PESTICIDE HAZARD ASSESSMENT PROJECT:

Harvester Exposure Monitoring Field Studies

(1980 - 1986)

VOLUME 2

A collection of 25 studies submitted to

U.S. Environmental Protection Agency
Office of Pesticide Programs
Hazard Evaluation Division
Washington, D.C. 20460

In conjunction with an InterAgency Agreement
with the Department of Labor (DOL)

Research Projects performed by

Mississippi State University
Medical University of South Carolina
Colorado State University
University of Iowa
University of California
Texas Tech University

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INTRODUCTION

On March 17, 1980, the Environmental Protection Agency (EPA) and the Department of Labor (DOL) entered into an Interagency Agreement (IAG) to study the effects of pesticides on youth working in agriculture. The research was needed to provide information and data about specific pesticides and crops in relation to waiver requests anticipated from growers which would authorize employment of 10 and 11 year-old children in activities normally under the Fair Labor Standards Act. The IAG provided that DOL and EPA would jointly fund these studies, and these resources were then used to fund research projects with appropriate institutions (universities and research firms).

The two major areas of EPA research, the Office of Health Research laboratory animal toxicology studies and the Office of Pesticide Program's harvester exposure field studies, were conducted to provide exposure/toxicity information necessary to evaluate the possible increased hazard of pesticides to young workers. Results of the toxicological research are available as published journal articles. (See attached listing of articles)

Regarding the field studies, the Office of Pesticide Programs funded worker exposure studies through university cooperative research agreements in California, Colorado, Florida, Iowa, Texas, Mississippi and South Carolina. Studies on monitoring pesticide exposure to children and adults during harvesting were conducted in California, Colorado, Florida, Maine, Mississippi, Michigan, North Carolina, South Carolina, Oregon, Texas and Wisconsin. The studies involved seventeen different crops, including: cucumbers, peas, sugarcane, peanuts, corn, grapes, strawberries, onions, tobacco, potatoes, blueberries, tomatoes, apples, blackberries, raspberries, okra and turnips. Thirty different chemicals were also involved in the studies. (See Matrix)

The following studies consist of the reports generated by the various university agreements. It should be noted that some of this data is also available as published journal articles.

HEALTH EFFECTS RESEARCH
FOR YOUTH IN AGRICULTURE PROGRAM
Office of Health Research
Health Effects Research Laboratory
Office of Research and Development
U.S.E.P.A.

I. Age Differences in Acute Oral Toxicity:

Gaines, T.B. and Linder, R.E. Acute Toxicity of Pesticides in Adult and Weanling Rats. Fund Appl. Toxicol. 7:299-308. 1986.

MacPhail, R.C., Padilla, S., and Reiter, L. Age-Related Effects of Pesticides. Presented at Second International Symposium on the Performance of Protective Clothing, Tampa, Florida, January 18-22, 1987 (In Press).

Padilla, S., MacPhail, R., and Reiter, L. Age-Related Effects of Pesticides Relevant to Youth in Agriculture. HERL Neurotoxicology Division Report, 1985.

II. Age Differences in Dermal Absorption of Pesticides:

Carter, S.D. et al. A Comparison of the Dermal Absorption of 2-^{14}C-Benlate in the Young and Adult Male Rat. Unpublished Research Report.

Fisher, H.L. et al. Dermal Absorption of Pesticides Calculated by Deconvolution. J. Appl. Toxicol. 5:162-177, 1985.

Hall, L.L. et al. Age-Related Percutaneous Penetration of Dinoseb in Rats. HERL Developmental and Cell Toxicology Division Report.

Hall, L.L. et al. Dermal Absorption and Disposition of Chlordecone in Young and Adult Rats. The Toxicologist 5:266, 1985 (Abstract only).

Hall, L.L. et al. Dose Response of Skin Absorption in Young and Adult Rats. HERL Developmental and Cell Toxicology Division Report.

II. **Age Differences in Dermal Absorption of Pesticides:**

Hall, L.L. et al. In Vivo and In Vitro Dermal Penetration of 2,4,5,2',4',5'-Hexachlorobiphenyl in Young and Adult Rats. HERL Developmental and Cell Toxicology Division Report.

Shah, P.V. et al. Dermal Penetration of Carbofuran in Young and Adult Fischer 344 Rats. J. Toxicol. Environ. Health (Accepted for publication).

Shah, P.V. et al. Penetration of Fourteen Pesticides Through the Skin of Young and Adult Rats: A Preliminary Screen: (Abstract in the Toxicologist 5:264, 1985). J. Toxicol. Environ. Health 21:353-366, 1987.

III. **Age Differences in Serum Chemistry Changes Following Pesticide Exposure:**

MacPhail, R.C., Padilla, S., and Reiter, L. Age-Related Effects of Pesticides. Presented at Second International Symposium on the Performance of Protective Clothing, Tampa, Florida, January 18-22, 1987 (In press).

Padilla, S., MacPhail, R., and Reiter, L. Age-Related Effects of Pesticides Relevant to Youth in Agriculture. HERL Neurotoxicology Division Report, 1985.

IV. **Age Differences in Motor Activity Following Pesticide Exposure:**

MacPhail, R.C., Padilla, S., and Reiter, L. Age-Related Effects of Pesticides. Presented at Second International Symposium on the Performance of Protective Clothing, Tampa, Florida, January 18-22, 1987 (In press).

Padilla, S., MacPhail, R., and Reiter, L. Age-Related Effects of Pesticides Relevant to Youth in Agriculture. HERL Neurotoxicology Division Report, 1985.

V. **Age Differences in Metabolism of Foreign Compounds:**

Chadwick, R.W. et al. Antagonism of Chlorobenzene-Induced Hepatoxicity by Lindane. Pest. Biochem. Physiol. 21: 148-161, 1984.

V. <u>Age Differences in Metabolism of Foreign Compounds:</u>

Copeland, M.F. <u>et al</u>. Use of γ-Hexachlorocyclohexane (Lindane) to Determine the Ontogeny of Metabolism in the Developing Rat. J. Toxicol. Environ. Health. <u>18</u>:527-542, 1986.

VI. <u>Effect of Pesticides on Behavioral Sex Differentiation:</u>

Gray, L.E., Jr. Alteration of Behavioral Sex Differen-iation by Exposure to Estrogenic Compounds During a Critical Neonatal Period: Effects of Zearalenone, Methoxychlor, and Estradiol in Hamsters. Toxicol. Appl. Pharmacol. <u>80</u>:127-136, 1985.

Gray, L.E., Jr. Compound-Induced Developmental Reproductive Abnormalities in Man and Rodents: A Review of Effects in Males. Repro. Toxicol. (Accepted for publication).

Gray, L.E., Jr. Neonatal Chlordecone Exposure Alters Behavior Sex Differentiation in Female Hamsters. Neurotoxicology <u>3</u>:67-80, 1982.

VII. <u>Development of a Male Rat Fertility Model:</u>

Carter, S.D. <u>et al</u>. Effect of Benomyl on the Reproductive Development of Male Rats. J. Toxicol. Environ. Health. <u>13</u>: 53-68, 1984.

Laskey, J.W. <u>et al</u>. Assessment of the Male Reproductive System in the Preweanling Rat. J. Toxicol. Environ. Health. <u>15</u>:339-350, 1985.

Rehnberg, G.L. <u>et al</u>. Age-Dependent Changes in Gastro-intestinal Transport and Retention of Particulate Manganese Oxide in the Rat. J. Toxicol. Environ. Health. <u>16</u>:887-899, 1985.

VIII. <u>Susceptibility to Renal Toxic Effects During Lactational and Prepubertal Period:</u>

Daston, G.P. <u>et al</u>. Toxicity of Mercuric Chloride in the Developing Rat Kidney. II. Effect of Increased Dosages on Renal Function in Suckling Pups. Toxicol. Appl. Pharmacol. <u>74</u>:35-45, 1984.

VIII. **Susceptibility to Renal Toxic Effects During Lactational and Prepubertal Period:**

Daston, G.P. et al. Toxicity of Mercuric Chloride to the Developing Rat Kidney. III. Distribution and Elimination of Mercury during Postnatal Maturation. Toxicol. Appl. Pharmacol. 85:39-48, 1985.

Kavlock, R.J., and Daston, G.P. Detection of Renal Dysfunction in Neonatal Rats: Methodologies and Applications in Abnormal Functional Development of the Heart, Lungs and Kidneys.

Kavlock, R.J., and Gray, J.A. Evaluation of Renal Function in Neonatal Rats. Biology of the Neonate 41:279-288, 1982.

Kavlock, R.J., and Gray, J.A. Morphometric, Biochemical and Physiological Assessment of Perinatally-Inducted Renal Dysfunction. J. Toxicol. Environ. Health 11:1-13, 1983.

Kavlock, R.J. The Ontogeny of the Hydropenia Response in Neonatal Rats and Its Application in Developmental Toxicology Studies. Banbury Report, Cold Spring Harbor Laboratory, 1982.

XI. **Development of Biochemical Indicators of Prenatal Organ Differentiation:**

Kavlock, R.J. et al. An Analysis of Fetotoxicity Using Biochemical Endpoints of Organ Differentiation. Teratology 26:183-194, 1982.

Kavlock, R.J., and Gray, J.A. Morphometric, Biochemical and Physiological Assessment of Perinatally-Inducted Renal Dysfunction. J. Toxicol. Environ. Health 11:1-13, 1983.

STUDY REF.#	PROJECT NAME (UNIV.)	STUDY SITE(S)	CHEMICAL/CROP	TYPE OF EXPOSURE
1	Mississippi State Univ.	Mississippi	Carbaryl-cucumbers,Carbaryl/Toxaphene/Treflan-peas, Carbofuran-sugarcane	Harvester Expos.
2	Mississippi State Univ.	Mississippi	Carbaryl-cucumbers,Aldicarb-peas,Toxaphene/Methyl parathion-peanuts	Harvester Expos.
3	Mississippi State Univ.	Mississippi	Endosulfan-peas,Endosulfan-corn,Benomyl-grapes	Harvester Expos.
4	University of Florida	Florida	Captan-strawberries	Foliar Residues
5	Medical Univ. of South Carolina	North Carolina	Acephate(methamidophos)-tobacco	Harvester Expos.
6	Medical Univ. of South Carolina	Maine	Aldicarb/Chlorothalonil/Dinoseb/Diquat/Endosulfan/Linuron/Polyram/Mancozeb/Methamidophos/Methomyl/Metribuzin/Demeton-potatoes	Soil Residues
7	Medical Univ. of South Carolina	North Carolina	Ethyl parathion/Malathion/Benomyl-blueberries	Harvester Expos.
8	Medical Univ. of South Carolina	Maine	Dinoseb-potatoes	Harvester Expos.
9	Medical Univ. of South Carolina	South Carolina	Endosulfan-tomatoes	Harvester Expos.
10	Medical Univ. of South Carolina	North Carolina	ULV Malathion-blueberries	Harvester Expos.
11	Colorado State Univ.	Colorado	Toxaphene/Malathion/parathion(ethyl & methyl)-onions	Harvester Expos.
12	Univ. of Iowa	Michigan	Malathion/Methiocarb/Captofol-blueberries	Harvester Expos.
13	Univ. of Iowa	Wisconsin	Captan/Guthion/Imidan-apples	Harvester Expos.
14	Univ. of California	California Oregon	Captan-strawberries	Harvester Expos.
15	Univ. of California	Oregon	Carbaryl-strawberries	Harvester Expos.
16	Univ. of California	Oregon	Vinclozolin-strawberries	Harvester Expos.
17	Univ. of California	California	Captan/Benomyl-strawberries	Harvester Expos.
18	Univ. of California	California	Captan-strawberries,Vinclozolin/Methiocarb/Carbaryl-blueberries	Harvester Expos. Foliage Residues
19	Univ. of California	California	N/A	Reentry Simulation Study(I&II)
20	Univ. of California	California	Methiocarb-blueberries,Benlate-blackberries,raspberries	Harvester Expos
21	Texas Tech Univ.	Texas	Carbaryl-okra	Harvester Expos.
22	Texas Tech Univ.	Texas	Azinphosmethyl-cucumber	Harvester Expos.
23	Texas Tech Univ.	Texas	Chlorothalonil-tomato	Harvester Expos.
24	Texas Tech Univ.	Texas	Lannate(methomyl)-cucumber	Harvester Expos.
25	Texas Tech Univ.	Texas	Phosdrin(mevinphos)-turnip/mustard greens	Harvester Expos.

Youth in Agriculture: Pesticide Exposure to
  Strawberry Pickers, 1981

Research performed by

University of California
Richmond, CA   94804

September 1982

Abstract

During five field studies in 1981, 78 field workers on three different strawberry farms in California and one in Oregon were monitored for dermal exposure to captan. Lower arms and hands were by far the areas of greatest dermal exposure. A comparison of dermal dose rate among children (- 11 years) or youths (- 13 years) and adults revealed lower doses to children and youths than adults. Age and productivity correlate positively with dermal dose. An increase in age results in higher productivity and consequently higher dermal exposure. A positive correlation was found between dislodgeable residues of captan on foliage and dermal exposure.

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SUMMARY

During five field studies in 1981, 78 field workers on three different strawberry farms in California and one in Oregon were monitored for dermal exposure to captan. Based on these results and a statistical analysis of these, the following conclusions were reached:

1. Lower arms and hands were by far the areas of greatest dermal exposure, ranging from 7-21% and 60-88% of total dermal exposure, respectively.

2. While a positive correlation was observed between aerosol concentration of captan and dermal exposure, the ratio of dermal and aerosol concentration doses was found to be approximately 100, suggesting that aerosols do not constitute a significant route of exposure.

3. The average hourly dermal exposure by strawberry pickers to captan ranged from 4.70 mg/hr to 17.41 mg/hr. Normalized for body weight, this exposure calculates to 0.082 mg/kg/hr and 0.310 mg/kg/hr, respectively. The standard deviations for these exposures were high, indicating large variability of dermal exposure among harvesters.

4. In terms of absolute dermal dose rate (mg/hr), a comparison between children ($\leq$ 11 years old) or youths ($\leq$ 13) and corresponding adult groups revealed a trend toward lower doses to children and youths than adults, but a statistically significant difference in only one field. When dermal doses are adjusted for body weight/mass (mg/kg/hr), the corresponding dose rates appear even more equal with higher doses only to youths in one field.

5. Age and productivity of strawberry pickers appear to correlate positively with dermal exposure; age and productivity are also cross correlated. Thus, one may conclude that increasing age results in higher productivity (experience and motivation); higher productivity results in higher dermal exposure, and consequently, increasing age of pickers results in higher dermal exposure.

6. No difference was found between dermal exposure by female and male strawberry harvesters.

7. A positive correlation was found between dislodgeable residues of captan on foliage and dermal exposure by strawberry pickers, suggesting that dislodgeable foliar residues represent an important route of dermal exposure of pesticides by strawberry pickers.

8. Dermal exposure of weeders in strawberry fields averaged 94.13 mg/hr, a concentration considerably higher than that observed for pickers. The distribution of dermal concentration on the body of weeders was extremely variable, the hands, however, receiving the lowest dermal dose, in contrast to the distribution found among pickers. While this operation is much less frequent than harvesting, the cause for this higher exposure is only speculative at this time.

Pesticide Exposure to Strawberry Pickers

1981 Studies

1.0 INTRODUCTION

In order to assess the exposure to pesticides by fruit harvesters of all
ages and both sexes, the California Project of the National Pesticide Hazard
Assessment Project (PHAP) of the EPA undertook a series of field studies during
1981 involving strawberry harvesters. These studies have now been completed,
and the results are given in this report. In order to simplify the chemical
analyses and interpretation of data during the first year's studies, we chose the
fungicide captan (N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide) for
detailed investigation. Statistical methods were applied to find significance of
difference and linear correlations between several variables like age, sex,
productivity, and groups of individuals, e.g., children (10-11 years old), youths
(less than 13 years of age) and adults.

2.0 EXPERIMENTAL PROCEDURES

All of the field studies which will be described in detail below were designed to monitor the dermal exposure of strawberry pickers during actual harvesting of the berries in the early spring (first fruit), middle and late summer in several locations in California and one location in Oregon. An attempt was made to select volunteers representing both sexes and children under the age of thirteen. This was not always successful (see Study No. 5) due to the lack of appropriate subjects in a particular field situation. Environmental samples like aerosols, dislodgeable residues on foliage and fruit, and soil residues were also taken in some of the field experiments. Sampling procedures and analytical methods will be described in later sections.

2.1 Field Studies

During the Summer of 1981, five pesticide residue studies on strawberry crops were conducted; four in the Salinas Valley of California and one in Corvallis, Oregon. The California studies were conducted on May 9, July 21, and two on August 21, 1981 and the Oregon study on June 22, 1981. The study dates had to be chosen in order not to inconvenience the cooperating growers and to obtain data from a variety of post-application dates.

In each of these field studies attempts were made to obtain the volunteer services of about 20 workers, including children and adults of both sexes. Due to the lateness in harvesting in August, the number of cooperating pickers was considerably lower, but the results of these studies will nonetheless be reported here.

For each study, the subjects' weight and height were measured before the pickers entered the field on that particular day. Personal dosimeters and some personal air samplers were placed on the subjects, as will be described in the next section, 2.2. Observations were made throughout the work day on personal clothing (removal of outer garments, etc.), work habits and peculair traits which might explain abnormal exposure values of individual pickers. At the end of the work day, each picker reported the total number of crates he harvested. The crates in California picked for market contain about 11 lbs of berries, while the Oregon crates, mostly picked for canning and processing, contained 13 lbs of strawberries. Distances covered by each picker throughout the day were estimated for Studies 1 and 3. Dosimeters (patches and gloves) were removed from the workers and stored in dry ice for future analysis.

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The following field experiments will now be described in greater detail:

Study Number	Site	Days Post-Application	Number of Subjects Youths *	Adults
1	Salinas, CA Farm A	10	8	11
2	Corvallis, OR	26	12 .	11
3	Salinas, CA Farm A	3	8	7
4	Salinas, CA Farm B	3	3	3
5	Salinas, CA Farm C	48	0	10

*
Youth defined as 13 years old or younger

A. Field Study No. 1

A Mexican-American farm cooperative located near Salinas, CA, consisted of two 40-60 acre plots, one of first year and the other of second year strawberry plants. This cooperative farm is owned and operated by member families who each maintain a designated section of the fields. Family members including children under the age of ten to eleven work in these fields during harvest time, which in California extends from about mid April until October-November.

The field study was conducted on a Saturday, May 9, 1981, in order to observe 10-11 year old pickers, who would be working in the fields only during the weekend because of school attendance. Ten days prior to the study date, the fields had been sprayed with several pesticides: captan, benomyl, and malathion as is shown in Table A-2. The fields on this farm are irrigated by drip irrigation and furrowed irrigation, and the study area included both sections of the farm. The study population was composed of 4 subjects age 11 and under and 16 subjects, 12 years of age and older.

Temperature was taken at mid-day and measured 73°F in the shade; humidity was 66%, and the wind speed ranged from 5.7 to 9.1 mph with a few gusts of 13 mph.

B. Field Study No. 2

The object of our studies on strawberry workers and their possible exposure to pesticides was to observe strawberry pickers in two divergently

different locations. The growing of strawberries in Oregon is quite different from the practices in California. For example, Oregon varieties of berries, Benton are usually harvested for about three weeks in June-July. Secondly, weather conditions might be quite diffrent from those encountered in California. For example rain fall during the Oregon harvest season is not uncommon. Also, heavy dew in the morning is much heavier in Oregon than might be found in California. Furthermore, strawberry harvesters in Oregon are hired hands and do not necessarily belong to the family which owns the farm. Many school children work on the strawberry farms during their summer vacation.

The particular site which was chosen for our study in Oregon was a privately owned strawberry farm in Corvallis, Oregon, and consisted of 15 acres of strawberries on leased land. The berries were of the Benton variety and two years old when the study was conducted.

The date of our Oregon-study was Monday, June 22, 1981. The fields had been previously sprayed on May 27, 1981 with captan, benomyl, and carbaryl, resulting in a 26-day post application date (see Table A-10). Twenty-three volunteer subjects ranging in age from 11 to 38 of both sexes were outfitted with dermal dosimeters as described in Section 2.2 of this report. In addition to all other observations made in the California studies, the hands of the subjects were traced on graph paper in order to estimate their surface area. The temperature during the day was cool (61-67°F), and some rain fell during parts of the work day. There was very little wind during the day ranging from 1.3 to 2.1 mph. Humidity ranged from 77 to 93% RH.

A map of this farm is shown in fig. 1 ; field observations were conducted in Areas A and C.
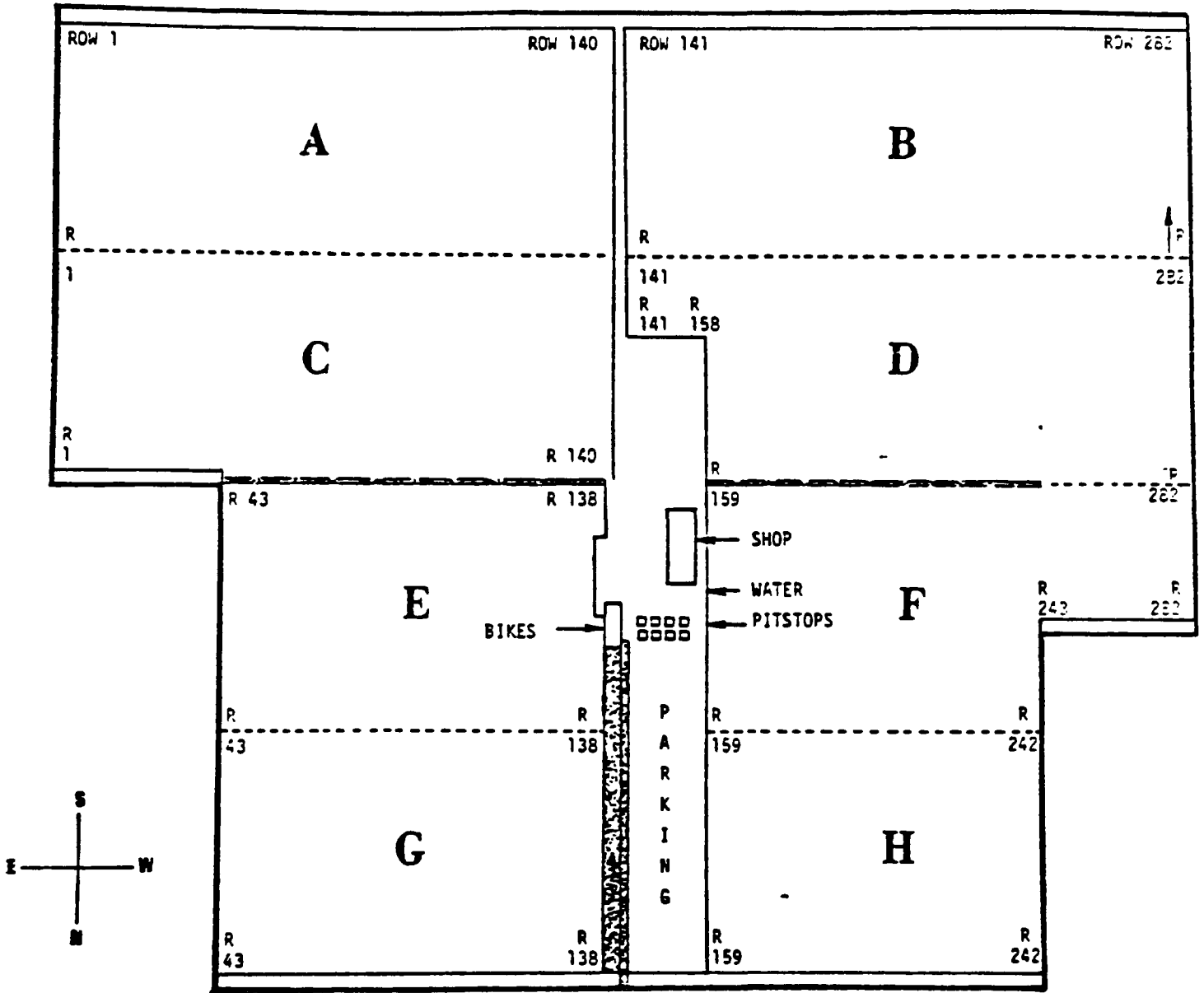
FIGURE 1. STRAWBERRY PLOTS FIELD STUDY NO. 2, CORVALLIS, OREGON

---- FOOT PATH

═══ TRUCK PATH

C. Field Study No. 3

This study was conducted on July 21, 1981 on the same cooperative strawberry farm as in Study No. 1. The study population consisted of 15 pickers (several other workers discarded their gloves or patches before the end of the workday and were thus removed from the study) and four weeders. Their ages ranged from 8 to 42 as is shown in Table   (Appendix). One of the "pickers" who was six years of age and who only picked less than one crate of berries during 3 1/2 hours was not included in the evaluation of harvesters' exposure and will be discussed separately under Results and Discussion, Section 3.

The weather early in the morning, from about 0730 until 0930, was foggy with the temperature increasing from 53°F to 59° with the relative humdity decreasing from 98% to 86%. During the early afternoon (1300), the temperature rose to 76°F and dropped back to 71°F at 1505 hours, the end of the work day. The wind speed in the morning ranged from 2:3-3.0 mph, but later during the day gusts of wind as high as 16-20 mph were recorded.

Different pesticides had been applied on various dates prior to this study, as is shown in Table A-2, and the latest captan application occurred three days prior to our investigation on July 21, 1981.

D. Field Study No. 4

This study was conducted during the morning of August 21, 1981 on Cooperative

Farm B near Salinas, California. Due to the lateness in the season, there

were few berries and only several families were in the fields picking berries.

Six harvesters were monitored for the same length of time (3.5 hours); their

ages ranged from 8 to 41. The temperature stayed fairly constant during the

time of the study (65 - 69.5°F) with the relative humidity ranging from

75 to 88%. Wind speed was recorded at 4.5 to 15 mph, and the day could best

be described as "cool and windy".

Pesticide applications were made according to the schedule found in Table A-21,

and the last application of captan had been made three days prior to the day

of the study.

E. Field Study No. 5

Due to the shortage of volunteer subjects found on Cooperative Farm B,

the study team was split up on August 21, 1981, and another group moved to

Cooperative Farm C to perform an additional study on the same day. This

farm was located just a few miles away from Farm B. Ten subjects were studied,

but no youths or children were working on that day. The weather conditions were

very similar to those recorded for Study No. 4. Pesticide applications had

been made throughout the season as is shown in Table A-28. The interval between

the day of last application of captan and the 21st of August, 1981 was 48 days.

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2.2 Sampling Procedures

Dermal Exposure to Pesticides —

This project employs a gauze pad as a dermal dosimeter for all areas of the worker's body except the hands (see Figure 2 and 3). This dosimeter consists of a 12-ply 3 x 3 inch gauze surgical sponge. A polyethylene "moisture barrier" is placed on the side of the pad facing the skin of the subject. All of this is held in a glossy paper envelope. The side of the envelope facing away from the skin has a circular hole 60 mm in diameter exposing 28 cm^2 of the gauze pad.

Body locations for mounting the gauze pad dosimeters are as follows:

Head -- mounted on the side of the head, roughly over one ear, either stapled to a stretchable head band or taped to the inside of the brim of the subject's hat (1);

Chest -- mounted over sternum between the pectoral muscles (1);

Back -- mounted over backbone between the scapulae (1);

Upper Arm -- mounted over the deltoid muscles (2);

Lower Arm -- mounted roughly midway between the elbow and wrist on the dorsal surface (2);

Lower Leg -- mounted roughly midway between the knee and the ankle on the anterior surface (2).

For ease of mounting and dismounting the patches, the chest, back and upper arm dosimeters are stapled to T-shirts which are dispensed to the subjects at the beginning of the work period and collected at the end. The T-shirts are worn next to the skin of the subject so that the dosimeters will be exposed to only that portion of the residues that would eventually reach the skin. Lower arm

FIGURE 2

Photograph of Strawberry Picker Outfitted with
Dosimeters on chest, head, upper and lower arms, and gloves
Farm A, Salinas, CA, 21 July, 1981
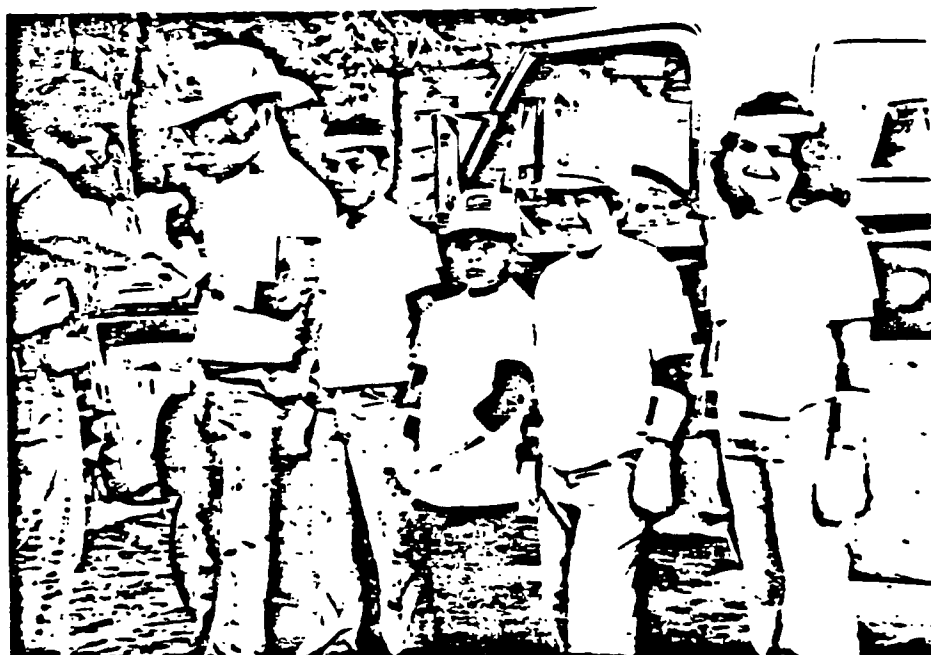
FIGURE 3

Photograph of Family and Friend Outfitted
with Dosimeters
from left to right: father (42yrs old) son(16), son (8), friend (11),
daughter(12)

and lower leg patches are taped directly to the skin in the appropriate location after the T-shirt is donned. The subjects then wear whatever clothing they would normally wear while working, except that if they were to strip to the waist (which some male workers in California do) they would continue to wear the T-shirt bearing the dosimeters.

A hand dosimeter consists of a light-weight cotton glove. For those subjects who feel uncomfortable wearing gloves picking strawberries, the finger tips of the thumb and first two fingers will be cut from the glove worn on the picking hand. This will allow stemming or other delicate manipulations the subject feels might be hindered by even the light-weight glove employed in this study.

Personal Aerosol Monitors —

Personal breathing zone air samples will be taken on at least two subjects each working period for two hours. An open-face, 37 mm Millipore cassette (0.8 µ pore size) is mounted on a subject's breathing zone and is aspirated at 2.0 ± 0.2 Lpm with a belt-mounted portable pump (Figures 4 and 5).

Foliar Samples —

Foliar sampling is accomplished by using a leaf punch equipped with a 3 cm diameter die (see Figure 6). The punch-through action of the device pushes the leaf disk into a 4-oz wide-mouth jar which is attached to the punch and which subsequently serves as the sample storage container. The punch is also equipped with a resettable counter.

Sample collection is accomplished by striking out diagonally across the area to be sampled, stopping every three or four rows to take a single leaf sample. The sampling points are to be distributed throughout the areas of the plants that the harvester will actually contact. For strawberries, this includes all
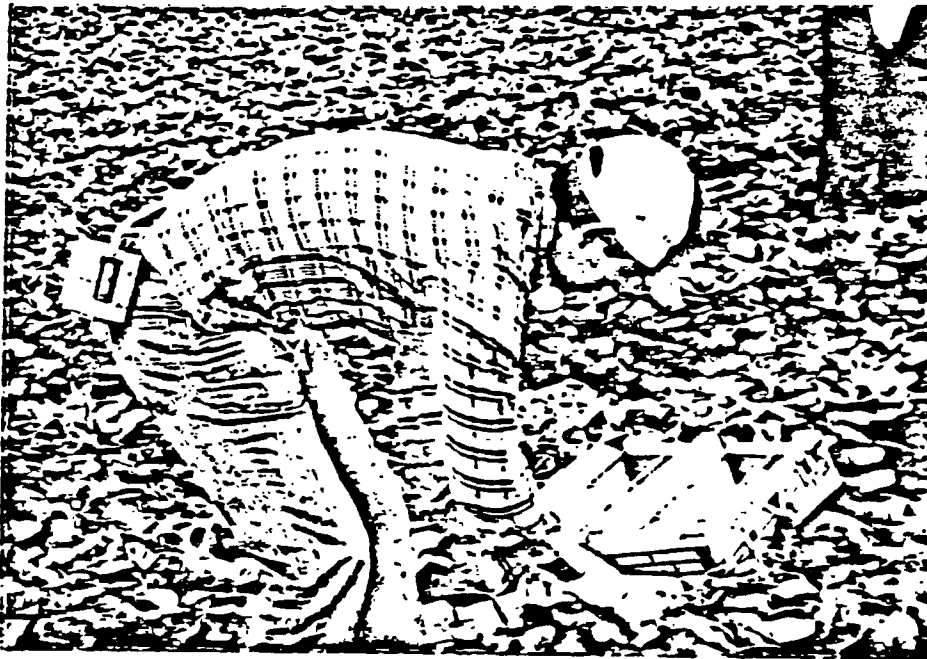
FIGURE 4

Photograph of Strawberry Picker Equipped with
Personal Air Sampler
Farm A, Salinas, CA; 21 July, 1981
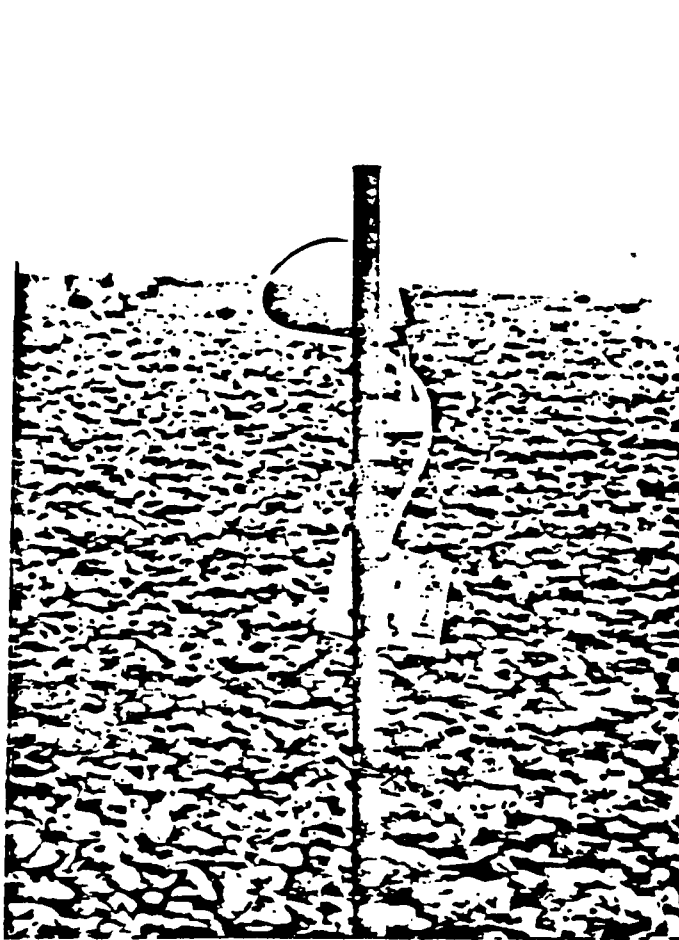
FIGURE 5

Air Sampler, Stationary Position
For Measuring Aerosol Concentrations (July 21, 1981)

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FIGURE 6

Mechanical Leaf Punch Being Operated by
Field Personnel

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parts of the plant, both outer and inner canopy leaves, from either side of the row, and from the center. The standard sample size is 48 disks. If the edge of the field is reached before the full complement of leaf disks has been obtained, the person collecting the sample merely reflects back into the field on a new diagonal.

Soil Samples —

The soil sampling device has two parts: a three-sided form 10 cm long by 8 cm wide and 8 cm high, which when pressed into the soil surface blocks out an area 80 cm^2; and a small rectangular shovel which fits just inside the form and has a 1 cm high rim around the sides and back (see Figure 7).

Sampling is accomplished by first shoving the form into the soil several centimeters. The shovel is then inserted vertically into the soil at the open face of the form, likewise, several centimeters; and the soil is scraped away from the form with it to a depth of several centimeters. The shovel is then run into the form horizontally so that it picks up a layer of surface soil the area of the form and 1 cm deep. The sampling pattern utilized for taking soil samples is the same as for taking foliage samples, being collected on a diagonal across the area being harvested by the cooperating pickers. However, since there are only six "scoops" taken, rather than the 48 sampling sites for the leaf punches, samples are taken every 8 to 10 rows. Furthermore, samples are taken in the area between the planted burms, which is where pickers are physically located, and where they contact the soil. Soil samples are held in a paper sack (=4 lunch bag) which is in turn placed in a plastic bag to reduce moisture loss in frozen storage.

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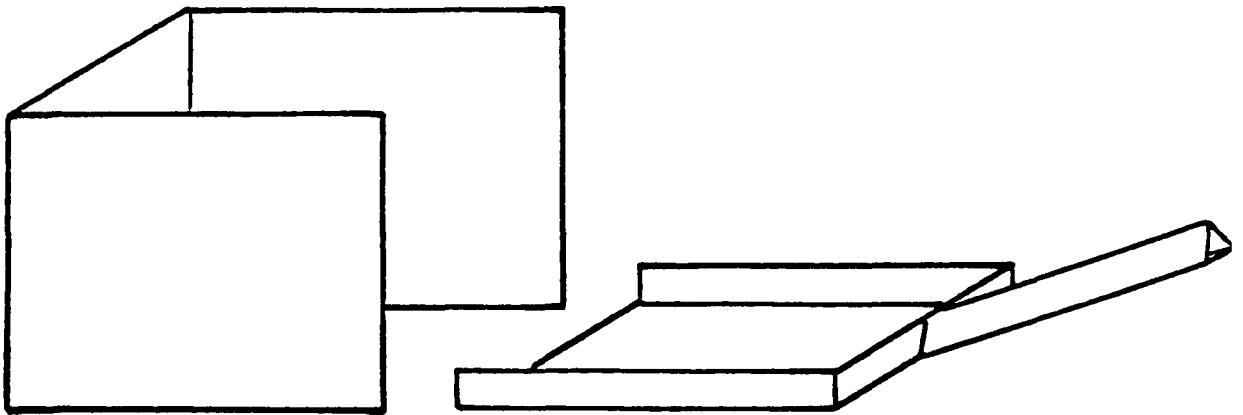
FIGURE 7   SOIL SAMPLER

2.3 Chemical Analyses

Dosimeters —

Samples consist of one or two pads (one for main trunk or two for limb sample sites) stapled inside paper application packs stored in an RRE Zip-lock bag in the freezer. After the samples were removed, the pad together with the plastic moisture barrier was transferred to a 125 mL LPE wide-mouth bottle. Thirty mL of toluene some of which is used to rinse the bag, were added and the sample shaken at about 200 Hz for one hour. Ten mL aliquot of the analysate was reserved in a glass polyseal vial, and an auto-sampler vial was prepared from the remainder.

The gloves were treated in a manner similar to that used for the patches and were also frozen, one pair to a sample bag. 100 mL of toluene was used to extract each pair. If a subject wore more than one pair, the solvent was increased only to the extent that an aliquot could easily be removed and the actual amount of solvent was noted.

Aliquots of the extracts were analyzed on a Tracor 222 gas-liquid chromatograph, using a mixture of argon-methane as carrier gas (65 ml/min), OV1 (10%) on Supelcoport (80/100 mesh), 3' x 2mm (i.d.) column at a column temperature of 210°C, using a ^{63}Ni-electron capture detector. Captan under these conditions elutes at 1.27 minutes. Quantification was performed by area-integration and expressed as "micrograms per sample." To calculate dose rate per person, the following calculations were made:

$$mg/hr = \frac{\text{μc pesticide x (cm}^2 \text{ surface area of body part)x F}}{(cm^2 patch) \text{ x nr x 1,000}},$$

where $cm^2 patch = 28 cm^2$; "cm^2 surface area, body part", see Table A-1, and

$$F = \frac{A \text{ indiv.}}{1.92} *$$

* Body surface of 50-percentile man is 1.92 m^2(Popendorf and Leffingwell, 1982)

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Strawberry Leaf Punch and Fruit Samples -

The standard leaf punch sample consisted of 48 3cm leaf disks frozen in a glass jar with a water-tight plastic cap. Berries were also kept frozen until being analyzed. After a half-hour thawing period, the leaves or fruit were placed into a one-pint square Mason jar with the standard lid and ring closure. Six drops of a 20 mg/L solution of dioctyl sodium sulfosuccinate was added to the sample jar. The surfactant and dust from the leaves were also transferred quantitatively to the Mason jar with 100 mL of distilled water. The samples were shaken for 30 min. on a mechanical shaker platform at about 140 Hz and the liquid decanted into 50 mL methylene chloride (dichloromethane) in a 500 ml separatory funnel, using a narrow stemmed funnel to avoid transferring the plant samples. The process of washing the samples with surfactant and water was repeated twice. The separatory funnel was shaken 30 times and the organic layer was drained through a small funnel plugged with glass wool and filled with anhydrous sodium sulfate into a 500 mL round-bottomed 24/40 flask. The extraction process was repeated twice more with fresh 50 mL aliquots of solvent and the combined solvent was rotary evaporated to about 1 mL. Ten mL of toluene was added and evaporated. This process was repeated twice more. The final residue was quantitatively transferred to a 10 mL volumetric flask. The sample was then ready for gas chromatographic analysis.

The dust which was washed from the leaf surfaces remained in the interfacial layer in the separatory funnel. This material was filtered onto a pre-weighed glass filter, dried at 110°C overnight and cooled in a desiccator. Post-weighing of the filter yielded the foliar dust weight.

Soil Samples -

The samples were sifted through a #10 sieve to break up lumps and remove rocks twigs and leaves. The sifted sample was mixed and a 250 mL portion was taken, placed in an ambient vacuum desiccator and dried for 24 hours or more until the residual moisture was less than 0.5%. A glass soxhlet thimble was prepared by placing 1.5 cm of acetone washed sand in the bottom to protect the extra-coarse frit from fouling by soil fines. The thimble was tared and about 30 gm of soil was added, the weight being taken to four significant figures. The thimble was then placed in a 250 mL soxhlet extractor and cycled for four hours. The solvent used is an azeotropic acetone-hexane mixture (59% - 41%). After extraction, the solvent was removed by rotary evaporation and replaced by a solvent compatible with the analytical method to be used - toluene for GC only, acetonitrile for GC plus HPLC.

Aerosol Samples -

Aerosol samples consisted of Millipore disposable cassettes with 37-mm membrane filters. The filters were dropped from the cassette directly into a 500-ml Nalgene LPE wide-mouthed rectangular bottle without the need for manual transfer. Loose dust was washed off the cassette with hexane which is allowed to evaporate on the bottom of the bottle. Captan was then extracted with 30 ml of toluene by a one-hour shake as is described under "Chemical Analyses - Dosimeters". The extract was concentrated or diluted, whichever was necessary, and analyzed by GLC as described above.

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3.0 RESULTS AND DISCUSSION

The primary aim of these studies was estimation of dermal exposure to pesticides by strawberry pickers of different ages. These studies were to be conducted under varying environmental conditions, different pesticide application schedules, and at two geographic locations on the West Coast. In the five studies reported here no attempt was made to conduct analyses of urinary excretion of pesticides or their metabolites. This will be the subject of subsequent studies. An effort was made to examine a broad spectrum of field workers and to determine if dermal exposure was related to their age. ·The exposures reported here are estimates for the fungicide captan as experienced by strawberry harvesters. Extrapolating these data to "dose" can be performed quantitatively only when the pharmacokinetics and dermal absorption of captan have been studied. If someone wishes to use these results to calculate absorbed "dose", he may be able to make an approximation by using generally accepted absorption rates (about 10%). Quantitative studies on the dermal absorption of C-14-captan in rats are being conducted presently by Dr. James Knaak at U.C. Davis in association with the California PHAP. Once these results have been reported, it may be possible to derive better quantitative data for dose of captan from dermal exposure.

Of the five studies on captan exposure conducted during 1981, four were performed on three different strawberry cooperatives in California and one farm in Oregon. The studies in California were run early in the season (May), during mid-summer (July) and late summer (August). The temperatures on the study days were moderate (61° to 76°F) at relative humidities ranging from 77 to 98%. Conditions during the Oregon study provided an interesting contrast to those encountered in California. The strawberry harvest season in Oregon lasts three

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weeks compared to 4-5 months in California. The temperature at the Oregon site in mid-June was about 10°F cooler than that found at the California study sites and rain fell at the Oregon site. Another difference which was found was the pesticide usage pattern (see Appendix).

In the five studies, a total of 73 strawberry pickers were monitored for dermal concentration of captan. Four weeders and one other atypical subject were included.

All five field studies were conducted under actual harvesting conditions. No arrangements for special pesticide applications or type of workers were made. Although this approach had the advantage of spontaneity, the disadvantage was that no control could be exerted on the choice of pesticides used or the number of children and adults who were harvesting fruit on a particular day. As a consequence, in Field Study No. 5, no subjects below the age of 13 yrs. were found, but this study, never-the-less, provided additional data points for over-all correlations and comparisons.

Dermal Exposure by All Subjects

Comparing dermal exposure to captan by strawberry pickers in all five studies, it may be seen in Table 1 that the exposures ranged from 4.70 mg/hr to 17.41 mg/hr; or 0.082 mg/kg/hr to 0.31 mg/kg/hr. The standard deviations from the means are very high, clearly illustrating the variability in exposure among different subjects on a particular harvest day. In Study No. 4, the standard deviation was much lower than in the other four studies, 16.37 mg/hr (S.D. 3.78). The smaller variability amoung subjects in this study might have been due to their small number (six), having the same working hours and being equally divided among males and females.

Dermal exposure to captan experienced by four weeders (Table II) showed an average concentration of 94 mg/hr (S.D. 120) or 1.7 mg/kg/hr. The variability

among these four workers was very high as seen in Table II. Worker No. 20 has

a dermal dose of 267 mg/hr compared to the next highest subject, No. 16 with

72 mg/hr. These results will be discussed below under "Dermal Exposure

Distribution."

Captan Dermal Exposure by Different Age Groups

In order to deal with the small target population of children under 12 years

of age, while assessing the importance of age in exposure, three statistical

approaches were used in the analyses of the results: (a) parallel comparison

between children (age $\leq$ 11) and "adults"*; "youth" (age $\leq$ 13) and "adults"*;

and (c) correlation analyses of different variables, e.g., exposure/age, exposure/

productivity, etc. The first approach is somewhat arbitrary but is mandated by

law. The second classification results in a more equally divided group. Further

statistical support of the 13-year cutoff point will be explored by examining

the effect of age on weight, body surface area, productivity, and exposure (as

is addressed by the third approach). The third approach is more general and

permits qualitative interpretations from viewing the x-y plots and quantitative

evaluations by calculating the correlation coefficients.

A comparison of dermal dose rates and age groups is shown in Tables III and

IV; a detailed statistical treatment of the data may be found in the respective

tables in the Appendix. To demonstrate that real differences existed between

exposure by age groups, three statistical tests were applied: (1) student's

t-test; (2) the same test on log-transformed data (environmental data is commonly

log-normally distributed, i.e., skewed), and (3) the Wilcoxon nonparametric test.

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* "Adults" are classified as being above the age of "children" or "youth".

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The p-value is the probability .that there is no difference between the two groups. (A probability of 0.05 or 5% is a common decision criteria.) By and large, all three statistical tests yielded similar trends, as may be seen in the respective Appendix tables.

Table III shows that a significantly lower _total_ dermal exposure exists for children versus adults in Field Study No. 3. Although a similar trend is evident in the results from Studies 1, 2, and 4 (i.e., lower exposure by children), a statistically significant difference could not be ascertained for these data.

It is noted, however, that all trends indicating any differences between children and adult exposures disappear when the exposure data are normalized for body weight (mg/kg/hr) (see bottom of Table III).

Comparing dermal exposure in youths and adults (Table IV), a similar trend of lower exposure by youths is observed in all four field studies analyzed, but in only one study (No. 1) is the difference between the groups statistically significant. Again, when the exposure data are normalized for body weight (bottom of Table IV), the difference in exposure between the two groups are not significant with the exception of Field Study 4, in which the dermal exposure for youth was higher. This result, however, must be tempered by the smallness of the study population (six subjects).

The conclusion one may draw from these results and their statistical analysis is that children and youths have lower dermal body exposure during strawberry harvesting, probably due to the smaller body weight and body surface compared to those of adults. This hypothesis is proven by positive linear correlations in three out of five studies. As is shown in Table V, the correlation coefficients in these three studies for exposure/body surface and exposure/body weight are all above 0.5 and $p \leq 0.05$. The fact that Field Study No. 5 has a negative

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has a negative correlation can be explained on the basis that the population

consisted only of a small group of ten adults.

Further evidence for age-related exposure may be found in Table 5. A

positive linear correlation is found in all five studies comparing age and

productivity (expressed in crates harvested per hour). The plot shown in Figure

8 depicts the data for all subjects in Field Study No. 1 along with the best-fit

straight line; and, the correlation coefficient is 0.67. The correlation between

age and dermal exposure is less clear and significant only for Study No. 1; this

is also graphically shown in Figure 9, depicting age versus total dermal exposure

of all subjects in this study with the best-fit straight line. A linear correla-

tion was found in three of the five field studies for dermal exposure versus

productivity as seen in Table V and Figure 10.

Although the field results are not completely consistent for all five studies,

we can advance a possible explanation for adults being dermally exposed to greater

concentrations of captan than youths or children. When one compares productivity

(number of strawberry crates harvested per hour) and age of workers, the product-

ivity appears to increase with greater age (or experience) of pickers. Thus,

a possible explanation for higher dermal exposure by adults might be that greater

productivity results in more contact with dislodgeable pesticide residues on

foliage and fruits. Further evidence for this hypothesis will be discussed in

greater detail under "Dislodgeable Residues and Dermal Exposure).

Individual Variability of Dermal Exposure

As previously discussed and seen from the data in Table 1, large variability

in dermal exposures among individuals is found even during one particular study.

The individual variability might be due to age, productivity, and work habits.

These factors are very difficult to separate and study out of context. However,

the 1981 field studies provided some, although limited, data on the intrapersonal

variability of strawberry harvesters. The way this came about was that Field Studies 1 and 3 were conducted on the same cooperative, and that fortuitously three pickers participated in both studies. These three individuals were monitored for captan dermal exposure on two separate dates (May and July). In Table IV, the dermal exposure for each of the three pickers is shown for Experiments 1 and 3. The ratio of the two sets of exposures was calculated for each worker, and two of the subjects had about the same ratio (2.51 and 2.56, respectively), while Subject "B.O." had a higher ratio. An explanation for the ratio being greater than 1 is that the post-application periods for Experiments 1 and 3 were 13 and 3 days respectively, and the resultant foliar dislodgeable residues were 2.36 $\mu g/cm^2$ and 3.85 $\mu g/cm^2$, respectively (see later discussion on page ___). It is highly speculative at this time to conclude that the fact that two workers had the same exposure ratio provides evidence that intrapersonal variability is smaller than interpersonal variability. Extensive field experiments are in progress during 1982 to study the variability of exposures among strawberry pickers.

Captan Exposure Experienced by Male and Female Strawberry Harvesters

The field studies reported here provided a basis to demonstrate whether the sex of harvesters is a factor in dermal exposure to pesticides. Table VII summarizes the results from these studies and shows that in one of the Studies (No. 1), the six females received significantly higher exposure than the corresponding 13 male workers (10.04 vs. 4.87 mg/hr). This difference could not be demonstrated in subsequent studies. It is concluded, therefore, that exposure differences due to the sex of the picker is probably not a general occurrence.

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Distribution of Dermal Exposure Over Different Parts of the Body

The agricultural practice of strawberry picking is a hand operation in which the harvester squats, kneels, and sometimes sits between rows of strawberry plants and picks with two hands. When berries are picked for the fresh-fruit market, the picker will grab the fruit at the stem about 2 cm below the crown and twist the fruit off with a fast wrist action. The experienced picker can perform this operation equally with both hands.

Fruit picked for canning or processing is handled in a different manner. The harvester will pick the fruit with one hand and pluck the stem off with the other hand. Strawberries harvested in Oregon went mostly to canneries, while in California during the early season, the berries were delivered to the fresh-fruit market. From these observations it appears reasonable to expect that different parts of the body receive varying concentrations of pesticides depending on the mode of picking as described above.

Table VIII clearly shows that the hands received the greatest amount of dermal exposure, ranging from 60 to 85% of total dermal body exposure. The next highest exposure was seen on the lower arms (7% to 21% of total) and the lower legs (1% to 10% of total). The remainder of the dermal dose was unevenly distributed with great variability among the other parts of the body which were monitored (head, chest, back and upper arms).

The sum of hand and lower arm exposure calculated to 81-98% of the total for all field experiments (see Table IX). From these results one may conclude that the major dermal exposure from hand-harvesting crops grown close to the ground (e.g., strawberries) occurs on the hands, lower arms and legs of the harvesters. If one wanted to minimize pesticide exposure to these field workers, one could provide suitable gloves with gauntlets and reduce dermal exposure considerably.

A possible explanation for the observation that the lower legs of the harvesters receive an appreciable concentration of pesticides is the occurrence of dew during the early morning hours which causes the lower pant legs to become water soaked and contaminated with dislodgeable pesticide residues.

An atypical case of abnormally high dermal exposure was found on one six-year old male picker (see Table X). Although classified as a picker, this young subject probably was playing in the strawberry plants and was becoming exposed to all parts of his body. Eighty-six percent (86%) of dermal exposure was concentrated on his chest and stomach.

Also atypical is the pesticide distribution on the body of the four weeders, previously discussed (see Table II). These subjects had small amounts of captan on their hands; Subjects 12 and 16 had the greatest amount on head and neck; Subject 20 on his head, neck and lower arm. This last subject also had, by far, the largest dermal exposure of all 78 subjects studied.

Weeders, as a group, exhibited about five times the dermal exposure found amoung the highest group of strawberry pickers (see Table 1). The possible explanation for this high exposure and atypical pesticide distribution on their bodies may be found in the finding of pesticide soil residues of 6.29 ppm in the fields where the weeders were employed. The stirring up of contaminated soil by weeders and playful children will stir up an aerosol which will settle on all parts of the body resulting in dermal exposure to pesticides adsorbed onto the dust particles.

Dislodgeable Foliar Residues and Dermal Exposure

A possible source of dermal exposure among strawberry pickers might be the dislodgeable pesticide residues found on foliage and fruit. As may be seen from the data in Table XI and Figure 11, a positive linear correlation exists between dislodgeable foliar residue and total dermal exposure (mg/hr). The data

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were obtained from the five sites where the studies were conducted and the
exposures are the mean volues of all subjects monitored; thus, large experimental
variability is to be expected and, indeed, was found. The plot in Figure 11
includes S.E.M.'s for all data points. A reasonably high correlation coefficient
(r^2 = 0.32) indicates that the two variables, dislodgeable residues and dermal
exposure, are dependent.

This correlation is compatible with those of the resuspension of dislodge-
able residues from foliage. In fact, the average ratio of foliar residue ($\mu g/cm^2$)
to dermal exposure rates (mg/hr) of 5.8 is quite comparable to that for other
crops (Popendorf and Leffingwell, 1982). However, the major deposition onto
the hands of strawberry harvesters (with the subsequent build-up of a detritus
layer on the hands or gloves) and the probable differential absorption among
various body parts may mitigate the health impact of these findings.

Dislodgeable captan residues on strawberry fruit, as shown in Table XII,
range from non-detectable to 1.20 ppm. The residues appear to be indirectly
correlated with time after last pesticide application; i.e., the shorter the
time period, the higher the dislodgeable residues. At 3 days after last applica-
tion of captan, the residues were about 1 ppm; at 26 days they were non-detectable
or 0.35 ppm, and at 48 days after the last application, the residues were 0.09
and 0.49 ppm. These findings are in agreement with the concept of pesticide
degradation in the field due to biological and environmental factors.

Dislodgeable Foliar Residue Decay Studies

In three of the field studies, leaf punches from strawberry plants were taken
at several post-application intervals. Dislodgeable foliar residues were deter-
mined and expressed both as concentration per unit leaf area ($\mu g/cm^2$) and per
dust weight (ppm in dislodgeable dust) and were plotted against time (days).

Figures 12 through 17 and Tables XIII - XV show the dislodgeable residue decline as straight lines on semilog plots with high correlation coefficients (-0.68 to -0.88). Extrapolation to "0: dislodgeable residues resulted in approximately 16, 26, and 26 days, respectively, for Field Studies Nos. 1, 2, and 3. There is no ready explanation for the shorter estimated time interval for Experiment 1, except to consider that weathering and decline of dislodgeable residues are complex processes, and that field experiments cannot be expected to be exactly replicable.

Similar observations have been made by Maddy and co-workers (1977) who studied the decline of total and surface captan residues from leaves of strawberry plants following pesticide treatment. In one experiment from Ventura County, surface residue decay was practically linear from 118 ppm on day-1 to 35.1 ppm on Day-9, following application. Another field observation near Watsonville (Santa Cruz County) resulted in a rapid decline of captan residues during the first 26 hours after application of captan, followed by an almost indiscernible decay during the next six days of observation. This latter observation is akin to our own Field Study No. 2 (see figure 14), except that a slow decline was observed during the second phase.

A comment regarding pesticide application practices in Oregon and California is in order at this point. Strawberries are continuously harvested in California from about May until sometime in October or November, and pesticides must be used continuously throughout this period, averaging about one application every two weeks. In Oregon, on the other hand, all pesticide applications are made prior to harvest, and rarely do additional applications occur during the short, three-week harvest period.

For Oregon conditions, therefore, one might be able to establish a practical reentry period for harvesters based on the time interval at which dislodgeable residues have disappeared, assuming dislodgeable residues are the major source of dermal exposure. This restriction would result in negligible pesticide exposure for strawberry harvesters. This approach, however, may not be feasible without additional safety factors, as is borne out by actual field observations (Experiment No. 2). The extrapolated reentry interval of 26 days (figs. 14 and 15) is contrasted with the occurence of measurable dislodgeable captan residues (o.71 $\mu g/cm^2$) and an average dermal exposure by 23 harvesters of 4.70 mg/hr 26 days post application (See Table XI).

The reason that this approach may not be feasible for California is that insect and disease infestation and a longer harvest period in California require the continuous application of pesticides; so that a negligible residue level may never be reached before another application is made.

Captan. Aerosol Concentrations

For particulate aerosols, the manual harvester is the proximate source of his own hazard. Measurements in a quiescent field, such as those by Carman, et al. (1952) found no aerosol and very low vapor levels shortly after application of pesticides to orange groves. However, the action of harvesters who may disturb the dust-laden foliage 20 to 30 days post-application, can generate locally high concentrations of pesticide contaminate aerosols. The spatial concentration gradient of such an aerosol near its source is so large that for a sample to accurately represent the hazard, it must be collected in the immediate breathing zone of the harvester. Concentrations measured by general area samplers show the effect of dilution by ambient breezes and

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and particle fallout. Therefore, "breathing zone" personal air samplers are the logical choice to avoid these interfering effects. Even then, the personal samplers are limited in their ability to collect all airborne particulates, but they do collect efficiently the small suspended particles which may be inhalable and respirable.

Unlike the harvesters of tree-borne crops, whose dermal exposure derives mainly from larger particles of dust falling on him, the harvester of hand-picked fruit grown close to the ground, like strawberries, is probably not exposed to these aerosols to a great extent. Yet it is surprising that there appears to be a good correlation between aerosol concentration and dermal exposure (see figure 18 and 19 and Table XVI). When dose was normalized for weight of harvester (mg/kg/hr), a linear correlation was retained, as shown in fig. 13. In these studies, eleven strawberry harvesters were equipped with personal air samplers with the filter holder positioned in a horizontal manner in order to collect mostly aerosol particles (see fig. 4). Fixed site samplers were positioned about 5 ft. above ground as shown in fig. 5. As shown in Table XIII, captan aerosol concentrations ranged from 2.7 $\mu g/m^3$ to 260. $\mu g/m^3$. Stationary sites for Field Studies 3 and 5 also had measurable concentrations of captan, but in Field Study No. 1, captan concentration in aerosols was nondectable.

Assuming that a strawberry harvester works at a moderate physical activity level and inhales about 1 m^3/hr, and assuming that all aerosol particles are inhalable, the average dermal concentration (see Table 1) is two to three orders of magnitude higher than the maximum inhalable amount. This observation is consistent with other crops, and assuming even a moderately low level of

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dermal absorption, clearly demonstrates that pesticide exposure through dermal contact is much more important than exposure due to inhalation for strawberry pickers. Obviously, exposure to highly volatile or gaseous pesticides would alter this ratio drastically.

Captan Soil Residues

Residues of captan on sieved soil taken from the strawberry plots on the days that the monitoring studies were performed, ranged from nondetectable to 10 ppm, as shown in Tables XVII - XIX.

A detailed soil degradation study of captan was conducted on the Corvallis strawberry plot (Field Study No. 2). Soil samples were taken on days 0, 1, 3, 7, 14, 21, 23, 26 (date of field study), and 29 post-application. Residues on Day 1 were 0.57 ppm and on Day 7, 6.56 ppm, and on all other sampling dates non-detectable. Leaving out the Day-7 sample as an aberration, one may conclude that the degradation of captan in Oregon soil proceeds rapidly within days of its application to strawberry plants. (See Table XVII)

Degradation studies on the California plots were complicated by the fact that pesticides were periodically re-applied, approximately at two week-intervals during the entire growing season. Thus, captan residues of soil samples from Coop A near Salinas, California, as may be seen from Table XVIII, appeared not to decline appreciably, with the exception of exhibiting some degree of variability, probably due to sampling techniques ($\bar{x}$=3.32 $\pm$ 2.91). Keeping in mind that only a single application was made over this period, no trend for residue decline could be discerned within the first 13 days. During a second sampling period, no decline of residues in the soil could be seen, as well; although it is possible that an additional pesticide application was made just

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Prior to July 31, 1981. Verification of the spray schedule is being made at this time. Table XIX shows that captan residues in soil did decline after 48 days at Coop C, which is located just a few miles north of Coop A. An attempt is being made to characterize the soils in both farms.

The literature on the decline of captan in soils of various types is in conflict. Munneck (1958) claims that fungicidal activity of captan in soil remained almost unchanged for 65 days, suggesting that little or no decline occurred during this period. Kluge (1969) partially confirmed this finding by demonstrating that the biological activity of captan did not decrease appreciably during the first six weeks in two different soils of "H's 7.4 and 5.1. After that, there was a rapid decline observed but unexplained resurgence of activity at 12 weeks. Griffith and Mathews (1969) using bioassays, showed a rapid decline of captan within 4 days after it had been mixed with soil. By applying captan as a simulated seed dressant on glass beads, the fungicidal activity was almost quantitatively retained even after 21 days.

In the experiments reported here, behavior of captan in soil varied from relatively high persistence in one soil (Coop A, Salinas, CA) to a rapid decline in the Oregon soil and a slower rate in another Salinas soil. Based on the few foil samples which were analyzed, it cannot be ascertained whether soil residues of captan represent a major source of dermal exposure to pickers. It is conceivable that weeders (see discussion above) who showed the greatest dermal exposure of captan of all the subjects studies, might be receiving some of their dermal dose from these soil residues. Weeding activity undoubtedly stirs up a large amount of dust which will settle on all parts of the body of the person present in the cloud.

Miscellaneous Correlations

In order to understand the major source of dermal exposure of strawberry harvesters to pesticides, several other attempts were made to perform regression analyses on a number of variables other than those already discussed above. Thus, for example, one might expect that the person who works longer hours picking fruit might receive a higher dermal dose. As seen in Table V, a trend for negative correlation is obtained for the relationship "hours worked" and dermal exposure (mg/hr). How can this be explained? We believe that the longer a person works in the field without changing his body dosimeters (patches and gloves), the more saturated they become and do not truly measure an accumulative daily exposure. Since this measure is expressed as an hourly rate, one might reason that a negative correlation would be predicted by this mechanism. In order to determine the linearity of dermal dosimeters used throughout these studies, detailed experiments are in progress during this growing season to investigate the "saturation points" of these devices.

It is reasonable to hypothesize that if such a saturation phenomenon affects the dosimeter then it may also affect the skin deposit. Studies incorporating urinary excretion monitoring next year may be useful in clarifying this year's results.

Another hypothesis to be tested by regression analysis is that daily exposure to pesticides might correlate with distance covered during a work day. In only two field studies (2 and 3) were measurements made of how many rows of strawberry plants each harvester covered during his working period. No such correlation could be found (Table V), and we must conclude, therefore, that distance covered is probably not a factor in dermal exposure.

REFERENCES

1. Popendorf, W. J. and Leffingwell, J. T. Regulating OP Pesticide Residues for Farmworker Protection. Residue Reviews 82, 125 (1982).

2. Carman, G. E., Gunther, F. A., Blinn, R. C., and Garmus, R. D. The Physical Fate of Parathion Applied to Citrus. J. Econ. Entomol. 45 (5), 767 (1952).

3. Spear, R. C., Popendorf, W. J., Leffingwell, J. T., Milby, T. H., Davies, J. E., and Spencer, W. F. Field Workers' Response to Weathered Residues of Parathion. J. Occup. Med. 19, 406 (1977).

4. Popendorf, W. J. Exploring Citrus Harvesters' Exposure to Pesticide Contaminated Foliar Dust. J. Amer. Industr. Hygiene Assoc. 41, 652 (1980).

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Table I

Mean Dermal Exposure to Captan by Strawberry Pickers and Weeders

(1981 — Field Studies)

No. of Experiment / Occupation	Days after last application	Numbers of Subjects		Dermal Exposure	
		≤11 yrs.	≥12 yrs.	mg/hr	mg/kg/hr
1 Pickers	3	4	16	6.50 (5.08)	0.108 (0.079)
2 Pickers	26	2	21	4.70 (4.11)	0.082 (0.077)
3 Pickers	4	5	10	17.41 (14.53)	0.310 (0.200)
3 Weeders	4	2	2	94.13 (118.4)	1.784 (2.177)
4 Pickers	3	2	4	16.37 (3.78)	0.411 (0.118)
5 Pickers	48	0	10	5.88 (3.70)	0.104 (0.072)

( ) = standard deviation.

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Table II

Physical Characteristics and Exposure Results of Strawberry Workers (Weeders)

(Field Study No. 3 — 1981)

Worker I.D.	Sex	Age	Weight kg	Hours Worked	Captan Dermal Exposure mg/hr							
					Head + Neck	Back + Shoulders	Chest	Lower Leg	Upper Arm	Lower Arm	Hands	Total
12	M	8	39	2.5	0.06	0.13	2.21	0.43	0.37	0.14	0.58	3.91
16	M	13	49	2.5	56.68	0.10	3.01	0.70	5.53	0.39	5.52	71.92
20	M	11	54	2.5	93.53	0.49	7.32	0.29	5.57	157.35	2.17	266.72
26	F	12	54	2.5	0.90	0.55	28.83	2.21	0.16	0.41	0.90	33.96
										MEAN		94.13
										S.D.		118.38

Table III

Comparison of Dermal Exposure to Captan Experienced by
Adult and Children Strawberry Pickers

(1981 — Field Studies)

Expt. No.	Children ($\leq$ 11)		Adults ($\geq$ 12)	
	No. of Subjects	Exposure mg/hr	No. of Subjects	Exposure mg/hr
1	4	4.04	15	7.16
2	2	1.96	21	4.97
3	5	7.74[+]	10	22.25[+]
4	2	12.64	4	18.24
		Exposure mg/kg b.w./hr	Exposure mg/kg b.w./hr	
1	4	0.112	15	0.107
3	5	0.240	10	0.345
4	2	0.483	4	0.376

[+]Statistically signficiant at p $\leq$ 0.05.

Table IV

Comparison of Dermal Exposure to Captan Experienced by
Adult and Youth Strawberry Pickers

(1981 — Field Studies)

Expt. No.	No. of Subjects	Group	Exposure mg/hr	No. of Subjects	Group	Exposure mg/hr
1	11	Adults ($\geq$ 14)	8.67[+]	8	Youths ($\leq$ 13)	3.53[+]
2	11		4.91	12		4.53
3	7		22.03	8	-	13.37
4	3		18.15	3		14.59
			Exposure mg/kg b.w./hr			
1	11		0.126	8		0.084
2	11		0.072	12		0.091
3	7		0.300	8		0.319
4	3		0.320[+]	3		0.503[+]

[+]Significant at $p \leq 0.05$.

Table V

Linear Correlations Between Selected Variables

(1981 — Field Studies)

Variables	Correlation Coefficients				
	Experiment Number				
	1	2	3	4	5
Age vs. productivity (crates/hr)	0.67^+	0.80^+	0.59^+	0.72	0.74 (p=0.09)
Exposure (mg/hr) vs. productivity	0.76^+	0.13	0.28	0.96^+	0.83^+
Log exposure vs. productivity	0.72^+		0.28	0.96^+	
Age vs. exposure	0.62^+	0.12	0.15	0.83	0.25
Hours worked vs. exposure	-0.37 (p=0.12)	-0.39^+	-0.14	n/a	-0.64^+
Total daily exposure vs. distance covered	--	-0.22	0.15	--	--
Exposure vs. body surface area	0.51^+	0.13	0.70^+	0.79^+	-0.21
Exposure vs. body weight	0.50^+	0.11	0.70^+	0.81^+	-0.33

$^+$Statistically significant, p=0.05.

Table VI

Individual Worker's Variability of Dermal Captan Exposure

| Subject's Initials | Dermal Exposure | | Ratio |
| | mg/hr | | |
	Expt. 1	Expt. 3	Expt. 3/Expt. 1
D.R.	3.87	9.70	2.51
B.O.	2.23	9.32	4.17
J.R.	1.70	4.36	2.56

Table VII

Dermal Exposure to Captan Experienced by Male and Female Strawberry Harvesters

Experiment No.	No. of Subjects	Dermal Concentration (mg/hr)
1	6 females 13 males	10.04 (6.63)[*] 4.87 (3.35)[+]
2	11 females 12 males	3.83 (3.32) 5.51 (4.71)
3	3 females 12 males	12.29 (3.74) 18.69 (16.04)
4	3 females 3 males	18.15 (2.63) 14.59 (4.38)
5	3 females 7 males	8.43 (4.55) 4.79 (3.00)

[*]Standard Deviation.

[+]Statistically significant at $p \leq 0.05$.

Table IX

Hand and Lower Arm Exposure to Captan by Strawberry Pickers

Expt. No.	Exposure		
	Total mg/hr	Hand + Lower Arm mg/hr	% of Total (Weighted av.)
1	6.51	6.15	92.93
2	4.71	3.29	80.80
3	17.41	15.13	80.82
4	16.37	16.04	97.87
5	5.88	5.04	86.00

Hand Exposure to Captan by Strawberry Pickers

(1981 — Field Studies)

Expt. No.	No. of Subjects	Exposure		
		Total mg/hr	Hand mg/hr	% of Total (Weighted av.)
1	19	6.51	5.53	85.73
2	23	4.71	2.83	67.52
3	15	17.41	11.16	59.55
4	6	16.37	14.32	87.69
5	10	5.88	4.38	76.07

Table X

Distribution of Captan Dermal Residues on Various Parts of the Body

Worker No. 29, Field Study No. 3

Body Part	Concn. Captan mg/hr	% of Total
Head + neck	0.39	0.60
Back + shoulders	0.30	0.46
Chest + stomach	55.96	86.53
Lower legs	0.90	1.39
Upper arms	0.47	0.73
Lower arms	1.42	2.20
Hands	5.23	8.09
TOTAL	64.67	100.00

Note: Subject is a six-year old male who worked for
3.5 hours in the field and picked one crate of
strawberries.

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Table XI

Relationship Between Hourly Dermal Exposure and Dislodgeable
Foliar Residues on Strawberry Plants

(1981 — Field Experiments)

Experiment No.	Dermal Exposure mg/hr	Dislodgeable Residue ug/cm^2
1	6.50 (5.08)	2.36 (0.60)*
2	4.70 (4.11)	0.71 (0.32)
3	17.41 (14.53)	3.85 (2.84)
4	16.37 (3.78)	1.42**
5	5.88 (3.70)	1.72 (1.04)

*( ) Values are standard deviations.

**Only two values reported; no standard deviation
calculated.

Table XII

Summary

Dislodgeable Captan Residues From Strawberry Fruits

(1981 — Field Studies)

Study No.	Days Since Last Application	Sample No.	PPM Captan
2	26	1	Nondetectable
2	26	2	0.35
3	4	1	1:11
3	4	2	1.20
4	3	1	1.13
5	48	1	0.49
5	48	2	0.09

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Table XIII

Decline of Foliar Dislodgeable Captan Residues

Field Experiment No. 1

Date of Harvester Monitoring: May 9, 1981

Place: Coop A, Salinas, CA

Temp.: 73°F, 66% RH

Wind Speed: 5.7 - 9.1 mph

Pesticide Treatment: 2 lb captan, April 15-18, 23, and 26, 1981

Days Post-Application	Date	Dislodgeable Residue	
		$\mu g/cm^2$	PPM on Dust
2	April 28, 1981	9.75	63,500
8	May 4, 1981	3.03	15,500
12	May 8, 1981	0.21	1,360
13 (1)	May 9, 1981	2.05	13,600
(2)		1.71	9,870
(3)		2.04	11,000
(4)		2.85	13,900
(5)		3.13	20,700

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Table XIV

Decline of Foliar Dislodgeable Captan Residues

Field Experiment No. 2

Date of Harvester Monitoring: June 22, 1981
Place: Strawberry Farm, Corvallis, OR
Temperature: 61-67°F; some rain
Pesticide Treatments: 2.5 lb captan on May 4,
21, and 27, 1981.

Days after Treatment	Date (1981)	Dislodgeable Residue	
		µg/cm²	PPM on dust
0	May 27	7.02	306,600
0	May 27	6.90	330,100
1	May 28	9.84	237,100
1	May 28	14.70	502,700
3	May 30	4.84	15,663
3	May 30	6.31	68,143
7	June 3	6.42	113,428
7	June 3	5.07	72,222
14	June 10	1.55	20,182
14	June 10	0.65	9,924
19	June 15	0.06	904
21	June 17	4.91	69,252
21	June 17	0.75	9,665
23	June 19	2.18	26,170
23	June 19	0.41	4,795
26	June 22	0.34	4,509
26	June 22	0.58	7,733
26	June 22	0.84	12,727
26	June 22	1.08	19,285

Table XV

Decline of Foliar Dislodgeable Captan Residues

Field Experiment No. 3

Date of Harvester Monitoring: July 21, 1981
Place: Co-op A, Salinas, CA
Temperature: 53-76°F
Pesticide Treatment: 2 lb captan on April 15-18,
April 23, April 26, May 10,
May 17, May 31, June 7, July 17, 1981

Days Post-Application	Date (1981)	Dislodgeable Residue	
		µg/cm^2	PPM on dust
4	July 21	6.70	21,300
4	July 21	3.39	8,627
4	July 21	5.22	18,514
21	Aug. 11	0.97	3,688
21	Aug. 11	1.77	6,756

Table XVI

Pesticide Aerosol Concentration (Captan) Vs. Dermal

Exposure of Individual Strawberry Pickers

| Subject No./ | Aerosol Concn. | Dermal Exposures | |
Experiment No.	ug/m³	mg/hr	mg/kg/hr
6/1	2.74	2.23	0.050
13/1	6.84	4.51	0.070
17/1	8.41	8.44	0.084
18/1	70.30	14.14	0.179
1/3	258.2	56.32	0.655
11/3	127.6	9.32	0.211
13/3	109.9	17.67	0.260
22/3	210.3	16.16	0.351
27/3	175.5	7.61	0.152
3/5	22.4	3.62	0.075
6/5	26.9	2.53	0.029

Fixed Sites			
Expt. 1	0		
Expt. 3	155.1		
Expt. 5	144.4		

54

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Table XVII

Captan Soil Residue Decay: Corvallis, OR

Days Since Last Application	Date (1981)	PPM Captan
0	May 27	0
1	May 28	0.57
3	May 30	0
7	June 2	6.56
14	June 9	0
21	June 17	0
23	June 19	0
26	June 22*	0
20	June 25	0

* date of human monitoring (Field Experiment No. 2)

Table XVIII

Captan Soil Residue Decay: Co-op A, Salinas, CA

Days Since Latest Application	Date (1981)	PPM Captan
2	April 28	3.47
2	April 28	1.58
8	May 4	3.40
9	May 5	0
13	May 9*	8.63
13	May 9*	2.89
4	July 21**	6.29
10	July 27	3.77
?	July 31	9.16
?	August 7	7.93

* date of human monitoring (Field Study No. 1)

** date of human monitoring (Field Study No. 3)

Table XIX

Captan Soil Residue Decay: Co-op C, Salinas, CA

Days Since Latest Application	Date (1981)	PPM Captan
27	July 31	4.10
34	August 7	0
48	August 21*	0

*Date of human monitoring (Field Experiment No. 5)
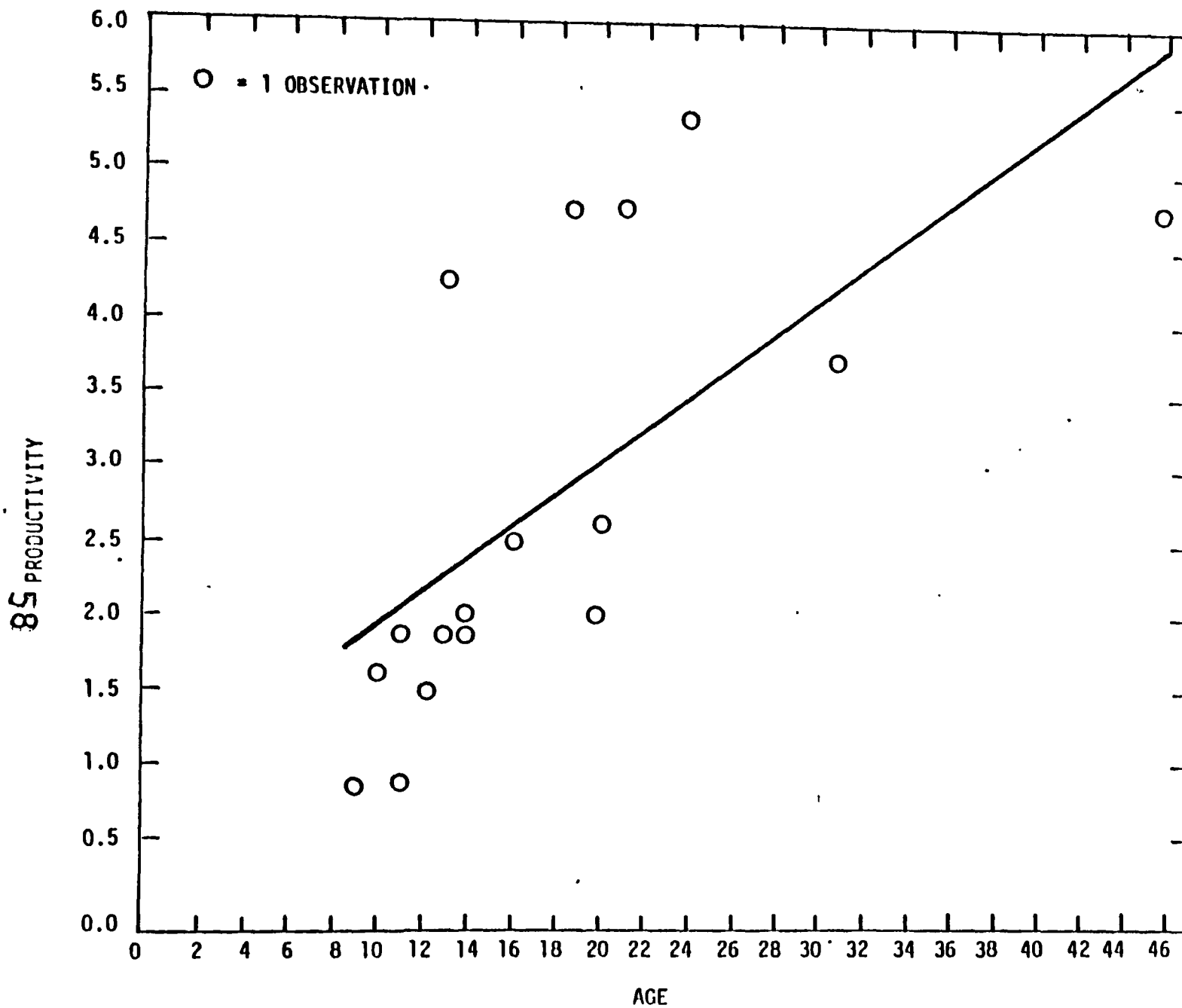
FIGURE 8.   AGE VS PRODUCTIVITY
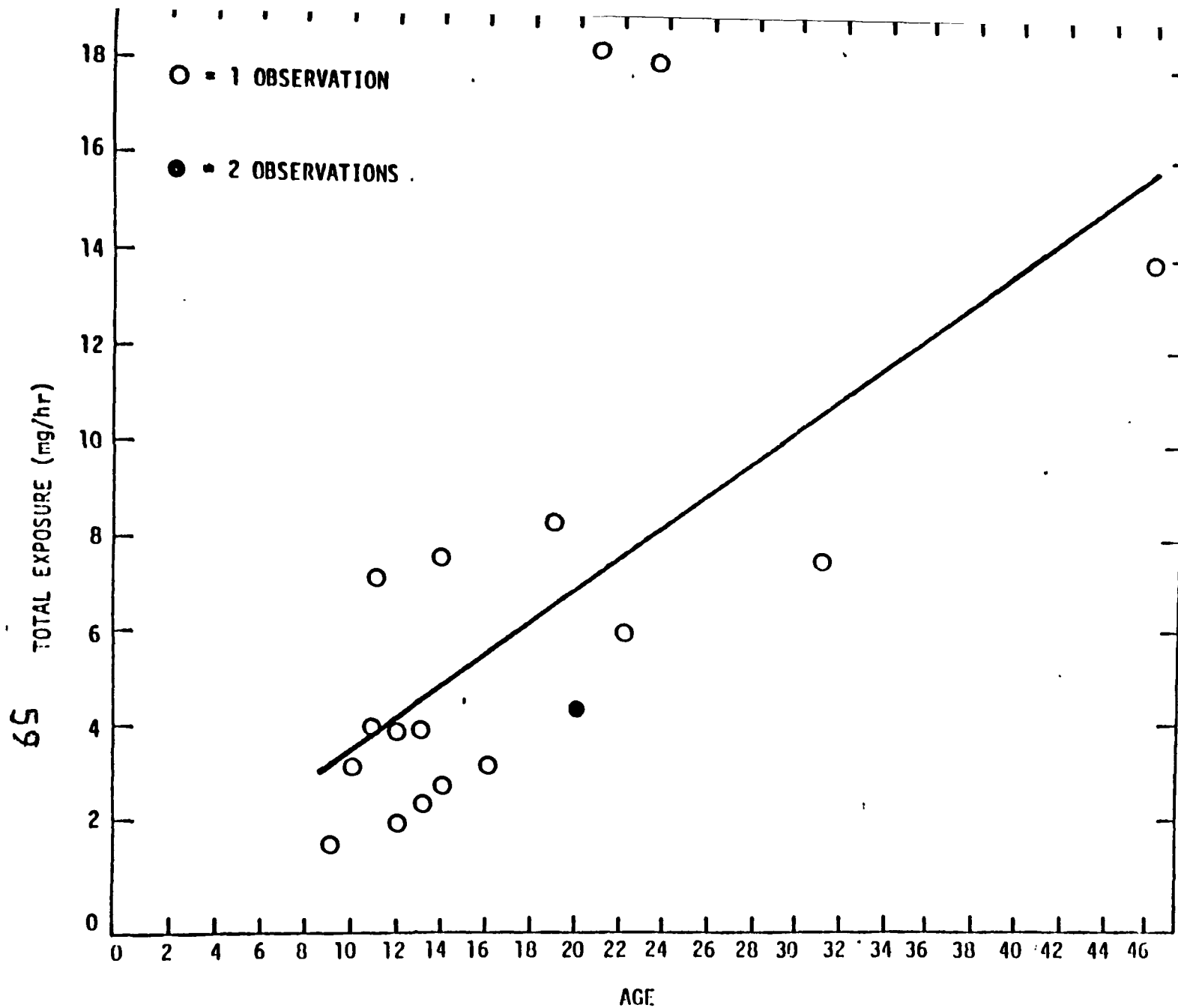
FIGURE 9. AGE VS TOTAL EXPOSURE
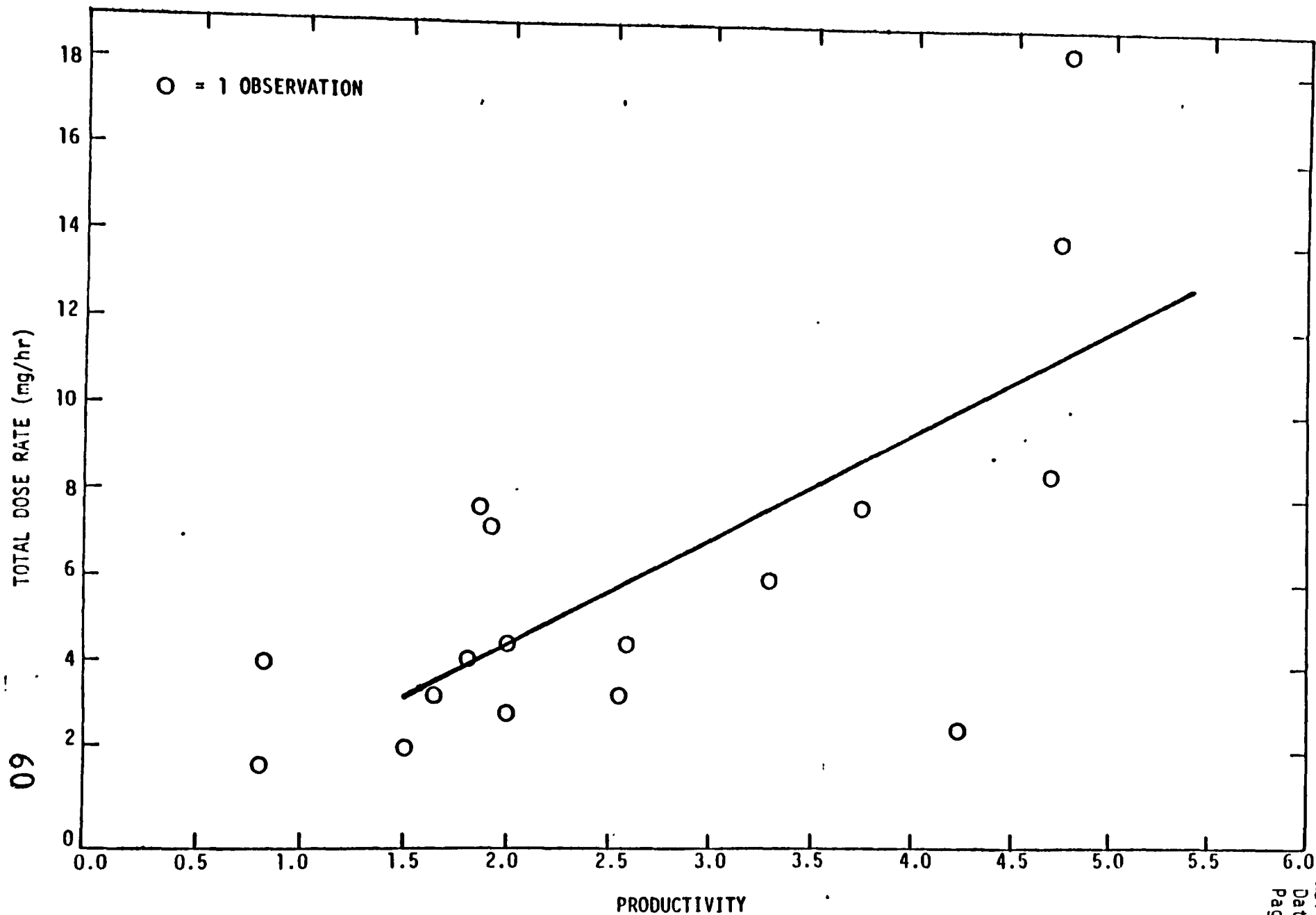
FIGURE 10. PRODUCTIVITY VS TOTAL EXPOSURE
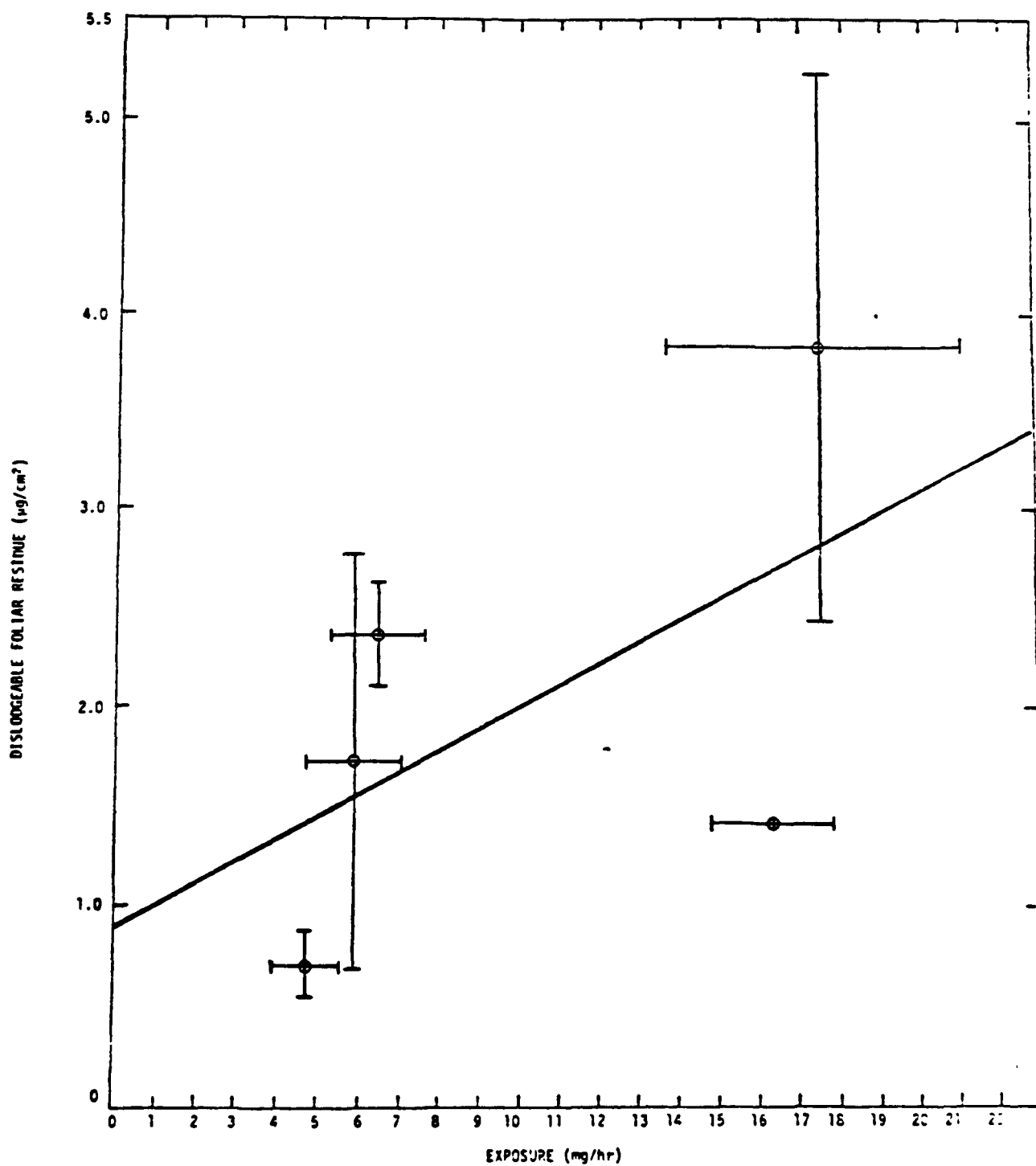
FIGURE 11. DISLODGEABLE FOLIAR RESIDUE VS, DERMAL EXPOSURE
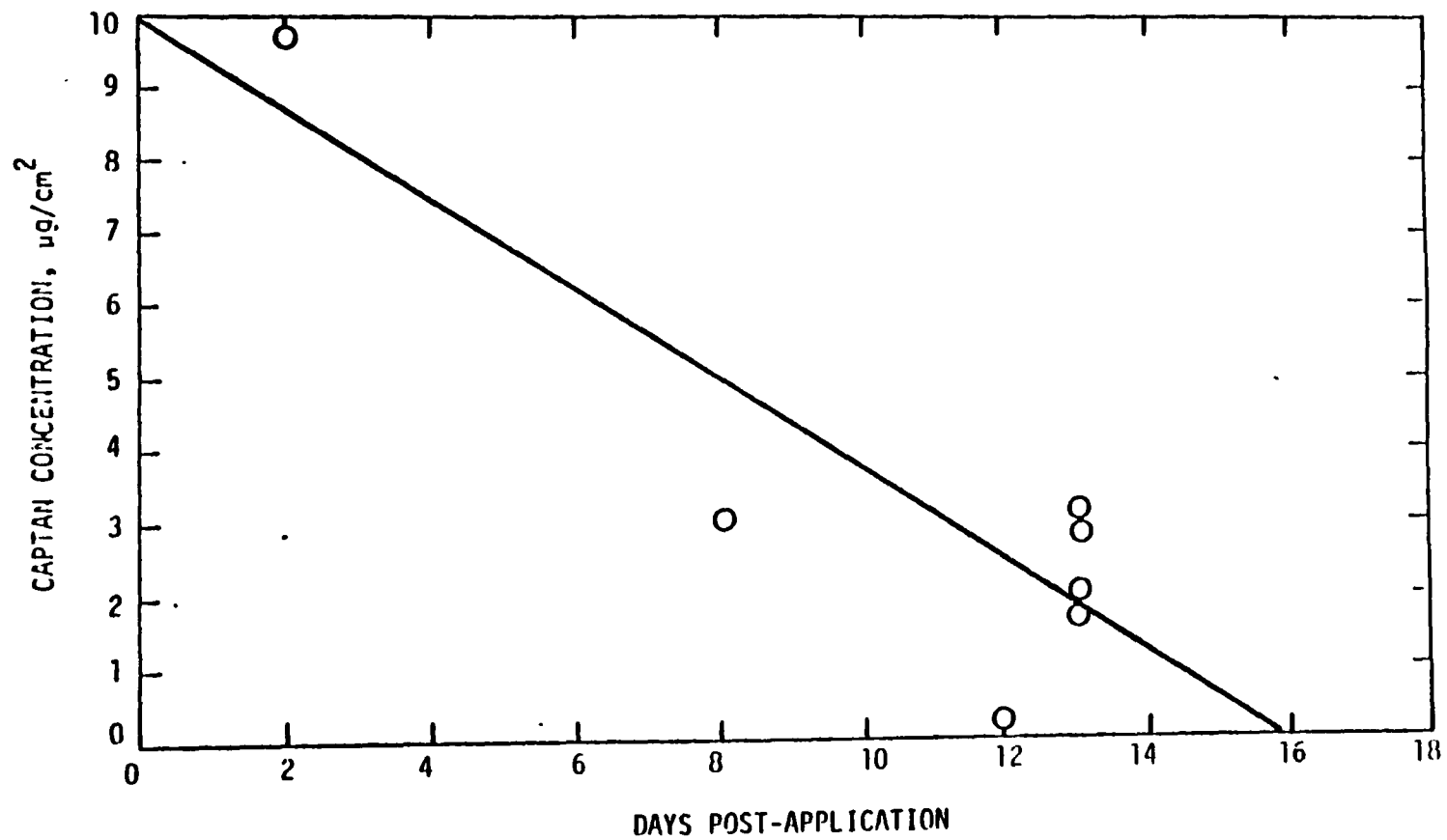
FIGURE 12.   FIELD EXPERIMENT NO. 1.   CAPTAN DISLODGEABLE RESIDUE DECLINE

DAYS POST-APPLICATION
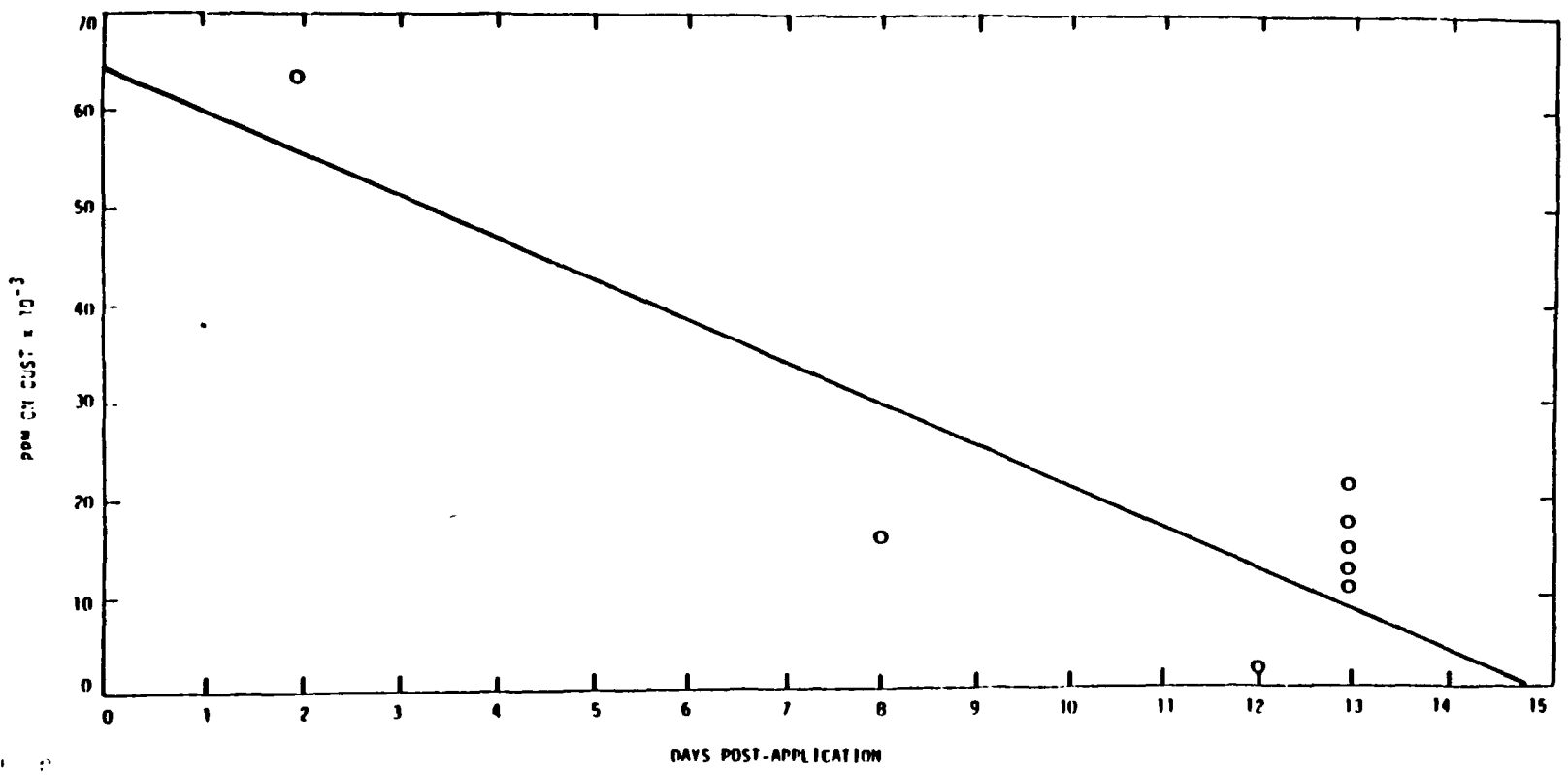
FIGURE 13. FIELD EXPERIMENT NO. 1. DISLODGEABLE FOLIAR RESIDUE DECLINE .
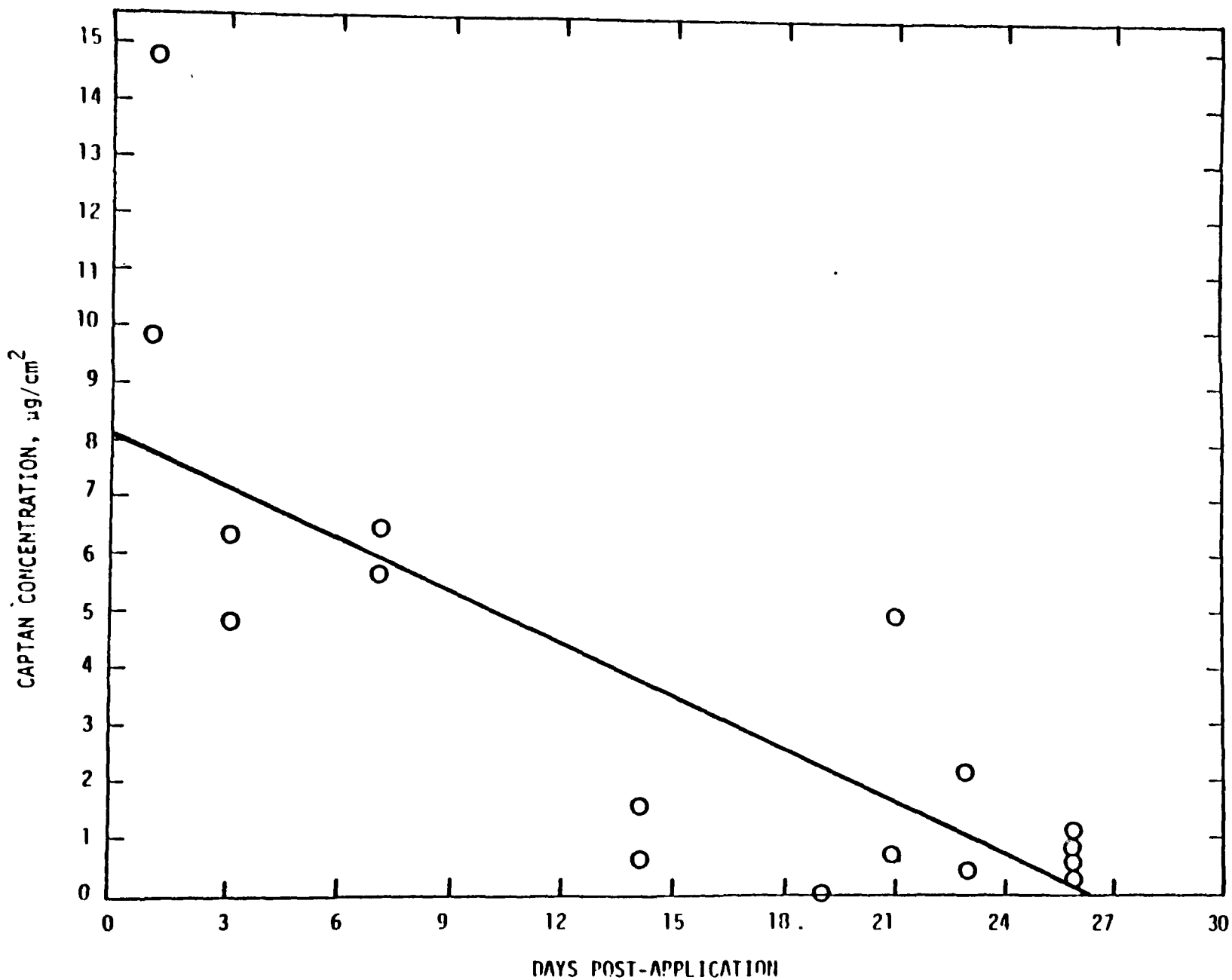
FIGURE 14.   FIELD EXPERIMENT NO. 2.   CAPTAN DISLODGEABLE RESIDUE DECLINE

PPM ON DUST x 10^{-3}

DAYS POST-APPLICATION
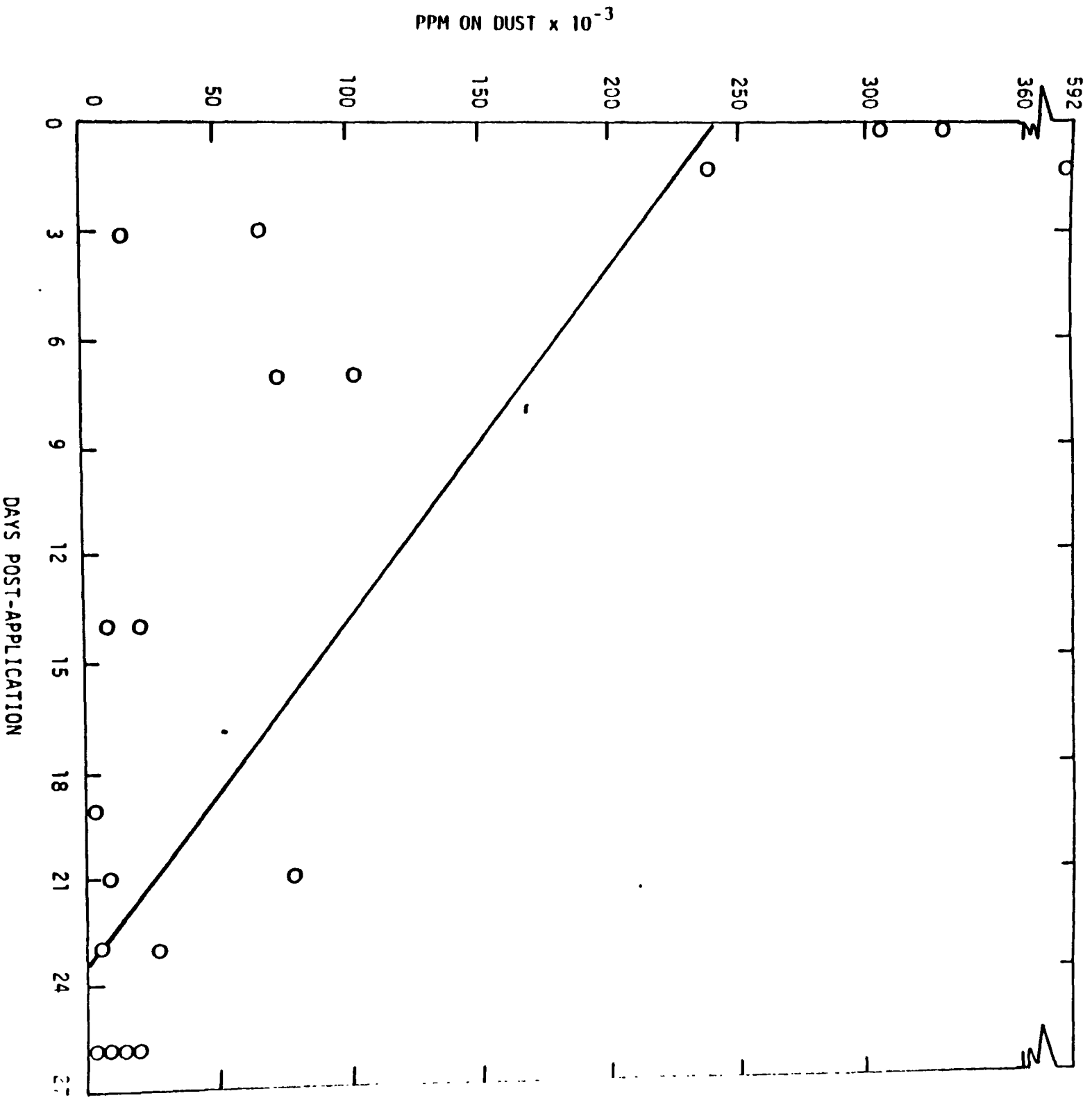
FIGURE 15. FIELD EXPERIMENT NO. 2. CAPTAN DISLODGEABLE RESIDUE DECLINE
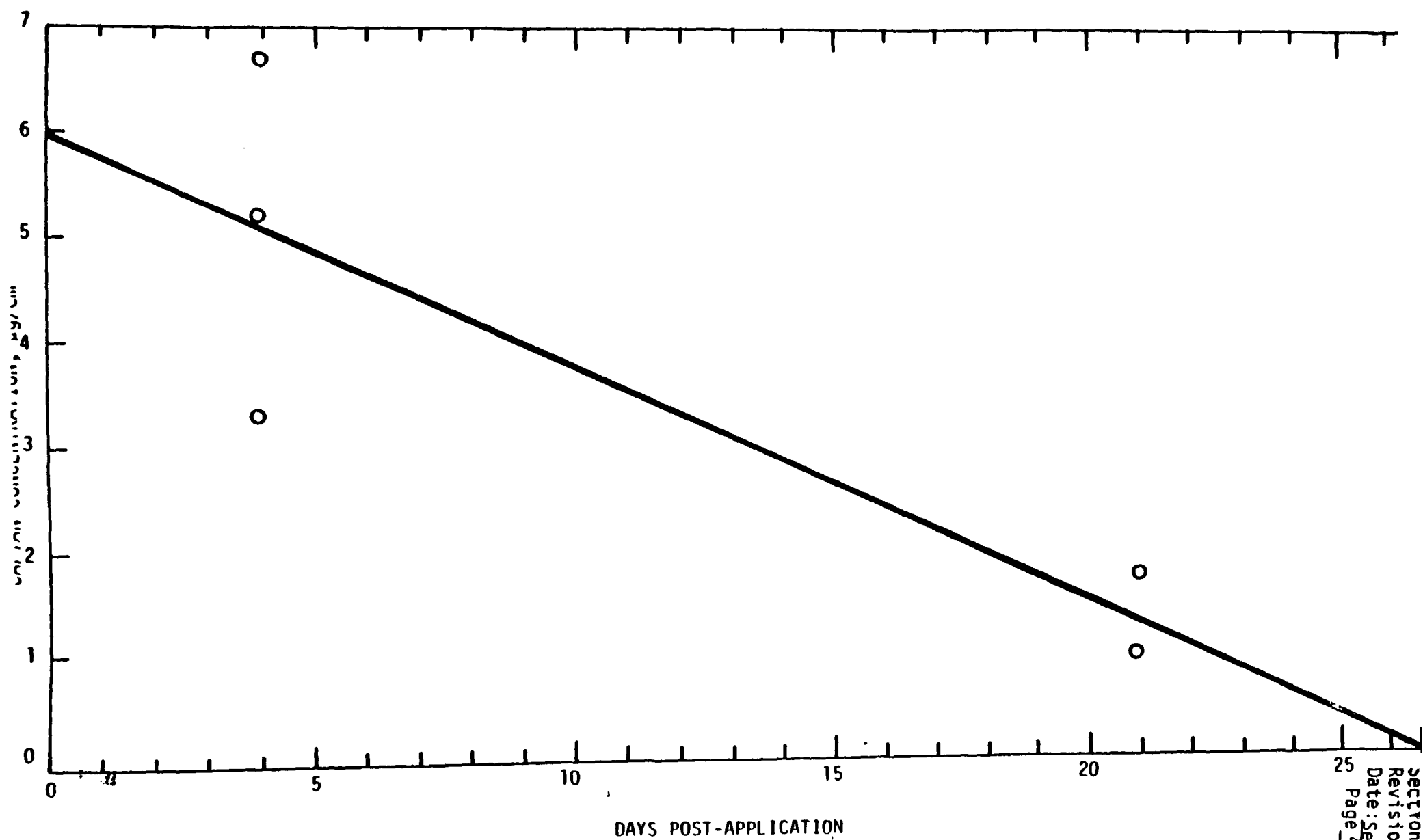
FIGURE 16. FIELD EXPERIMENT NO. 3. CAPTAN DISLODGEABLE RESIDUE DECLINE

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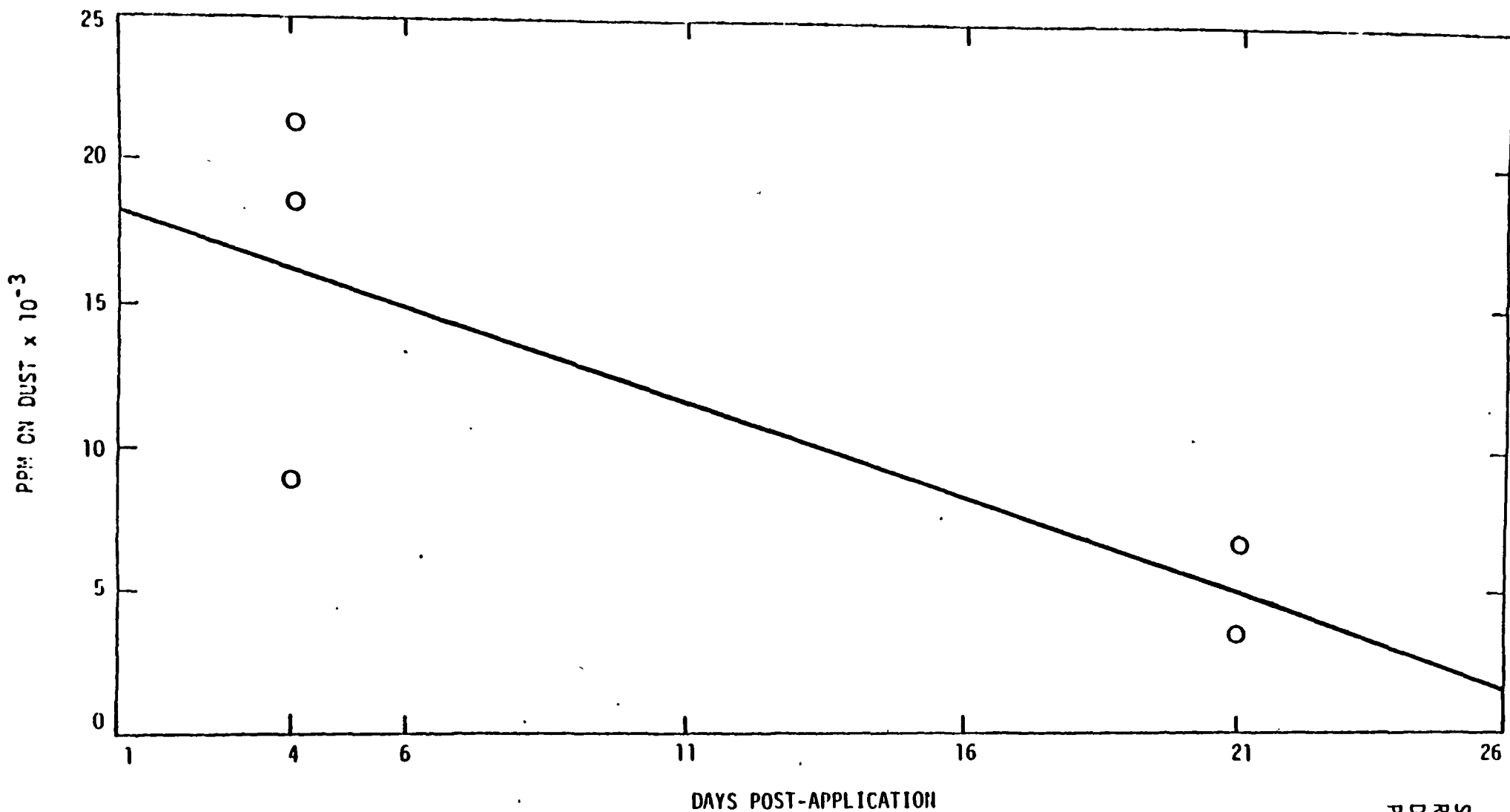
FIGURE 17. FIELD EXPERIMENT NO. 3. DISLODGEABLE FOLIAR RESIDUE DECLINE
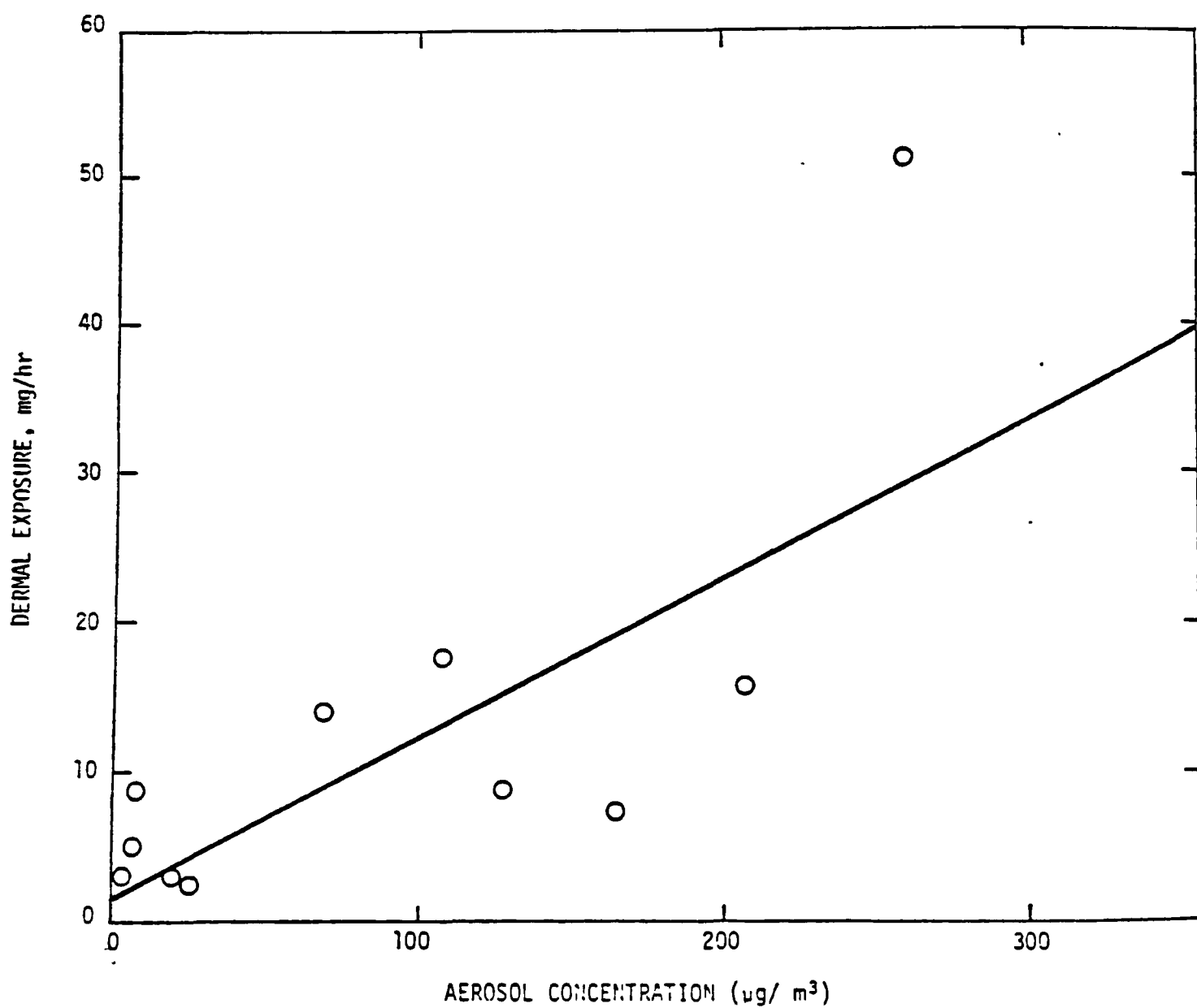
FIGURE 18.   AEROSOL CONCENTRATION VS. DERMAL EXPOSURE (mg/hr)

AEROSOL CONCENTRATION (µg/ m³)
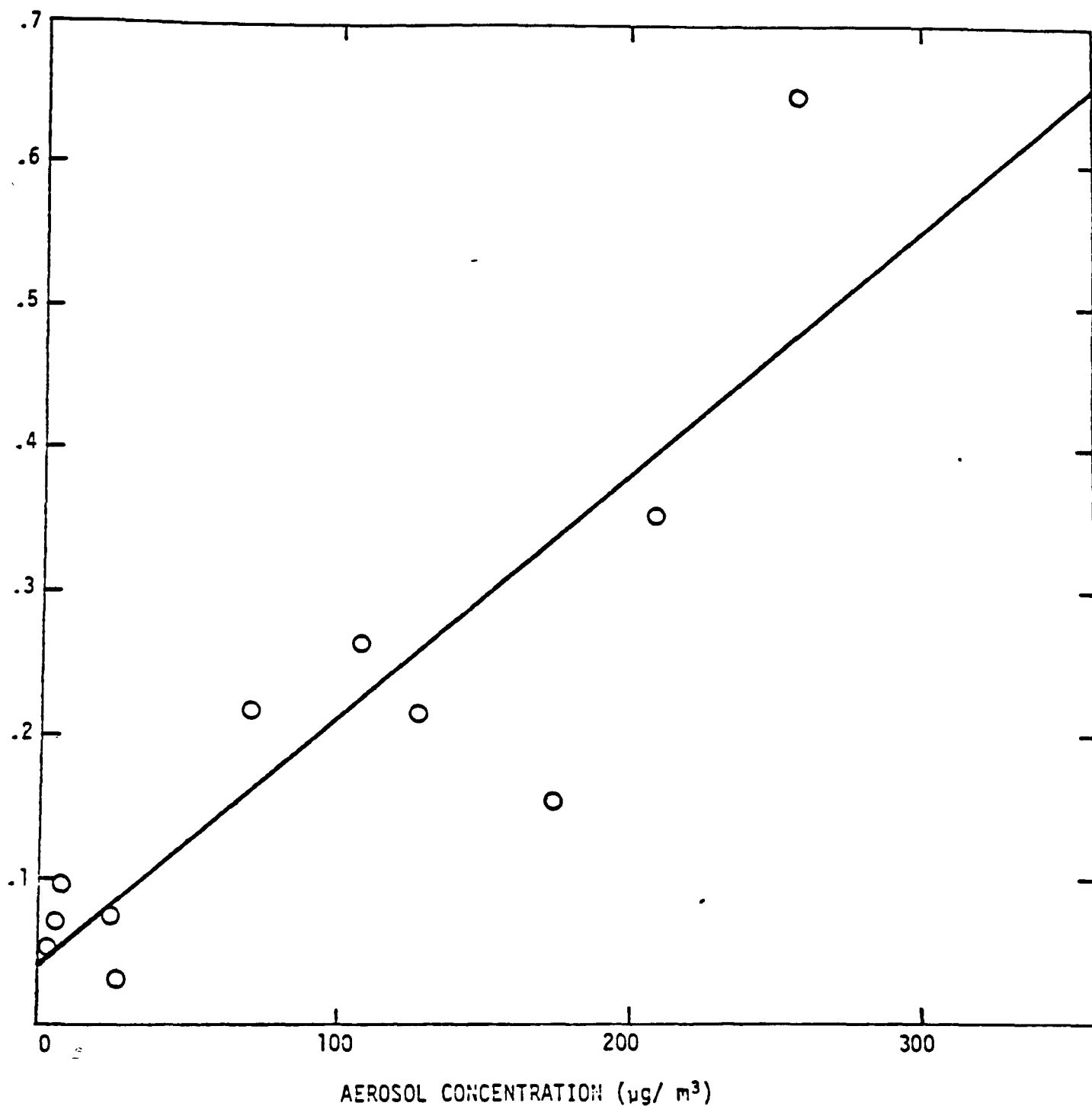
FIGURE 19. AEROSOL CONCENTRATION VS. DERMAL EXPOSURE (mg/kg b.w./hr)

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REFERENCES

1. Carman, G. E., Gunther, F. A., Blinn, R. C. and Garmus, R. D. The
   Physical Fate of Parathion Applied to Citrus. J. Econ. Entomol.
   45 (5), 767 (1952).

2. Griffith, R. L. and Mathews, S. The Persistence in Soil of the
   Fungicidal Seed Dressings of Captan and Thiram. Ann. Appl. Biol. 64.
   113-118 (1969).

3. Kluge, E. Der Einfluss der Bodenreaktion auf den Abbau und die Wirkungsdauer
   von Thiuram, Ferbam, und Captan im Boden. Arch. Pflanzenschutz, 5,
   263-271 (1969).

4a. Maddy, Keith, T., Kahn, C. S., Riddle, L., and Alexander, J. A Breakdown
    Study of Captan (Orthocide) on Strawberry Foliage and Fruit in
    Ventura County, California, April, 1977. Worker Health and Safety
    Unit, Div. of Pest Management, Environmental Protection and Worker
    Safety, CDFA, Sacramento, California, Report No. HS-372 (June 20, 1977).

4b. Maddy, Keith, T., Edminston, S., Kahn, C. S., Jackson, T., and Frederickson,
    A. Scott. A Study of the Decay of Captan on the Foliage and Fruit of
    Strawberries in Santa Cruz County, May 1977. Ibid., ACF 59-376
    (June 16, 1977).

5. Munnecke, Donald E. The Persistence of Nonvolatile Diffusible Fungicides
   in Soil. Phytopathology, 48, 581-585 (1958).

6. Popendorf, W. J. Exploring Citrus Harvesters' Exposure to Pesticide
   Contaminated Foliar Dust. J. Amer. Industr. Hygiene Assoc. 41,
   652 (1980).

7. Popendorf, W. J. and Leffingwell, J. T. Regulating OP Pesticide Residues
   for Farmworker Protection. Residue Reviews 82, 125 (1982).

8. Spear, R. C., Popendorf, W. J., Leffingwell, J. T., Milby, T. H.,
   Davies, J. E., and Spencer, W. F. Field Workers' Response to
   Weathered Residues of Parathion. J. Occup. Med. 19, 406 (1977).

APPENDIX

. Body Surface of the 50-Percentile Man

. Data From Field Study 1

. Data From Field Study 2

. Data From Field Study 3

. Data From Field Study 4

. Data From Field Study 5

Table A-1

Body Surface of the 50-Percentile Man

Body Parts	Surface Area (cm^2)
Head and neck	1300
Back and shoulder	2190
Chest and stomach	2190
Upper leg	3460
Lower leg	2590
Feet	1230
Upper arm	1860
Lower arm	1290
Hands	1075*

1
 Popendorf and Leffingwell, 1982

*
 Hand surface was not used for total body exposure because glove dosimeter covered entire surface of hand (see text for details).

Field Study No. 1

Site and Location: Cooperative Farm A, Salinas, California

Date of Study: May 9, 1981

Weather: temp.: med. 73°F; humidity: 66% R.H.; wind speed: 5.7-9.1 mph

Number and age of subjects: age 11 and under: 4; age 12 and over: 16

Table A-2

Pesticide Spray History, 1981, Cooperative A, California

Date of Application	Pesticides	Product/A	AI/A	Method of Application/ Final Volume
2/7/81	Lannate SP (90%)	1.0 lb.	0.9 lb.	Ground
	Thiodan 2E	1.0 gal.	2.0 lb.	3-400 gal/A
	Dithane Z 78 (75%)(ziram)	3.25 lb.	2.4 lb.	
2/25/81	Sevin Bait (5%)	1.5 lb.	0.075 lb.	Ground
3/23 - 3/24/81	Plictran 50W	1.5 lb.	0.75 lb.	Ground
	Diazinon 50W	2.0 lb.	1.0 lb.	3-400 gal/A
	Topsin M 70W	1.0 lb.	0.7 lb.	
3/25/81	Topsin M 70W	1.0 lb.	0.7 lb.	Ground
	Plictran 50W	2.0 lb.	1.0 lb.	3-400 gal/A
	Diazinon 50W	1.0 lb.	0.5 lb.	
	Bufferol, Spray Film B			
	Cytrol (amitrole) (2 lb./gal.)	1.0 gal	1.0 lb.	
4/15 - 4/18/81	Ortho Plictran 50W	2.0 lb.	1.0 lb.	Ground
	Ortho Malathion 25WP	3.0 lb.	0.75 lb.	3-400 gal/A
	Dupont Benlate 50W	1.0 lb.	0.5 lb.	
	Ortho Orthocide 50W	4.0 lb.	2.0 lb.	
4/23/81	Orthocide 50W	4.0 lb.	2.0 lb.	Air
	Benlate DP 50	1.0 lb.	0.5 lb.	20 gal/A
	Bufferol			
4/26/81	Orthocide 50W	4.0 lb.	2.0 lb.	Air
	Benlate 50W	1.0 lb.	0.5 lb.	20 gal/A
	Malathion 25	4.0 lb.	1.0 lb.	
	Bufferol	1.0 pt.	1.0 pt.	

Table A-2 (continued)

Date of Application	Pesticides	Product/A	AI/A	Method of Application/ Final Volume
5/10/81	Mevinphos 4E	1.5 pt.	0.75 lb.	Air
	Benlate DP	1.0 lb.	0.5 lb.	20 gal/A
	Orthocide 50W	4.0 lb.	2.0 lb.	
	Bufferol	1.0 pt.	1.0 pt.	
5/17/81	Dibrom 8E	1.0 pt.	1.0 lb.	Air
	Benlate 50W	1.0 lb.	0.5 lb.	20 gal/A
	Orthocide 50W	4.0 lb.	2.0 lb.	
	Bufferol	1.0 pt.	1.0 pt.	
5/31/81	Plictran 50W	2.0 lb.	1.0 lb.	Ground
	Dibrom 8E	1.0 pt.	1.0 lb.	3-400 gal/A
	Topsin M (70W)	1.0 lb.	0.7 lb.	
	Orthocide (50W)	3.0 lb.	1.5 lb.	
	Bufferol	1.0 gal.	1.0 gal.	
6/7/81	Dibrom 8E	1.0 pt.	1.0 lb.	Air
	Benlate 50W	1.0 lb.	0.5 lb.	20 gal/A
	Orthocide 50W	4.0 lb.	2.0 lb.	
	Bufferol	1.0 pt.	1.0 pt.	
6/27 - 6/28/81	Diazinon 50W	2.0 lb/A	1.0 lb.	Ground rig
	Dicofol 4E	2.0 qt.	2.0 lb.	3-400 gal/A
	Topsin M 70W	1.0 lb.	0.7 lb.	
	Bufferol	1.0 gal.	1.0 gal.	
6/28/81	Dibrom 8E	1.0 pt.	1.0 lb.	Air
	Oxyflow Sulfur (6 lb./gal.)	1.0 qt.	1.5 lb.	10-20 gal/A
	Bufferol	1.0 gal.	1.0 gal.	

Table A-2 (continued)

Date of Application	Pesticides	Product/A	AI/A	Method of Application/ Final Volume
7/7/81	Dicofol 4E	2.0 qt.	2.0 lb.	Ground
	Dibrom 8E	1.0 pt.	1.0 lb.	3-400 gal/A
	Thiram 65W	2.0 lb.	1.3 lb.	
	Bufferol	1.0 gal.	1.0 gal.	
7/17/81	Phosdrin 4E	1.0 qt.	1.0 lb.	Air
	Oxyflow Sulfur (6 lb./gal)	1.0 qt.	1.5 lb.	20 gal/A
	Orthocide 50W	4.0 lb.	2.0 lb.	

Table A-3

Physical Characteristics and Work Habits of Strawberry Pickers

Field Study No. 1 - 1981

Worker I.D.	Sex	Age	Weight kg	Productivity crates/hr	Hours Worked	Body Surface m^2
1	M	10	34	1.64	5.50	1.2
3	M	9	34	0.82	9.78	1.1
4	F	11	39	0.82	9.78	1.2
6	M	13	44	4.27	6.33	1.4
7	M	11	36	1.88	5.33	1.2
8	M	12	52	n/a	4.0	1.5
9	F	14	54	1.76	6.25	1.6
10	M	14	66	2.03	4.92	1.7
11	M	12	59	1.46	8.25	1.6
12	M	20	61	2.57	8.17	1.7
13	M	20	64	1.98	6.58	2.0
14	F	24	86	5.39	7.42	2.0
15	M	22	73	3.10	5.17	1.8
16	M	31	75	3.73	4.83	1.9
17	F	19	100	4.72	7.42	2.1
18	M	46	79	4.76	5.25	1.9
19	M	16	70	2.56	6.25	1.9
22	F	21	52	4.80	4.17	1.5
23	F	13	66	1.82	5.50	1.7
24	M	50	66	4.09	5.62	1.6

Table A-4

Exposure Results of Strawberry Pickers

Field Study No. 1 - 1981

Worker I.D.	Dermal Exposure (Captan)				
	Total			Hands Only	
	mg/kg	/hr*	mg/hr	mg/hr	%Total
1	0.099	3.37		3.09	91.79
3	0.050	1.70		1.53	90.15
4	0.099	3.87		3.30	85.32
6	0.050	2.23		1.98	88.47
7	0.200	7.20		6.39	88.74
8	0.076	3.94		3.62	91.91
9	0.139	7.53		6.41	85.14
10	0.045	2.98		2.85	95.67
11	0.035	2.04		1.93	94.46
12	0.075	4.60		3.71	80.65
13	0.070	4.51		4.07	90.34
14	0.209	18.00		12.88	71.50
15	0.080	5.86		5.37	91.63
16	0.102	7.64		6.67	87.32
17	0.084	8.44		8.06	95.44
18	0.179	14.14		11.25	79.61
19	0.045	3.14		1.56	49.54
22	0.356	18.51		17.27	93.30
23	0.059	3.89		3.02	77.76
MEANS	0.108	6.50		5.53	85.73
S.D.	(0.079)	(5.08)		(4.25)	(10.89)

* kg of body weight

Table A-5

Comparison of Captan Exposure By Different Groups of Strawberry Pickers
Total Dermal Exposure (per hour)

Field Study No. 1 - 1981

Group	Average Age	No. of Subjects	Captan Concentration (mg/hr)		Statistics p-Values*		
			Mean	S.D.	(1)	(2)	(3)
Adults ($\neq$12)	19.8	15	7.16	5.46	0.286	0.250	0.211
Children ($\doteq$11)	10.25	4	4.04	2.31			
Adults ($\leq$14)	22.5	11	8.67+	5.67	0.015	0.008	0.012
Youths ($\geq$13)	11.4	8	3.53+	1.74			
Female		6	10.04+	6.63	0.120	0.036	0.059
Male		13	4.87+	3.35			

*(1) Assuming normal distribution of data
 (2) Assuming nat. log normal distribution of data (skewed)
 (3) Wilcoxon nonparametric test

+p $<$ 0.05 is considered significantly different (95% probability)

Table A-6

Comparison of Captan Exposure by Different Groups of Strawberry Pickers

Total Dermal Exposure Normalized for Body Weight (mg/kg/hr)

Field Study No. 1 - 1981

Group	No. of Subjects	Captan Concentration (mg/kg/hr)		Statistics p-Values*		
		Mean	S.D.	(1)	(2)	(3)
Adults ($\geq$12)	15	0.107	0.085	0.915	0.690	0.582
Children ($\geq$11)	4	0.112	0.063			
Adults ($\geq$14)	11	0.126	0.093	0.262	0.231	0.302
Youths ($\geq$13)	8	0.084	0.053			
Female	6	0.158	0.110	0.174	0.057	0.059
Male	13	0.085	0.051			

*(1) Assuming normal distribution of data
(2) Assuming nat. log normal distribution
(3) Wilcoxon nonparametric test

Table A-7

Captan Dermal Exposure to Various Parts of the Body

Field Study No. 1 - 1981   (19 subjects)

Body Part	Exposure		Weighted average
	mg/hr		Percent of total *
	Mean	S.D.	
Head + neck	- 0.032	(0.040)	0.65%
Back + shoulder	0.084	(0.186)	1.37
Chest + stomach	0.044	(0.078)	1.17
Lower leg	0.165	(0.179)	3.30
Upper arms	0.034	(0.054)	0.59
Lower arms	0.622	(1.179)	7.20
Hands	5.525	(4.248)	85.73
Total	6.505	(5.080)	100.00
Other than hands	0.981	(1.202)	14.27

*

Note: Average percentages are calculated as averages of individual percentages which explains the discrepancy between these values shown in the table and calculated percentages based on the means.

Table A-8

Aerosol Concentration of Captan on Individual Workers

Field Study No. 1 - 1981

Subject No.	Aerosol Concn. $\mu g/m^3$	Dermal Exposure mg/hr	Dermal Exposure mg/kg/hr
6	2.74	2.23	0.050
13	6.84	4.51	0.070
17	8.41	8.44	0.084
18	70.3	14.14	0.179

Table A-9

Pearson Correlation Coefficients for Variables

Field Experiment No. 1 - 1981

Variables	Correlation Coefficients
Age vs productivity	0.669^{+}
Total exposure vs productivity	0.755^{+}
Log total exposure vs productivity	0.715^{+}
Age vs. total exposure	0.615^{+}
Hours worked vs total exposure	$- 0.369$ (p=0.12)

$^{+}$ Statistically significant at $p \leq 0.05$

Field Study No. 2

Site and Location: Farm in Corvallis, Oregon

Date of Study: June 22, 1981

Weather: temp.: 61-67°F; some rain; 77-93% R.H.; no wind (1.3÷2.1 mph)

Number and age of subjects: 23 (ages 11-38)

Table A-9

Pearson Correlation Coefficients for Variables

Field Experiment No. 1 - 1981

Variables	Correlation Coefficients
Age vs productivity	0.669[+]
Total exposure vs productivity	0.755[+]
Log total exposure vs productivity	0.715[+]
Age vs. total exposure	0.615[+]
Hours worked vs total exposure	- 0.369 (p=0.12)

Statistically significant at $p \leq 0.05$

Field Study No. 2

Site and Location: Farm in Corvallis, Oregon

Date of Study: June 22, 1981

Weather: temp.: 61-67°F; some rain; 77-93% R.H.; no wind (1.3-2.1 mph)

Number and age of subjects: 23 (ages 11-38)

Table A-10

Pesticide Spray History; Strawberry Farm in Crovallis, Ore. During 1981

Crop: Strawberries (Benton)

Acres: 15

Application Equip: Side delivery air blast sprayer
                     @ 20 gallons finished spray/acre

Date	Pesticide	Formulation	Rate Form	AI	PHI
May 4	Thiodan	50% WP	2 lb/ac	1.0 lb/ac	
	Captan	50% WP	5 lb/ac	2.5 lb/ac	49 days
	+ B-1956 (spr-stick)				
May 11	Benlate	50% WP	1 lb/ac	0.5 lb/ac	42 days
	+ Ag-98 (spr-stick)				
May 21	Captan	50% WP	5 lb/ac	2.5 lb/ac	32 days
May 27	Captan	50% WP	5 lb/ac	2.5 lb/ac	26 days
	Benlate	50% WP	1 lb/ac	0.5 lb/ac	
	Sevin	80% WP	1 1/3 lb/ac	1.0 lb/ac	
	MSR	2 ℓ/G	1 1/2 pts/ac	0.38 lb/ac	
	+ AG-98 (spr-stick)				
June 22	Harvest				0 days

Table A-11

Captan Dermal Exposure By Various parts of the Body

Field Study No. 2 - 1981 (23 subjects)

| Body Part | mg/hr | | Exposure |
	Mean	S.D.	Weighted Average Percent of Total
Head + neck	0.174	0.573	2.92
Back + shoulder	0.247	0.982	3.36
Chest + stomach	0.047	0.106	1.15
Lower legs	0.503	1.565	6.96
Upper arms	0.452	1.800	4.82
Lower arms	0.460	0.594	13.28
Hands	2.825	2.862	67.52
Total	4.707	4.107	100.00
Other than hands	1.882	2,806	32.48

Table A-12

Physical Characteristics and Work Habits of Strawberry Pickers

Field Study No. 2 - 1981

Worker I.D.	Sex	Age	Weight kg	Productivity crates/hr	Distance covered ft	Hours worked	Body Surface m²
1	F	26	57	1.45	202	6.92	1.6
2	F	15	60	1.01	225	5.92	1.6
3	F	38	60	1.59	225	5.92	1.6
4	F	13	41	1.28	180	6.25	1.3
5	M	38	68	1.90	324	6.85	1.8
6	F	37	82	1.65	324	6.85	1.9
7	M	13	49	0.85	180	6.57	1.4
8	M	17	71	1.26	270	6.33	1.9
9	M	13	70	0.92	174	6.50	1.2
10	M	13	70	0.92	180	6.50	1.8
11	F	13	42	0.71	90	6.50	1.4
12	F	13	79	0.31	59	6.50	1.8
13	F	20	70	1.57	239	6.37	1.8
14	M	17	72	1.04	180	6.25	1.9
15	M	13	60	1.20	180	5.75	1.7
16	M	12	43	0.64	119	6.38	1.4
17	F	26	93	0.97	180	6.58	2.1
18	F	38	67	1.73	225	6.92	1.8
19	F	13	48	0.82	225	6.50	1.5
20	M	11	35	0.64	180	6.25	1.2
21	M	11	44	0.54	90	6.28	1.4
22	M	12	45	0.83	180	6.50	1.4
23	M	14	61	1.36	324	6.85	1.6

Table A-13

Exposure Results of Strawberry Pickers

Field Study No. 2 - 1981

Worker I.D.	Dermal Exposure (Captan)			
	Total		Hands Only	
	mg/kg / hr*	mg/hr	mg/nr	% Total
1	0.104	5.94	2.86	48.14
2	0.038	2.26	1.72	76.18
3	0.073	4.39	4.34	98.80
4	0.011	0.45	0.30	66.16
5	0.155	10.51	1.18	11.22
6	0.058	4.72	2.48	52.70
7	0.240	11.77	4.43	37.64
8	0.019	1.37	1.32	95.80
9	0.055	3.86	2.36	61.23
10	0.041	2.87	1.58	55.20
11	0.293	12.32	3.09	25.09
12	0.027	2.16	1.65	78.45
13	0.061	4.27	3.75	87.94
14	0.205	14.73	13.38	90.80
15	0.154	9.24	8.00	86.44
16	0.076	3.26	2.31	70.80
17	0.011	1.05	0.70	66.58
18	0.053	3.53	3.07	86.98
19	0.021	1.00	0.87	87.00
20	0.033	1.16	0.93	80.14
21	0.063	2.77	0.64	23.09
22	0.077	3.45	3.06	88.65
23	0.020	1.19	0.93	77.77
MEANS	0.082	4.70	2.83	67.52
S.D.	(0.077)	(4.11)	(2.86)	(24.68)

* kg of body weight

Table A-14

Comparison of Captan Exposure by Different Groups of

Strawberry Pickers

Field Study No. 2 - 1981

Dermal Exposure Expressed in mg/hr

Group	Average Age	No. of subjects	Captan Conc. mg/hr		Statistics p-Values *		
			Mean	S.D.	(1)	(2)	(3)
Adults (≥12)	19.71	21	4.97	4.20	0.33	0.35	0.25
Children (≤11)	11.00	2	1.96	1.14			
Adults (≥14)	26.00	11	4.91	4.24	0.83	0.67	0.48
Youths (≤13)	12.50	12	4.53	4.16			
Females		11	3.83	3.32	0.34	0.36	0.56
Males		12	5.51	4.71			

Dermal Exposure Expressed in mg/kg/hr

Group	Average Age	No. of subjects	Captan Conc. mg/hr		Statistics p-Values *		
Adults (≥12)			0.085	0.080	0.52	0.76	0.79
Children (≤11)			0.048	0.021			
Adults (≥14)			0.072	0.060	0.57	0.74	0.74
Youths (≤13)			0.091	0.091			
Females			0.068	0.080	0.42	0.24	0.65
Males			0.095	0.075			

*(1) Assuming normal distribution of data
(2) Assuming natural log normal distribution
(3) Wilcoxon nonparametric test

Table A-15

Pearson Correlation Coefficients for Variables

Field Experiment No. 2 - 1981

Variables	Correlation Coefficient
Age vs Productivity	0.795 [+]
Hours worked vs total exposure	-0.394 [+]
Productivity vs total exposure	0.127
Productivity vs log total exposure	0.173
Age vs total exposure	0.120

[+] Statistically significant at $p \leq 0.05$

Field Study No. 3

Site and Location: Cooperative Farm A, Salinas, California

Date of Study: July 21, 1981

Weather: fog early morning; temp. 53-59°F, early morning, rising to 76°
in the afternoon. little wind in the morning (2.3-3.0 mph).
gusts of wind in the afternoon (16-20 mph).

Number and age of subjects: 15 pickers (ages 8-42); 4 weeders, 1 extra (6 yrs)

Table A-16

Physical Characteristics and Work Habits of Strawberry Pickers

Field Study No. 3 - 1981

Worker I.D	Sex	Age	Weight kg	Distance covered ft	Productivity crates/hr	Hours Worked	Body Surface m^2
1	M	21	96	n/a	3.49	5.73	2.00
3	M	42	68	1800	2.23	6.70	1.75
4	F	11	41	3000	3.04	5.92	1.30
5	F	11	32	1200	0.84	7.17	1.10
7	M	9	27	600	1.02	3.92	1.00
9	M	10	35	1500	1.69	5.90	1.00
10	M	17	61	2700	2.79	7.17	1.70
11	M	13	44	1800	2.02	6.42	1.40
13	M	18	68	2400	2.51	7.17	1.80
14	F	27	71	675	1.82	5.50	1.80
15	M	15	51	1800	1.67	7.17	1.50
17	M	27	84	1200	3.75	4.80	1.95
18	M	41	73	6000	7.69	6.50	1.80
19	F	23	50	1200	3.20	3.75	1.45
21	M	11	36	n/a	n/a	4.67	1.20
22	M	13	46	1800	1.71	7.00	1.35
23	F	27	60	1500	2.15	6.50	1.55
27	M	17	50	1200	2.61	3.83	1.50
28	M	12	54	600	1.14	3.50	1.50
29	M	6	22	600	0.29	3.42	0.90

Table A-17

Exposure Results of Strawberry Pickers

Field Study No. 3 - 1981

Worker [1] I.D.	Dermal Exposure (Captan)			
	Total		Hands Only	
	mg/kg b.w./hr	mg/hr	mg/hr	% Total
1	0.655	56.32	36.82	65.38
3	0.169	11.53	5.19	45.04
4	0.237	9.70	7.04	72.61
5	0.331	10.59	3.29	31.09
7	0.470	12.70	8.14	64.10
9	0.125	4.36	3.00	68.80
10	0.360	21.91	13.84	63.15
11	0.211	9.32	6.85	73.50
13	0.260	17.67	13.95	78.91
14	0.233	16.57	4.62	27.87
17	0.270	22.62	14.65	64.74
21	0.038	1.37	0.36	25.95
22	0.351	16.16	11.33	70.09
27	0.152	7.61	4.86	63.79
28	0.791	42.74	33.43	78.22
(29	2.940	64.67	5.23	8.09)
MEAN VALUES	0.310	17.41	11.16	59.55
S.D.	(0.200)	(14.53)	(10.66)	(18.03)

Subjects 15, 19, and 23 were deleted due to failure to wear gloves throughout the study. Subject 29 was deleted as explained in the text.

Table A-18

Comparison of Captan Dermal Exposure by Different Groups

of Strawberry Pickers

Field Study No. 3 - 1981

Exposure expressed in milligrams/hour

Group	Average Age	No. of subjects	Captan Conc mg/hr		Statistics p-Values*		
			Mean	S.D.	(1)	(2)	(3)
Adults (≥12)	20.7	10	22.25+	15.52	0.07	0.01	0.03
Children (≤11)	10.4	5	7.74+	4.70			
Adults (≥14)	24.14	7	22.03	16.04	0.26	0.13	0.09
Youths (≤13)	11.25	8	13.37	12.72			
Females		3	12.29	3.74	0.52	0.90	0.72
Males		12	18.69	16.04			

*
 (1) Assuming normal distribution of data
 (2) Assuming log normal distribution of data
 (3) Wilcoxon nonparametric test

+
 Statistically different at $p \leq 0.05$

Exposure Expressed in mg/kg b.w./hour

Group	Mean	S.D.	(1)	(2)	(3)
Adults (≥12)	0.345	0.213	0.35	0.20	0.43
Children (≤11)	0.240	0.170			
Adults (≥14)	0.300	0.171	0.86	0.77	0.95
Youths (≤13)	0.319	0.234			
Females	0.267	0.055	0.69	0.91	0.94
Males	0.321	0.223			

Table A-20

Correlation Coefficients for Variables of Strawberry Pickers

Field Experiment No. 3 - 1981

Variables	Correlation Coefficient[*]
Age vs. Productivity	0.59^{+} (S)
Hours vs. total hourly exposure	-0.14
Productivity vs. total hourly exposure	0.28
Productivity vs log total hourly exposure	0.28
Age vs. total hourly exposure	0.15
Total daily exposure vs. distance covered	0.15

[*] (S)= Spearman correlation coefficient; all others are Pearson's

[+] Significant at $\leq$ 0.05 p

Field Study No. 4

Site and Location: Cooperative Farm B, Salinas, California

Date of Study: August 21, 1981

Weather: Temp.: 65-69.5°F; 75-88% R.H.; wind speed; 4.5-15 mph.

Number and age of subjects: 6 harvesters (ages 8-41)

Table A-21

Pesticide Spray History, Cooperative Farm B, California, 1981

Date of Application	Pesticides	Product/A	AI/A	Method of Application/ Final Volume
4/26/81	Diazinon		24 oz	300 gal water
	Orthocide		4.5 lb	
	Benlate 50W		12 oz	
	Kelthane		24 oz	
6/24/81	Malathion 25W	4.0 lb.	1.0 lb.	Hand rig
	Benlate 50W	0.75 lb.	0.37 lb.	300 gal/A
	Orthocide 50W	4.5 lb.	2.25 lb.	
8/5/81	Malathion 25W	4.0 lb.	1.0 lb.	Hand rig
	Benlate 50W	0.75 lb.	0.37 lb.	300 gal/A
	Orthocide 50W	4.5 lb.	2.25 lb.	
8/19/81	Plictran 50W	2.5 lb.	1.25 lb.	Hand rig
	Malathion 25W	4.0 lb.	1.0 lb.	300 gal/A
	Benlate 50W	0.75 lb.	0.37 lb.	
	Orthocide 50W	4.5 lb.	2.25 lb.	
8/19/81	Kelthane 25W	6.75 lb.	1.7 lb.	Hand
	Malathion 25W	4.0 lb.	1.0 lb.	Applied only to 2nd year berries
	Benlate 50W	1.0 lb.	0.5 lb	
	Orthocide 50W	4.0 lb.	2.0 lb.	

Table A-22

Physical Characteristics and Work Habits of Strawberry Workers

Field Study No. 4 - 1981

Worker I.D.	Sex	Age	Weight kg	Productivity crates/hr	Hours worked	Body Surface m^2
2	F	41	72	1.44	3.48	1.70
9	M	3	25	0.57	3.48	1.00
10	F	14	50	1.15	3.48	1.50
12	M	9	27	0.57	3.48	1.00
15	F	15	50	1.15	3.48	1.50
16	M	13	34	1.44	3.48	1.30

Table A-23

Exposure Results of Strawberry Pickers

Field Study No. 4 - 1981

Worker I.D.	Dermal Exposure (Captan)			
	Total		Hands Only	
	mg/kg b.w./hr	mg/hr	mg/hr	% Total
2	0.294	21.18	18.71	88.32
9	0.394	9.84	9.17	93.14
10	0.330	16.52	13.62	82.45
12	0.571	15.44	12.84	83.21
15	0.335	16.75	14.57	86.97
16	0.544	18.49	17.01	92.01
MEANS	0.411	16.37	14.32	87.69
S.D.	(0.118)	(3.78)	(3.34)	(4.40)

Table A-24

Comparison of Captan Exposure by Different Groups of Strawberry Pickers

Dermal Exposure in milligrams/hour

Study No. 4 - 1981

Group	Average Age	No. of subjects	Captan Concn mg/hr		Statistics p-Values*		
			Mean	S.D.	(1)	(2)	(3)
Adults ($\geq$12)	20.8	4	18.24	2.15	0.08	0.08	0.11
Children ($>$11)	8.5	2	12.64	3.96			
Adults ($\geq$14)	23.3	3	18.15	2.63	0.29	0.30	0.38
Youths ($\leq$13)	10.0	3	14.59	4.38			
Females		3	18.15	2.63	0.29	0.30	0.38
Males		3	14.59	4.38			

Dermal Exposure in milligrams/kg$^+$/hour

Group	Mean	S.D.	(1)	(2)	(3)
Adults ($\geq$12)	0.376	0.113	0.35	0.32	0.25
Children ($\leq$11)	0.483	0.126			
Adults ($\geq$14)	0.320$^+$	0.022	0.032	0.024	0.08
Youths ($\geq$13)	0.503$^+$	0.096			
Females	0.320$^+$	0.022	0.032	0.024	0.08
Males	0.503$^+$	0.096			

*
(1) Assuming normal distribution of data
(2) Assuming log normal (natural log) distribution of data
(3) Wilcoxon nonparametric test

$^-$ kg of body weight

$^+$ Statistically significantly different at $p \leq 0.05$

Table A-25

Captan Exposure by Various Parts of the Body of Strawberry

Pickers. Field Study No. 4 (6 subjects)

Body Part	Exposure		
	mg/hr	S.D.	% of total (weighted average)
Head + neck	0.057	0.056	0.32
Back + shoulder	0.067	0.073	0.39
Chest + stomach	0.035	0.017	0.25
Lower leg	0.161	0.169	0.95
Upper arms	0.038	0.037	0.24
Lower arms	1.691	0.801	10.18
Hands	14.320	3.340	87.69
Total	16.370	3.776	100.00
Other than hands	2.050	0.828	12.31

Table A-26

Spearman Correlation Coefficients for Different Variables

Field Experiment No. 4 - 1981

Variables	Correlation Coefficient
Age vs productivity	0.717
Age vs total dose	0.829[+]
Productivity vs total dose	0.956[+]
Log (ln) total dose vs productivity	0.956[+]

+ Significant at ≤ 0.05 p

Table A-27

Dislodgeable Captan Residues from Strawberry Leaves

Field Study No. 4 - 1981

Sample No.	Captan Concentration	
	$\mu g/cm^2$	PPM on dust
3.1	2.74	8867
3.2	0.10	376

Field Study No. 5

Site and Loacation: Cooperative Farm C, Salinas, California

Date of Study: August 21, 1981

Weather: Temp.: 65-6915°F; 75-88% R.H.; wind speed: 4.5-15 mpn.

Number and age of subjects: 10 pickers (above age 11)

Table A-28

Pesticide Spray History. Cooperative Farm C, California, 1981

Date of Application	Pesticides	Product/A	AI/A	Method of Application/ Final Volume
3/31 - 4/1/81	Plictran 50W	2 lb.	1.0 lb.	Ground
	Diazinon 50W	1 lb.	0.5 lb.	600 gal/A
	Topsin M (70W)	1 lb.	0.7 lb.	
	Thiodan 2E	1 gal.	2.0 lb.	
	Moretrol 4E	1 qt.	1.0 lb.	
4/17/81	Benlate 50W	1 lb.	0.5 lb.	Air
	Orthocide 50W	4 lb.	2.0 lb.	20 gal/A
	Bufferol	1 pt.	1.0 pt.	
5/17/81	Dibrom 8E	1 pt.	1.0 lb.	Air
	Oxyflow Sulfur	1 qt.	1.5 lb.	20 gal/A
	Topsin M	1 lb.	0.7 lb.	
	Bufferol	1 pt.	1.0 pt.	
6/7/81	Dibrom 8E	1 pt.	1.0 lb.	Air
	Benlate 50W	1 lb.	0.5 lb.	20 gal/A
	Orthocide 50W	4 lb.	2.0 lb.	
	Bufferol	1 pt.	1.0 pt.	
7/4/81	Phosdrin 4	1 qt.	1.0 lb.	40 Acres sprayed by air
	Benlate	1 lb.	0.5 lb.	20 gal/A
	Orthocide 50	2 lb.	1.0 lb.	
	Bufferol	1 pt.	1.0 pt.	
7/30/81	Phosdrin 4	1 pt.	1.0 lb.	Helicopter
	Oxyflow Sulfur	1 qt.	1.5 lb.	20 gal/A
	Topsin M (70W)	1 lb.	0.7 lb.	
	Bufferol	1 pt.	1.0 pt.	
8/14/81	Endosulfan 2E	1.5 gal.	3.0 lb.	Ground
	Thylate 65W (thiram)	2.5 lb.	1.6 lb.	600 gal/A
	Oxyflow Sulfur	2.0 qts.	3.0 lb.	32 acres were treated
	Bufferol. Spray-			

Table A-28 (continued)

Date of Application	Pesticides	Product/A	AI/A	Method of Application/ Final Volume
8/17/81	Thiodan 2E	1.5 gal.	3.0 lb.	Ground
	Thylate 65W	2.5 lb/A	1.6 lb.	600 gal/A
	Oxyflow Sulfur	2.0 qts.	3.0 lb.	8 acres were
	Bufferol			treated (see
	Sprayfilm B			8/14/81 appli-cation)

Table A-29

Physical Characteristics and Work Habits of Strawberry Workers

Field Study No. 5 - 1981

Worker I.D.	Sex	Age	Weight kg	Productivity crates/hr	Hours worked	Body Surface m^2
1	M	19	64	n/a	3.33	1.80
3	F	16	48	n/a	3.58	1.40
6	M	24	86	1.53	4.58	2.00
8	M	28	57	1.40	3.58	1.60
13	F	34	48	2.73	4.40	1.40
14	F	18	51	n/a	3.58	1.50
17	M	17	59	1.09	4.58	1.60
18	M	19	66	1.53	4.58	1.70
25	M	27	66	n/a	2.92	1.80
30	M	17	54	1.68	3.58	1.60

Table A-30

Exposure Results of Strawberry Pickers

Field Study No.5 - 1981

Worker I.D.	Dermal Exposure (Captan)				
	Total			Hands Only	
	mg/kg	/hr *	mg/hr	mg/hr	%Total
1	0.151	9.66		4.92	50.96
3	0.075	3.62		1.43	39.41
· 6	0.029	2.53		1.91	75.68
8	0.081	4.60		3.80	82.52
13	0.188	9.01		7.18	79.68
14	0.248	12.66		9.27	73.26
17	0.057	3.38		2.60	76.94
18	0.032	2.10		1.89	90.00
25	0.126	8.31		8.01	96.49
30	0.055	2.95		2.82	95.71
MEANS	0.104	5.88		4.39	76.07
S.D.	(0.072)	(3.70)		(2.83)	(18.36)

*·kg of body weight

Table A-31

Captan Exposure of Various Parts of the Body of Strawberry

Pickers. Field Study No. 5 - 1981 (10 subjects)

Body Part	Exposure		
	mg/hr	S.D.	% of total (weighted average)
Head + neck	0.180	0.189	3.66
Back + shoulder	0.203	0.216	3.26
Chest + stomach	0.231	0.247	3.68
Lower leg	0.132	0.170	1.93
Upper arms	0.091	0.087	1.47
Lower arms	0.659	0.820	9.93
Hands	4.384	2.832	76.07
Total	5.882	3.698	100.00
Other than hands	1.498	1.543	23.93

Table A-32

Comparison of Dermal Exposure of Captan by Sex

of Strawberry Pickers

Field Study No. 5 - 1981

Sex	No. of subjects	Captan Exposure Mean	S.D.	Statistics p-Values* (1)	(2)	(3)
		mg/hr				
F	3	8.43	4.55	0.16	0.19	0.17
M	7	4.79	3.00			
		mg/kg b.w./hr				
F	3	0.170	0.088	0.05	0.08	0.11
M	7	0.076	0.047			

*

(1) Assuming normal distribution of data
(2) Assuming log normal distribution of data
(3) Wilcoxon nonparametric test

Table A-33

Correlation Coefficients for Different Variables

Field Study No. 5 - 1981

Variables	Correlation Coefficient*
Age vs productivity	0.74 (P) (p=0.09)
Productivity vs total dermal exposure	0.83 (P) [+]
Total dermal exposure vs hours worked	-0.64 (S) [+]
Age vs total exposure	0.25 (P)

*

P=Pearson correlation coefficient
S=Spearman correlation coefficient

[+]

Significant at $\leq$ 0.05 p

Youth in Agriculture: Dermal Exposure to
Carbaryl by Strawberry Harvesters 1982

Research performed by

University of California
Richmond, CA   94804

December 1983

Abstract

Dermal exposure to carbaryl of 18 fieldworkers harvesting strawberries was measured on three consecutive days in June 1982 on a farm in Corvallis, Oregon. The study was designed to measure productivity vs age, exposure vs productivity, exposure vs age and to test for exposure by different age groups and gender. A significant difference in productivity was detected between youth and adults. Age and productivity exhibited significant positive correlations. Dermal exposure for youths (14 years and younger) was lower than adults for all three days. No significant correlations were observed between dermal dose rate and physical characteristics of the harvesters, e.g. sex, body weight, and height.

1.0 INTRODUCTION

In order to complement the 1981-studies on the assessment of pesticide exposure by strawberry pickers, an additional detailed field study was conducted during June of 1982 in Oregon. The site of the study, a commercial strawberry farm near Corvallis, OR, was the same as that chosen for Study 2 in 1981.

The design of this study was to measure dermal exposure to several pesticides which had been used on this plot. Since in the 1981-studies it was shown that dermal exposure among strawberry pickers mainly consisted of pesticide deposits to hands, forearms and lower legs, only these three anatomical regions were monitored. Observations were made in the morning and afternoon of three consecutive harvesting days. Of the 23 volunteers who started out, only 18 completed the three-day course. The statistical analyses presented in this report, therefore, deal with these 18 subjects.

The major aim of this study was to examine the variance of dermal exposure among individuals and the group as a whole. Results of such studies might aid in the experimental design of future field studies. There was some anticipation that the findings of this study might elucidate whether dermal exposure is affected by individual work characteristics or environmental factors or both.

Two approaches for the statistical analysis of the results were applied. The first considered the variance of individuals and the group. In the second approach, each of the six monitoring periods (AM and PM of three days) were considered as separate

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experiments. Similar to the 1981-studies the following correlat-
ions were tested: age vs. productivity; exposure vs. producti-
vity; exposure vs. age; t-test for exposure by different age
groups and gender.

This is the first report of a series and deals exclusively
with the results obtained from exposure to carbaryl.

2.0 EXPERIMENTAL DESIGN

2.1 Field Study.

A privately owned strawberry farm near Corvallis, OR was
chosen as the site of the field experiment. The dates of the
study were June 22-24, 1982. The field had been sprayed prior to
the study date with 3 pesticides as follows: carbaryl, 2 lbs/A, 7
June , 1982: vinclozolin, 1 lb/A, 3 applications on 5, 15, and 22
May, 1982; endosulfan, 1 lb/A, 15 May, 1982.

Twenty-three harvesters volunteered to participate in the
study initially, but only 18 workers completed the three-day
exercise. At the beginning of each workday (between 0600 and 0800
hr) , the workers were outfitted with dermal monitors*, light
cotton gloves for the hands and cotton patches on the forearms
and ankles. A description of these dermal monitors has been given
in the 1982-final report on the 1981-studies. Patches were kept

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* The term "monitor" as used throughout this report, refers to
cotton gloves and gauze pads which measure dermal exposure. These
devices are intended to yield information on the quantity of
pesticide residue deposited on the skin surface but does not
address the issue of percutaneous absorption.

on the subjects during the entire working period (about 6 to 8 hrs). Gloves, however, were removed in the morning after the first or second crate of strawberries had been brought to the weighing station. Another set of gloves was issued after the lunch break to be worn till the end of the workday. The morning gloves were usually worn for one to two hours, depending on the work efficiency of individ-ual harvesters, while the afternoon gloves were worn for a slightly longer period. Since the time periods during which the gloves and patches were worn might be critical in the estimation of hand-exposure to pesticides, this information is given in the Appendix.

The procedure for hand monitoring was changed on the second day of the study when it was observed that a large amount of dew on the strawberry foliage appeared to contribute a great deal of moisture to the glove. It was believed that the moist condition of the gloves might possibly impair the absorptive capacity of the cotton cloth. Consequently, on the second day the volunteers were provided with patches at the beginning of their workday and gloves about one to two hours later after the initial dew on the leaves had dried.

At the completion of the monitoring period, gloves and patches were removed from each subject, stored individually in plastic Zip-closure type bags over dry-ice, transported to the laboratory , and placed in the deep-freeze until the samples could be extracted and analyzed. The gloves were peeled from the hands inside-out in order to minimize contamination.

Forty-eight leaf disks from strawberry plants were sampled

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with a mechanical punch, designed so that the leaf disks dropped
directly into a glass storage bottle. The punch was equipped with
a mechanical counter to facilitate the sampling. The procedures
for sampling and collecting leaf disks and the analysis of
dislodgeable foliar pesticide residues have been described in the
1982-Report to EPA (Popendorf, et al. 1982).

2.2 Sample Extraction and Analysis.

Gloves were thawed to room temperature placed into a 500-mL
wide-mouthed LP-plastic bottled fitted with a screw cap and
extracted with 100-mL acetonitrile by shaking on a reciprocal
shaker for two hours. Ten-mL aliquots were filtered through
0.22u Millipore filters and directly analyzed by HPLC as des-
cribed below.

Dislodgeable foliar pesticide residues and dust were iso-
lated from leaf punches according to methods developed by Gunther
(1973, 1974), Iwata (1977) and Popendorf and Leffingwell (1977).
Leaf punches were surface-extracted with 100 mL of a 60-
ppb aqueous solution of dioctyl sodium sulfosuccinate (Surten°)
by agitation on a reciprocal-action mechanical shaker for 30 min.
The liquid phase was carefully separated from the plant tissue
and extracted three times successively with 50 mL each of
dichloro-methane in a 500-mL separatory funnel. If an emulsion
formed at this stage, the addition of a few mls. of sat. aqueous
sodium sulfate was usually sufficient to separate the phases. The
combined organic extracts (bottom phase) were filtered through
glass wool and a bed of anh. sodium sulfate and evaporated in
vacuo to complete dryness. The residue was finally taken up in
10.0 to 25.0 mL of acetonitrile. Aliquots of this solution were

directly analyzed for carbaryl as will be described below.

Leaf dust, originally washed off with the surfactant, re-
mained in the interfacial solvent—water layer in the separatory
funnel and was quantitatively transferred after the last solvent-
extraction to a pre—weighed glass filter. After drying at 110°
overnight, the filter was reweighed, and the weight of the foliar
dust was calculated by difference in weights.

Carbaryl residues were analyzed by reverse-phase HPLC using
a Waters 6000A Solvent Delivery System, WISP Automatic Sample
Processor, Waters Data Module with Automatic Integrator, and
Model 450 Variable Wave Length Detector. The chromatographic
column was uBondapack C_{18}. The experimental conditions were:
mobile phase , acetonitrile – water (40:60); flow rate 2 mL/min,
and detection at 230 nm. Under these conditions, carbaryl has a
retention time of 4.61 min and its metabolite, 1-naphthol, 5.1
min; absolute sensitivity as limited by background noise and
automatic integration was 2 ng.

Laboratory recovery studies for carbaryl and 1-naphthol were
performed with cotton patches and detergent extracts as follows:
Known amounts of carbaryl (69 to 173 ug) and 1-naphthol (76 to
152 ug) were added to "control" patches which were extracted as
described above. Known amounts of carbaryl (828 ug) were added to
100 mL of the aqueous Surten° solution containing 48 leaf disks,
and the aqueous phase was then extracted as described above.
Recoveries of added carbaryl and 1-naphthol were almost quantita-
tive. as may be seen in Table 1.

2.3 Statistical Analysis

Statistical analyses of experimental data were performed using SAS, a statistical computer software program developed by Statistical Analysis Systems, Inc.

3.0 RESULTS AND DISCUSSION

3.1 Dermal Exposure

Eighteen strawberry harvesters were monitored for the entire course of the study consisting of three days, morning and afternoon. Physical characteristics (sex, age, weight, height, and body surface [Sendroy and Cecchini, 1952]) were recorded (Table 2-1). Individual productivity, expressed as crates of strawberries harvested per hour, as shown in Table 2-2, is further broken down into productivity in the morning (AMPROD), afternoon (PMPROD), and all-day (DAYPROD). As will be discussed later, these data were used in an attempt to correlate productivity with dermal exposure, age, sex, and other variables.

Tables 3-1, 3-1, and 3-3 show individual daily exposures to carbaryl, mean values, standard deviations (S.D), maxima and minima, and coefficients of variation (C.V). Hand exposures were broken down into morning (AM), afternoon (PM), and all-day (HANDS). Furthermore, left and right hand and lower arm exposures were measured or calculated and are listed in these tables.

A three-day summary of these data may be found in Table 4-1. All exposure values are expressed as mg carbaryl/hr/person. 1-Naphthol was not detected in any of the field samples and was not reported. Dermal pesticide concentration of lower legs (ankles) was low or nondetectable and was excluded, therefore, from estim-

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ations of total body exposure.

By visual inspection of Table 3-1, 3-2, and 3-3, it appears that dermal exposure on Day-1 was generally higher than was found on subsequent days. This impression is supported by statistics, demonstrating that the daily mean exposure variables for the three days differ significantly (see Table 4-2), with the possible exception of lower arm exposures (ARMS).

The experimental protocol was changed due to observations while the experiment was in progress. Whereas gloves were placed on the workers' hands on Day-1 and Day-3 as soon as the workers entered the field early in the morning, gloves on Day-2 were supplied two hours after the harvest had begun. The reason for this change is our observation that early morning dew on the leaves of the strawberry plants caused the cotton gloves to become saturated quickly with water and fruit juice. It was then reasoned that wet gloves might no longer possess linear absorptive capacity for dislodgeable residues from foliage and, therefore, would no longer serve as a suitable monitor for dermal exposure. Since on the third day the morning dew did not appear to be a serious problem, the original procedure was followed by placing gloves on the workers' hands as soon as they began to harvest.

Contrary to what we believed might happen with a "saturated, wet glove", namely the loss of its absorptive capacity, it is the gloves of Day-1 which exhibit a higher carbaryl concentration than either Day-2 or Day-3 gloves. It appears, therefore, that wet gloves may be more "efficient" exposure monitors by being more

absorptive than dry gloves, perhaps due to the partitioning of the pesticides from the dislodgeable foliar residues into the aqueous phase contained in the cotton cloth. This transfer due to water solubility of pesticide residues might be an alternative or additional explanation to the current view expressed by Popendorf and Leffingwell (1982) that dermal exposure is the result of contact-transfer from dislodgeable foliar residues, mainly composed of pesticide residues absorbed or adsorbed on dust.

With patch monitors, dislodgeable pesticide residues are presumably entrapped or absorbed by the cloth mesh of the multi-layered gauze of which the patches are composed. Cotton gloves, on the other hand, are made of smooth cotton material, and the partitioning theory of the pesticide transfer from foliage to cloth seems more plausible.

Indirect evidence for the partitioning theory may be found in the experimental finding that dose rates for hands were significantly higher in the morning (AM) than afternoon (PM) on Days-1 and -3 (T 3.5; df=34; p <0.01), but that no such differences existed on Day-2. It was that day that the gloves were placed on the workers' hands after the dew had dried, and the gloves re-mained relatively dry during the monitoring period.

3.2 Comparison of Dermal Exposure by Workers Grouped by Age or Body Weight

One of the goals of this study was to determine if the age of strawberry harvesters affected dermal exposure to pesticides. Since there were no subjects in this study 11 years and younger, the 18 pickers were divided into two separate groups, youths

(<=14 years of age) and adults (>=15 years of age).

Comparing these two age groups, the only difference in dermal exposure was the right-hand exposure rate (RIGHT) of youths, as defined above, which was lower than the corresponding values for adults (see Table 5). No other significant differences of dermal exposure of these two groups were found.

Since there were no 10-11 year old harvesters in this study, an attempt was made to use surrogate variables in place of age, namely body weight (<=50 kg), height (< 165 cm), and body surface (< 1.50 m²). The two group classified by physical characterist-ics were compared for correspond-ing hand exposures. T-Tests and nonparametric Kruskal-Wallis tests revealed no significant dichotomies in mean exposure values (expressed in mg/hr) for any of the physical characteristics tested, with the exception of body weight (see Table 5). For harvesters, weighing less than 50 kg, the overall mean afternoon exposure to carbaryl was lower than the corresponding value for the other group (> 50 kg).

3.3 Left- Versus Right-Hand Exposure

In a study with captan and benomyl exposure by strawberry pickers (Zweig, et al., 1983), it was found that right- or left-handed preference by pickers could be observed by measuring individual hand and lower arm exposures. Similar studies have now been made with carbaryl, as is shown in Tables 3-1, 3-2, and 3-3. However, in this study no significant differences were found between exposure rates for the left and right hands in the morn-ing, afternoon, the combination of mornings and afternoons, or for lower arm patches worn all day. This finding indicates that

there is no particular hand preference among this group of straw-
berry harvesters, even though some of them might demonstrate
handed preference for some other manual activity. The only sig-
nificant correlation was demonstrated with worker height (r= -
0.404; N=53; p<0.01), as is shown in figure 1, indicating that
left arm carbaryl exposure was predominant among shorter straw-
berry harvesters in this study. The significance of this curious
correlation is not within the scope of this study.

3.4 Worker Exposure Variability

One of the objectives of this study was to investigate the
variability of worker dermal exposure (in mg/hr) as affected by
environmental and other factors. To determine the
significance of individually consistent behavioral patterns,
which may have influenced the pattern of dermal exposure of the
individual, an analysis of variance was performed. The models
used were intended to predict AM, PM, HANDS, and TOTAL exposures.
Models including only DAY as a categorical predictor variable
were compared to models incorporating both DAY and individual
identity (ID number). The models including DAY only are equiva-
lent to tests of homogeneity of the means of the exposure variab-
les over the 3 days of the study. The latter means are, indeed,
significantly nonhomogeneous with respect to DAY value (as pre-
viously discussed), as the following analysis of variance (ANOVA)
statistics indicate:

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Variables	F Value	Degrees of Freedom	p
AM	12.70	2,51	0.0001
PM	5.06	2,51	0.0099
HANDS	10.60	2,51	0.0001
TOTAL	10.88	2,50	0.0001

From this analysis it is apparent that DAY is a highly signific-
ant predictor for these exposure variables.

Adding the individual(ID) as a categorical predictor
variable did not significantly improve exposure predictions for
any of these variables according to F-tests comparing the
simpler, nested model with the more complex model:

Variables	F-Values	Degrees of Freedom	p
AM	0.922	17,34	>0.05
PM	1.415	17,34	>0.05
HANDS	-.0.802	17,34	>0.05
TOTAL	0.805	17,33	>0.05

The above tabulation illustrates the predominant influence of
factors other than individual behavioral patterns on dermal expo-
sure as measured in this study.

Another analysis was performed to investigate the variance
of hand exposures (as measured in mg/hr) of individual pickers
over the three days of the study. There are six values for each
worker (AM and PM for three days). The analysis was performed
with and without normalizing hand exposure for the influence of
picking time period (AM or PM) or day. A summary of the results
from this analysis may be found in Table 6.

Comparing the individual variances of the unnormalized indi-
vidual dermal exposures (Table 6), it is seen that the exposure

of Picker No. 14 was more consistent than that of the group as a whole, and Picker No. 22's exposure was more variable than that of the group. Primarily as a result of these two cases, the exposure variabilities of the individual pickers cannot be considered homogeneous (Bartlett's $X^2=41.63$, df=17, p <0.01). It is noted that Picker No. 22 had the highest AM hand exposure on Days 1 and 3 of the study, compared to that of the other workers.

The exposures were normalized by subtracting the corresponding time- and day-specific hand exposure means. It is seen from Table 10 that the variance of the normalized hand exposure of Picker No. 22 remains significantly greater than that of the group. The variances of the group, despite this one high value, can be considered homogeneous (Bartlett's $X^2=22.60$, df=17, p 0.10). Thus, by controlling for day- and time-specific exposure variability, intrapersonal exposure variabilities are rendered statistically homogeneous for the pickers in this study.

3.5 Productivity

Productivity, expressed as crates harvested/hr, of all workers over the three days may be seen in Table 2-2. The mean values for A.M., P.M. and daily productivity for the three days are not significantly different, respectively (Kruskal-Wallis $X^2=0.63-4.18$; df = 2; p >0.10). When examining the two age groups (<14 and >15 yrs old), however, it was found that the daily productivity of youths was lower than that of the adult group (0.72 cr/hr vs. 0.89 cr/hr; F=11.56; df=1,48; p=0.0014). This is in agreement with the finding that over the 3 days of the study, each worker's daily productivity was positively correlated

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· = 0.459) with his/her age to a significant degree (N = 51; p
).0007). However, age did not correlate significantly with
ther morning productivity (AMPROD) or afternoon productivity
1PROD), which are the productivity variables associated with
e times during which the gloves were worn.

3.6 Dislodgeable Foliar Residues

Samples of leaf disks to determine dislodgeable carbaryl
sidues were taken 3,7,14,15,16, and 17 days post application (2
s/A carbaryl), and the results of the analyses may be found in
ble 7. From these data and a plot of log. concn. vs time (see
g. 2), it appears that the decline of foliar dislodgeable
sidue obeys first-order kinetics. Days-15, 16 and 17 of the
cline study are identical with Days-1,2,and 3 of the exposure
udy. It is possible, therefore, to calculate the transfer
efficients of strawberry harvesters from their dermal exposure
ceived on these days.

The transfer coefficient (k_d) may be considered to represent the
action of dislodgeable foliar residue transferred to the exposed
in of field workers during normal work activity in unit time. The
mensions of k_d are area (cm^2) per time. The larger the k_d, the
eater the transfer efficiency.

The calculated k_d values for Days-1,2,and 3 are 4.34,2,82,
d 6.17 x 10^3 cm^2/hr, respectively (see Tables 3-3 and 7 for
perimental data). Table 8 is a comparison of transfer coeffic-
nts from this and other studies. It may be seen that the trans-
r coefficients for pickers are similar regardless of chemical
d crops. This observation further tends to support the current
ew that dermal exposure by fruit harvesters arises from foliar

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contact with plants which have been previously sprayed with
pesticides.

Mailen et al. (1982) have studied the dermal exposure to
carbaryl by pesticide applicators and thinners in apple orchards.
From their reported values of hand exposure and total extractable
carbaryl residues, the calculated k_s is about 600, which is
considerably lower than our values found in Table 8. This appar-
ent discrepancy can be explained by the fact that these workers
measured total and not dislodgeable foliar residues which would
result in a lower transfer coefficient.

Literature Cited

Iwata, Y.; Spear, R.C.; Knaak, J.B; Foster, R.J. Bull. Environm. Contam. Toxicol. 1977,18, 649-53.

Gunther, F.A.; Westlake, W.E.; Barkley, J.H.; Winterlin, W.; Langbehn, L. Bull. Environm. Contam. Toxicol. 1973, 9, 243-49.

Gunther, F.A.; Barkley, J.H.; Westlake, W.E. Bull. Environm. Contam. Toxicol. 1974, 12, 641-44.

Maitlen, J.C.;Sell, R.C.; McDonough, L.M.; and Fertig, S.N. In "Pesticide Residues and Exposure"(Plimmer, J.R., ed.); ACS Symp. Series 182, Amer. Chem. Soc., Washington, D.C.,1982,pp.83-103

Popendorf, W.J. and Leffingwell, J.T. Bull..Environm. Contam. Toxicol. 1977, 18, 787-88.

Popendorf, W.J.; Leffingwell, J.T. Residue Reviews 1982, 82, 125-201.

Popendorf, W.J.; Leffingwell, J.T.; McLean, H.R.; Zweig, G.; Witt, J.M. "Youth in Agriculture. Pesticide Exposure to Strawberry Pickers —1981 Studies", Final Report, 2nd Draft, EPA Office of Pesticide Programs, Washington, D.C. 20460, Sept. 1982.

Sendroy, J. Jr.; Cecchini, L.P. J. Appl. Physiol. 1954, 7, 1-12.

Zweig, Gunter; Gao, Ru-yu; Popendorf, W.J. J. Agric. Food Chem. 1983,31, 1109-1113.

SUMMARY AND CONCLUSIONS

Dermal exposure to the insecticide carbaryl experienced by 18 fieldworkers harvesting strawberries, was measured on 3 consecutive days in June, 1982 on a commercial farm in Corvallis, OR. Left and right hand exposures were measured by means of cotton gloves. Lower arm and lower leg.exposures were measured by the use of cotton gauze pads. Gloves were changed for the afternoon work period, while gauze pads remained on the persons for the entire work day. Leaf disks from strawberry plants were sampled randomly on several dates prior to the study days and on the third day of the study and were analyzed for carbaryl dislodgeable residues.

The experimental data associated with glove and lower arm patch exposure measurements were analyzed statistically, and the following conclusions were reached:

1. Dose rates, expressed in mg/hr, for hands from Day-1 and Day-3 were significantly higher in the morning than afternoon. The higher morning values may have been caused by the accumulation of morning dew on the plants which might have either facilitated the transfer of dislodgeable residues from leaves to the gloves and/or rendered the gloves more absorptive or retentive.

2. No significant correlations were observed between dermal dose rate and physical characteristicss of the harvesters, e.g. sex, body weight, and height.

3. Right-hand exposure of youths of age 14 or younger was significantly lower than that of adults (15 years and older) when analyzing data for all three days. The corresponding exposure values were 0.54 mg/hr and 0.74 mg/hr, respectively.

4. The mean afternoon hand exposure of pickers weighing less than 50 kg was lower than that of the group of heavier persons (0.80 mg/hr vs. 1.27 mg/hr, respectively).

5. Left- and right mean exposure values for hands and lower arms did not differ significantly. However, a trend towards left hand and left lower arm exposures was discerned among the workers regardless of age. Left lower arm exposure did correlate negatively with body height, reflecting the predominance of left-hand and -arm exposures among shorter workers in comparison with their taller counterparts in this study.

6. The statistical analyses revealed that the particular day on which exposure occurred had a highly significant influence on most types of exposure measured, including morning hand exposure, afternoon hand exposure, total hand exposure, and total (hand plus arm) exposure. In contrast, individual worker identity did not explain exposure variability to any significant degree, indicating strongly that variables other than those associated with the individual (e.g., age, picking behavior) had a predominant influence on exposure in this study. No significant difference could be shown between intra- and inter-personal hand exposure variabilities in this study, again suggesting that individual picker characteristics and picking behavior are not influential determinants of dermal exposure.

7. The calculated transfer coefficient (k_d) (relating dermal exposure to dislodgeable foliar residues) for strawberry harvesters exposed to carbaryl was of the same order of magnitude as those previously determined for captan and benomyl exposures and O-P exposure in tree crops (citrus and peaches). Due to the similarity of values for k_d for various pesticides and crops, it appears that the main source of dermal exposure of fruit harvesters is the pesticide present as dislodgeable foliar residues.

8. Productivity of the group of strawberry harvesters studied was found not to be significantly different on different days or times of day. A significant difference in productivity was detected between youths and adults (0.72 crates/hr vs. 0.89 cr/hr, respectively). Age and productivity also exhibited a significant positive correlation.

FIGURE 1

LEFT-RIGHT PLOT FOR AAN   LEGEND: A = 1 OBS, B = 2 OBS, ETC.
PLOT OF LNROWEIGHT

r = -0.404

(p<.01)
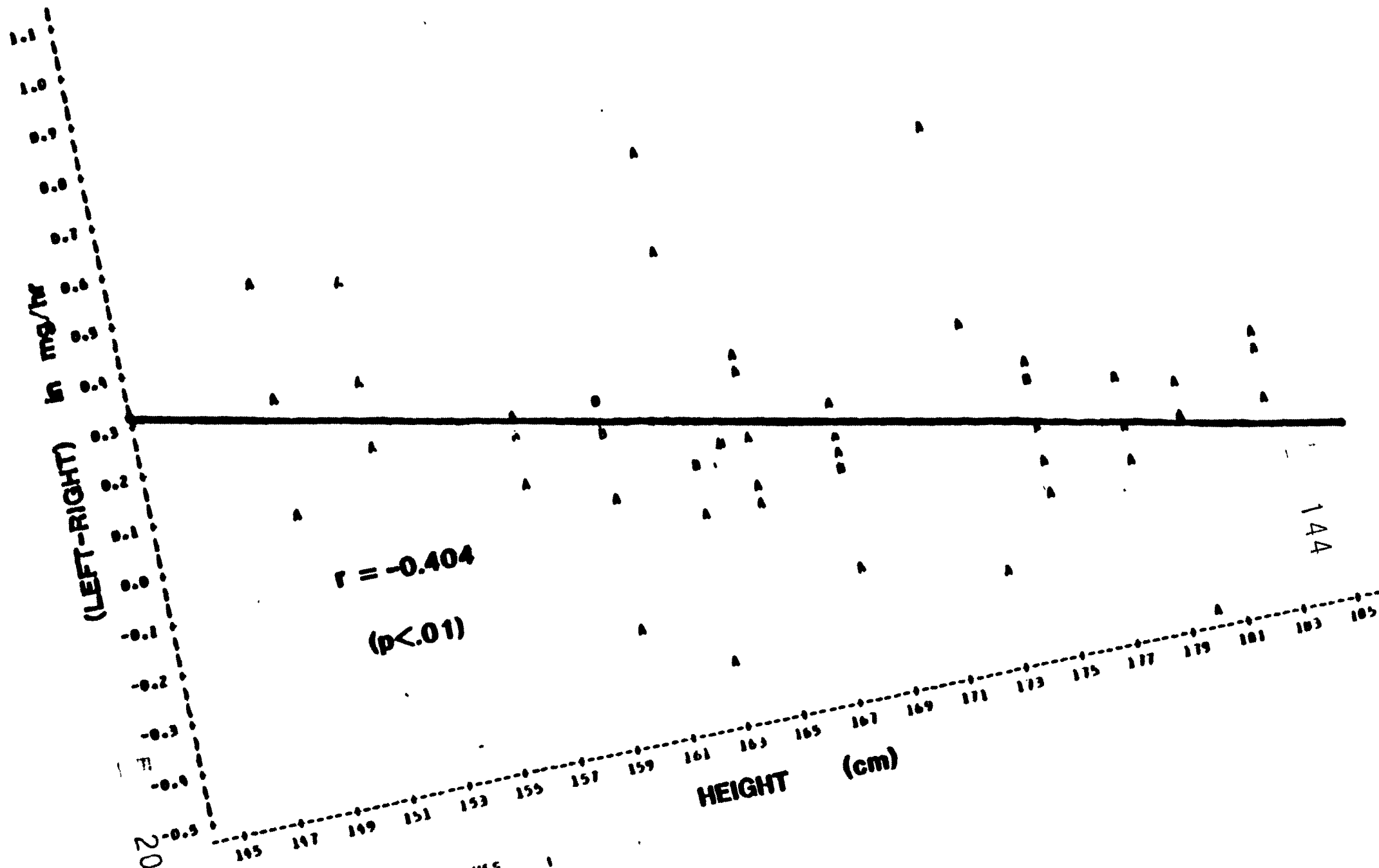
NOTE: 1 OBS HAD MISSING VALUES
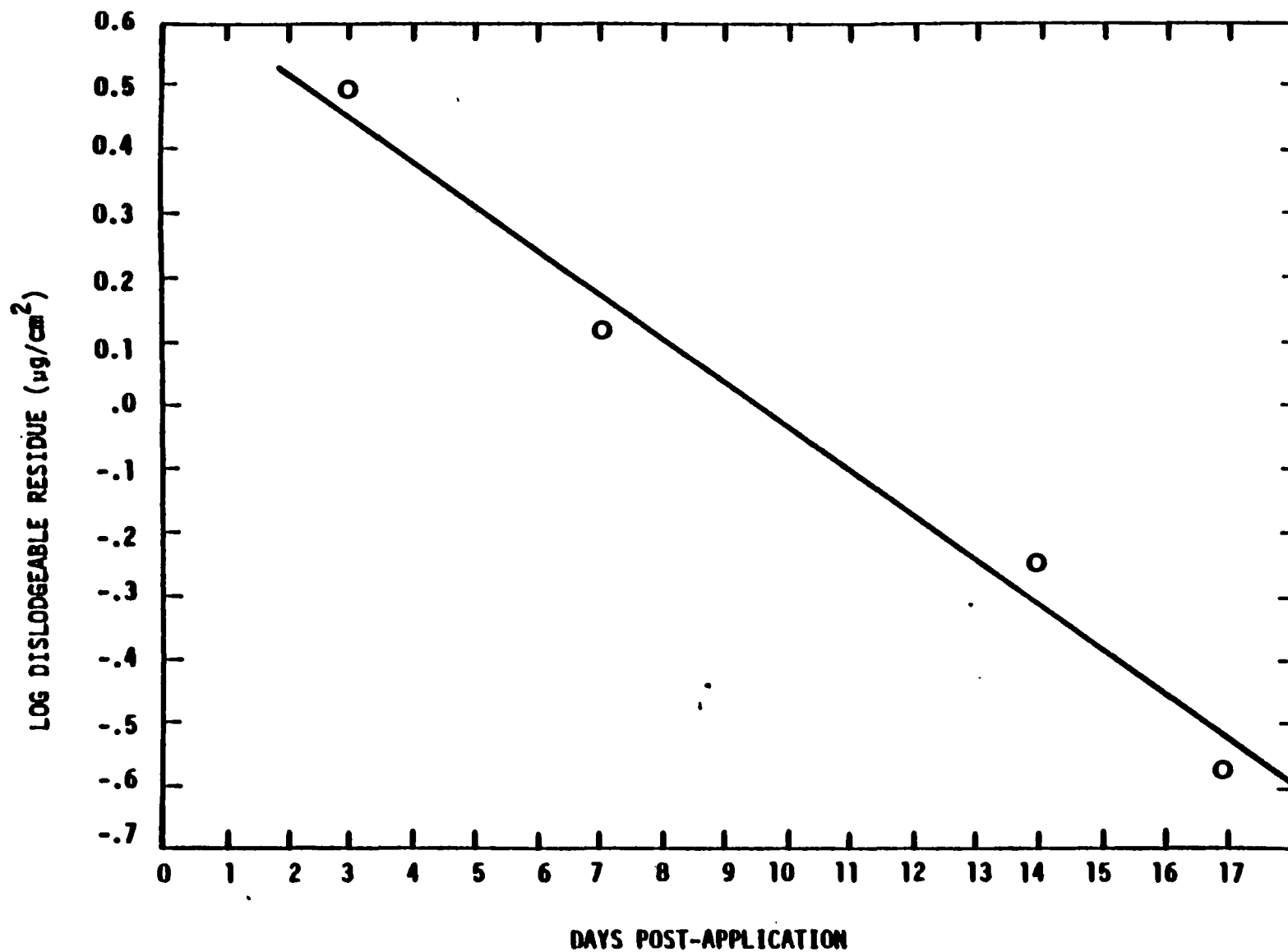
FIGURE   CARBARYL DISLODGEABLE FOLIAR RESIDUE DECLINE — STRAWBERRY LEAVES

GLOSSARY OF TERMS USED IN TABLES

eneral

Term	Explanation	Units
SEX	0=female, 1=male	
WEIGHT	individual body weight	kg
HEIGHT	individual height	cm
AREA	body surface area	m^2
AMPROD	productivity, morning	crates/hr
PMPROD	productivity, afternoon	crates/hr
DAYPROD	productivity, all day	crates/hr
AMHOURS	hours monitored, a.m. (gloves)	hr
PMHOURS	hours monitored, p.m. (gloves)	hr
DAYHOURS	total hours monitored (arm patches)	hr
ID	worker identification number	

xposure Tables

Terms	Explanation
AMLEFT	left glove (hand), a.m.
PMLEFT	left glove (hand), p.m.
AMRIGHT	right glove (hand), a.m.
PMRIGHT	right glove (hand), p.m.
AM	AMLEFT + AMRIGHT
PM	PMLEFT + PMRIGHT
LEFT	(AMLEFT*AMHOURS + PMLEFT*PMHOURS)/(AMHOURS+PMHOURS)[1]
RIGHT	(AMRIGHT*AMHOURS + PMRIGHT*PMHOURS)/(AMHOURS+PMHOURS)[1]
HANDS	LEFT + RIGHT
ARMLEFT	left arm patch (all day)
ARMRIGHT	right arm patch (all day)
ARMS	ARMLEFT + ARMRIGHT
TOTAL	HANDS + ARMS

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[1] In Tables 6-9, simple averages were used in place of ese time-weighted averages; e.g., LEFT = (AMLEFT+PMLEFT)/2.

Table 1

Recovery Studies for Carbaryl and 1-Naphthol

Compound	Sample No.	Amount added μg	found	Per Cent Recovery
Carbaryl	Patch-1	69.0	62.2	92.6
			65.5	
	Patch-2	69.0	67.2	93.9
			62.4	
	Patch-3	172.5	184.2	106.7
	Patch-4	172.5	180.0 -	104.3
	Leaf punch-1	828.0	700.8	84.9
			705.6	
	Leaf punch-2	828.0	828.0	97.3
			782.4	
	Leaf punch-3	828.0	679.2	85.3
			734.2	
	Leaf punch-control	0	2.0	n/a
1-Naphthol	Patch-3-1	76.0	77.2	101.5
	Patch-3-2	152.4	153.1	106.5
	Patch-3-3	152.4	150.7	98.9

Table 2-1

PHYSICAL CHARACTERISTICS [1]

ID	SEX	AGE	WEIGHT	HEIGHT	AREA
6	0	40	65.5	166	1.77
7	0	12	42.3	163	1.52
8	0	18	63.6	175	1.78
9	0	29	56.7	164	1.56
10	0	13	43.1	149	1.35
11	0	22	61.3	175	1.72
12	0	15	59.0	160	1.62
13	0	16	50.4	173	1.56
14	1	13	63.6	178	1.76
15	1	13	70.4	166	1.76
17	0	12	45.4	157	1.42
18	0	12	49.9	163	1.52
20	1	14	56.7	180	1.70
21	0	14	54.5	165	1.55
22	0	37	49.9	152	1.46
23	0	16	45.9	165	1.53
25	1	22	45.4	160	1.43
26	1	15	63.6	183	1.84

[1] (0=FEMALE, WT IN KG, HT IN CM), Area in m^2.

Table 2-2

PRODUCTIVITY (CRATES/HR)

ID	DAY=1			DAY=2			DAY=3		
	AMPROD	PMPROD	DAYPROD	AMPROD	PMPROD	DAYPROD	AMPROD	PMPROD	DAYPROD
6	1.47	1.33	1.17	1.01	0.42	1.03	0.95	0.68	0.93
7	0.61	0.47	0.56	0.70	1.40	0.67	0.86	1.03	0.82
8	0.64	1.00	0.85	0.99	0.92	0.97	0.95	1.23	0.91
9	0.70	1.00	0.86	1.02	0.52	1.00	0.37	1.17	1.10
10	0.35	0.63	0.92	1.17	0.22	0.75	0.70	0.46	0.67
11	0.99	1.05	1.00	1.15	1.11	1.05	0.97	0.79	0.89
12	0.90	1.15	1.08	0.93	0.41	0.98	1.00	1.37	0.93
13	0.66	1.35	0.79	0.77	0.56	0.78	0.61	0.68	0.50
14	0.99	0.88	0.84	1.09	0.67	1.08	1.02	1.43	1.00
15	0.97	0.55	0.55	0.76	0.80	0.62	1.54	0.74	0.53
17	1.00	0.92	.	0.52	0.62	0.55	1.16	0.98	0.92
18	0.66	0.72	0.63	0.52	0.25	0.42	0.95	0.30	0.74
20	2.50	0.86	1.29	0.45	0.65	0.81	1.04	0.64	1.03
21	0.65	0.47	0.54	0.67	0.50	0.56	0.37	0.64	0.71
22	0.99	0.66	.	0.91	0.86	0.77	1.01	1.03	1.01
23	1.25	0.56	1.00	1.25	1.25	0.71	1.55	1.94	1.09
25	0.60	0.84	0.86	0.67	0.62	0.60	0.70	0.90	0.65
26	0.57	.	.	0.83	0.74	0.74	0.72	0.58	0.71
Mean	0.94	0.88	0.85	0.85	0.70	0.78	0.92	0.92	0.85

Note: "." = missing value

DATA SUMMARY: DOSE RATES, IN MG/HR
LEFT, RIGHT & HANDS ARE TIME-WEIGHTED AVERAGES

DAY=1

ID	AMLEFT	AMRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
6	1.49	0.99	1.01	0.99	0.35	2.48	2.00	1.25	0.99	2.24	2.59	0.14	0.21
7	3.82	0.81	0.26	0.48	0.33	4.63	0.74	1.47	0.59	2.06	2.39	0.17	0.16
8	1.00	1.22	0.19	0.16	0.66	2.22	0.35	0.53	0.61	1.14	1.80	0.29	0.37
9	1.38	1.69	1.52	1.20	1.74	3.07	2.72	1.47	1.38	2.85	4.59	0.88	0.86
10	0.39	0.18	0.34	0.51	0.23	0.57	0.85	0.36	0.37	0.73	0.96	0.14	0.09
11	0.42	0.60	0.57	0.56	0.28	1.02	1.13	0.52	0.57	1.09	1.37	0.04	0.24
12	1.36	0.86	0.59	0.51	0.27	2.22	1.10	0.95	0.67	1.62	1.89	0.12	0.15
13	4.12	0.84	1.07	2.10	0.77	4.96	3.17	2.60	1.47	4.07	4.84	0.22	0.55
14	0.99	0.33	0.58	1.08	0.59	1.82	1.66	0.77	0.96	1.74	2.33	0.29	0.30
15	2.35	1.91	1.37	0.56	0.63	4.26	1.93	1.73	1.05	2.79	3.41	0.19	0.44
17	0.76	1.50	0.71	0.57	0.55	2.26	1.28	0.73	0.94	1.67	2.22	0.36	0.19
18	0.36	0.44	0.05	0.27	0.19	0.80	0.32	0.22	0.36	0.58	0.77	0.09	0.10
20	0.81	1.09	0.46	0.49	1.47	1.90	0.95	0.57	0.68	1.25	2.72	0.48	0.99
21	1.74	2.18	1.15	1.25	0.84	3.92	2.40	1.37	1.60	2.98	3.82	0.50	0.34
22	3.80	3.20	0.60	0.50	0.97	7.00	1.10	1.51	1.27	2.77	3.74	0.73	0.24
23	2.36	2.52	0.33	0.32	0.65	4.88	0.65	0.80	0.83	1.63	2.28	0.27	0.38
25	1.57	0.69	0.89	0.34	0.77	2.26	1.23	1.20	0.50	1.70	2.47	0.24	0.53
26	2.26	1.61	0.75	1.18	0.55	3.87	1.93	1.51	1.40	2.91	3.46	0.28	0.27
ean	1.72	1.29	0.69	0.73	0.66	3.01	1.42	1.09	0.90	1.99	2.65	0.30	0.36
.D.	1.19	0.78	0.41	0.48	0.41	1.70	0.80	0.59	0.39	0.92	1.14	0.22	0.25
in.	0.36	0.18	0.05	0.16	0.19	0.57	0.32	0.22	0.36	0.58	0.77	0.04	0.09
ax.	4.12	3.20	1.52	2.10	1.74	7.00	3.17	2.60	1.60	4.07	4.84	0.88	0.99
.V.	69.07	60.79	59.22	66.56	62.93	56.49	56.57	54.51	43.20	46.15	43.14	73.38	69.30

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Table 3-2

Table 3-2

DAY=2

ID	AMLEFT	AMRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
6	0.98	0.83	0.52	0.38	0.21	1.81	0.90	0.76	0.61	1.37	1.58	0.14	C.07
7	0.12	0.14	0.09	0.10	0.16	0.26	0.19	0.10	0.12	0.22	0.38	0.03	0.13
8	0.21	0.16	0.54	0.42	0.41	0.37	0.96	0.43	0.33	0.76	1.17	0.23	0.18
9	0.68	0.82	1.15	1.37	.	1.50	2.52	1.01	1.20	2.21	.	.	1.21
10	0.83	0.53	0.65	0.35	0.97	1.36	1.00	0.76	0.46	1.22	2.19	0.75	0.22
11	0.19	0.12	0.55	0.86	0.10	0.31	1.41	0.36	0.48	0.84	0.94	0.07	C.03
12	1.03	0.78	0.67	0.47	0.30	1.81	1.14	0.85	0.62	1.47	1.77	0.23	0.07
13	1.12	0.54	0.97	0.53	0.95	1.66	1.50	1.04	0.53	1.58	2.53	0.76	0.19
14	1.07	0.74	1.30	0.13	0.47	1.81	1.43	1.19	0.42	1.61	2.08	0.18	0.29
15	0.69	0.78	0.10	0.08	0.00	1.47	0.18	0.40	0.44	0.84	0.84	0.00	0.00
17	0.74	0.80	0.16	0.14	0.26	1.54	0.30	0.49	0.52	1.01	1.27	0.20	0.06
18	0.47	0.23	0.27	0.51	0.64	0.70	0.78	0.40	0.32	0.73	1.37	0.64	0.00
20	1.96	0.29	0.27	1.83	0.32	2.25	2.10	1.04	1.13	2.17	2.49	0.15	0.17
21	0.37	0.61	0.27	0.00	0.34	0.98	0.27	0.30	0.21	0.51	0.85	0.18	0.16
22	0.20	0.15	0.98	0.91	0.57	0.35	1.89	0.65	0.59	1.25	1.82	0.37	0.20
23	0.84	0.89	0.10	0.13	0.31	1.73	0.23	0.47	0.51	0.98	1.29	0.12	0.19
25	1.26	0.12	1.78	0.38	0.33	1.38	2.16	1.51	0.24	1.75	2.08	0.21	0.12
26	0.57	0.34	0.77	0.48	0.70	0.91	1.25	0.65	0.40	1.05	1.75	0.37	0.33
Mean	0.74	0.49	0.62	0.50	0.41	1.23	1.12	0.69	0.51	1.20	1.55	0.27	0.20
S.D	0.47	0.30	0.47	0.48	0.27	0.62	0.73	0.36	0.28	0.54	0.61	0.23	0.27
Minimum	0.12	0.12	0.09	0	0	0.26	0.18	0.10	0.12	0.22	0.38	0	0
Maximum	1.96	0.89	1.78	1.83	0.97	2.25	2.52	1.51	1.20	2.21	2.53	0.76	1.21
C.V.	62.79	59.89	76.28	94.73	66.18	50.13	65.08	52.40	54.53	44.78	39.54	86.09	133.3

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Table 3-3

DATA SUMMARY: DOSE RATES, IN MG/HR
LEFT, RIGHT & HANDS ARE TIME-WEIGHTED AVERAGES

DAY=3

ID	AMLEFT	AMRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
6	1.09	1.25	0.42	0.59	0.44	2.34	1.01	0.82	0.98	1.79	2.23	0.20	0.24
7	0.49	0.69	0.46	0.63	0.60	1.18	1.09	0.47	0.65	1.12	1.72	0.51	0.09
8	1.09	1.10	0.39	0.33	0.58	2.19	0.72	0.66	0.63	1.30	1.88	0.31	0.27
9	0.16	0.14	0.24	0.25	0.23	0.30	0.49	0.20	0.19	0.39	0.62	0.13	0.10
10	1.41	1.15	0.32	0.14	0.83	2.56	0.46	0.74	0.52	1.26	2.09	0.57	0.26
11	1.08	0.63	0.29	1.52	0.14	1.71	1.81	0.65	1.12	1.77	1.91	0.00	0.14
12	0.71	0.81	0.27	0.27	0.26	1.52	0.54	0.52	0.58	1.11	1.37	0.21	0.05
13	0.45	0.20	0.39	0.26	0.26	0.65	0.65	0.43	0.22	0.65	0.91	0.21	0.05
14	0.80	0.59	0.33	0.74	0.83	1.39	1.07	0.50	0.69	1.18	2.01	0.34	0.49
15	0.29	0.56	0.20	0.18	0.07	0.85	0.38	0.22	0.27	0.49	0.56	0.00	0.07
17	0.28	0.59	0.20	0.27	0.05	0.87	0.47	0.23	0.39	0.62	0.67	0.05	0.00
18	0.81	0.30	0.11	0.14	0.71	1.11	0.25	0.50	0.23	0.73	1.44	0.16	0.55
20	0.56	0.59	0.26	0.28	0.20	1.15	0.54	0.33	0.35	0.68	0.88	0.05	0.15
21	2.03	0.21	0.20	0.80	1.01	2.24	1.00	1.04	0.53	1.57	2.58	1.01	0.00
22	1.22	1.88	0.70	0.20	0.78	3.10	0.90	0.89	0.82	1.72	2.50	0.54	0.24
23	0.46	1.86	0.19	0.22	0.24	2.32	0.41	0.26	0.65	0.91	1.15	0.22	0.02
25	0.24	0.16	0.30	0.10	0.10	0.40	0.40	0.27	0.13	0.40	0.50	0.10	0.00
26	0.47	0.15	0.36	0.35	0.33	0.62	0.71	0.41	0.26	0.67	1.00	0.12	0.21
Mean	0.76	0.71	0.31	0.40	0.43	1.47	0.72	0.51	0.51	1.02	1.45	0.26	0.16
S.D.	0.49	0.54	0.13	0.35	0.30	0.82	0.38	0.25	0.28	0.47	0.69	0.26	0.16
Minimum	0.16	0.14	0.11	0.10	0.05	0.30	0.25	0.20	0.13	0.39	0.50	0	0
Maximum	2.03	1.88	0.70	1.52	1.01	3.10	1.81	1.04	1.12	1.79	2.58	1.01	0.55
C.V.	64.32	76.14	42.65	86.24	71.46	55.80	52.76	48.80	55.06	46.41	47.69	97.41	98.38

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DATA SUMMARY: DOSE RATES, IN MG/HR
LEFT, RIGHT & HANDS ARE TIME-WEIGHTED AVERAGES

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	C.V.
DAYHOURS	54	5.664	1.049	2.950	7.420	18.530
AMHOURS	54	1.364	0.476	0.550	2.710	34.864
PMHOURS	54	1.776	0.596	0.730	3.180	33.538
DAYPROD	51	0.831	0.201	0.420	1.290	24.138
AMPROD	54	0.907	0.343	0.370	2.500	37.876
PMPROD	53	0.832	0.365	0.220	1.940	43.804
ARMLEFT	53	0.279	0.234	0.000	1.010	83.765
ARMRIGHT	54	0.240	0.241	0.000	1.210	100.294
ARMS	53	0.501	0.350	0.000	1.740	69.838
AMLEFT	54	1.073	0.902	0.120	4.120	84.010
AMRIGHT	54	0.831	0.658	0.120	3.200	79.159
AM	54	1.904	1.377	0.260	7.000	72.201
PMLEFT	54	0.541	0.398	0.050	1.780	73.561
PMRIGHT	54	0.545	0.453	0.000	2.100	83.210
PM	54	1.086	0.712	0.180	3.170	65.613
LEFT	54	0.761	0.483	0.101	2.595	63.443
RIGHT	54	0.641	0.366	0.115	1.602	57.073
HANDS	54	1.402	0.784	0.216	4.065	55.921
TOTAL	53	1.068	1.000	0.376	4.835	52.999

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Table 5

Dermal Exposure by Age and Weight of Strawberry Harvesters

Variable	Dermal Exposure mg/hr	Type	Kruskall-Wallis x^2	p
Youths (<14)	0.54	RIGHT (3 days)	4.94	0.026
Adults (>15)	0.74			
Small (<50 kg)	0.80	PM (3 days)	-5.87	0.015
Big (>50 kg)	1.27			
Small	0.88	PM (Day-1)	$T_{uneq.var.}$ =3.10 df =14.4 p=0.0076	
Big	1.76			

Table 6

Analysis of Variance of Dermal Exposure to Carbaryl[1]
by Strawberry Harvesters

Picker ID	Mean Dermal Exp.[2]	Variance unnormalized	Mean Dermal Exp.	Variance normalized
	mg/hr		mg/hr	
6	1.76	0.443	0.26	0.286
7	1.35	2.752	-0.15	0.997
8	1.14	0.739	-0.36	0.455
9	1.77	1.405	0.27	0.941
10	1.13	0.591	-0.36	1.356
11	1.23	0.300	-0.26	1.161
12	1.39	0.350	-0.11	0.206
13	2.10	2.817	0.60	1.138
14	1.53	0.084*	0.04	0.406
15	1.51	2.244	0.02	0.652
17	1.12	0.532	-0.38	0.186
18	0.66	0.104	-0.84	0.532
20	1.48	0.485	-0.01	0.718
21	1.80	1.746	0.31	0.536
22	2.39	6.01*	0.90	3.055*
23	1.70	3.085	0.21	1.138
25	1.31	0.658	-0.19	0.547
26	1.55	1.52	0.05	0.365
Group Mean	1.50	1.359	0.00	0.836

[1]Left + Right Hands, all day (time averaged)
[2]Average of six monitoring periods (AM,PM for 3 days)
*significantly different from corresponding group variance at p<0.01, if tested individually.

Table 7

Dislodgeable Foliar Residues of Carbaryl on Strawberry Leaves

Sample ID	Days Post-Harvest	Dislodgeable Residue	
		$\mu g/cm^2$	PPM(dust) $\times 10^3$
8202.3.1 P	3	3.36	57.10
8202.3.2 P	3	2.98	56.53
8202.3.3 P	3	1.35	16.45
8202.7.1 P	7	1.32	22.55
8202.14.1 P	14	0.56	8.30
8202.14.2 P	14	0.51	12.43
8202.15.1 P	15	0.77	16.06
8202.15.2 P	15	0.45	6.53
8202.16.1 P	16	0.41	9.42
8202.16.2 P	16	0.69	14.57
8202.17.1 P	17	0.32	2.92
8202.17.2 P	17	0.15	1.67

Pesticide Treatment: 2 lbs carbaryl/A (Sevin*4F Flowable)

on June 7, 1982

Table 8

Dermal Exposure Transfer Coefficients for Fruit Harvesters

Pesticide	Crop	$k_a \times 10^3$	Lit.Cit.
Carbaryl(Day-1)	Strawberries	4.34	This study
Carbaryl(Day-2)	Strawberries	2.82	This study
Carbaryl(Day-3)	Strawberries	6.17	This study
Captan	Strawberries	8.57	Zweig et al.,1983
Captan	Strawberries	2.90	Popendorf,et al.,1982
Captan	Strawberries	8.00	Popendorf et al.,1982
Captan	Strawberries	2.62	Popendorf et al.,1982
Captan	Strawberries	5.97	Popendorf et al.,1982
Captan	Strawberries	4.73	Popendorf et al.,1982
Benomyl	Strawberries	7.19	Zweig et al.,1983
OP Compounds	Citrus	5.1*	Popendorf and
OP Compounds	Peaches	1.9**	Leffingwell,1982

*geometric means from 14 observations

**geometric means from 9 observations

Hours Monitored for Individuals on Each of Three Days

DATA SUMMARY: HOURS MONITORED, BY DAY

OBS	ID	DAY=1 AMHOURS	PMHOURS	DAYHOURS	DAY=2 AMHOURS	PMHOURS	DAYHOURS	DAY=3 AMHOURS	PMHOURS	DAYHOURS
1	6	1.36	1.36	5.36	1.98	1.05	3.90	1.05	0.73	4.82
2	7	1.63	3.18	7.16	1.43	2.38	7.42	1.16	2.46	7.26
3	8	1.46	1.96	5.90	1.10	2.16	6.45	1.05	1.63	5.48
4	9	1.40	2.50	6.41	0.96	2.20	7.05	2.71	2.56	6.38
5	10	1.15	1.58	5.41	2.41	1.58	7.30	1.20	2.08	5.87
6	11	1.01	1.90	5.65	1.93	1.80	6.60	1.03	1.26	6.16
7	12	1.12	1.30	5.07	1.21	1.23	3.32	1.00	0.73	4.32
8	13	1.15	1.15	5.07	1.30	1.33	3.65	1.63	0.73	4.30
9	14	2.01	2.25	5.95	1.83	1.96	6.47	0.98	1.75	5.50
10	15	1.63	1.80	6.15	1.31	1.25	6.43	0.65	2.03	5.62
11	17	1.60	1.53	5.11	1.61	1.21	4.97	0.87	1.53	5.42
12	18	1.50	1.26	4.77	1.98	0.98	2.95	1.05	0.83	4.38
13	20	0.60	1.73	5.15	1.28	1.53	6.85	0.96	3.11	7.01
14	21	1.30	2.13	5.51	1.48	2.81	6.95	2.65	3.10	7.01
15	22	1.01	2.55	5.88	1.23	1.71	6.50	0.86	1.46	5.43
16	23	0.80	2.66	6.00	1.60	1.60	3.75	0.55	1.55	6.40
17	25	1.48	1.76	4.62	1.48	1.33	6.11	1.28	1.66	5.37
18	26	1.75	1.73	5.58	2.41	1.66	5.63	1.38	1.71	5.63
mean		1.28	1.91	5.60	1.59	1.70	5.71	1.23	1.72	5.69
S.D.		0.33	0.55	0.62	0.42	0.47	1.49	0.58	0.74	0.90

Grand Means: AM 1.36 $\pm$ 0.48
(± S.D.) PM 1.78 $\pm$ 0.60
DAY 5.66 $\pm$ 1.05

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ARM PATCH EXPOSURES (IN MG/PATCH)

	DAY 1			DAY 2			DAY 3		
ID	ARMLEFT	ARMRIGHT	ARMS	ARMLEFT	ARMRIGHT	ARMS	ARMLEFT	ARMRIGHT	ARMS
6	0.034	0.052	0.086	0.025	0.013	0.038	0.044	0.053	0.097
7	0.065	0.061	0.126	0.012	0.052	0.063	0.199	0.035	0.234
8	0.078	0.100	0.178	0.068	0.053	0.121	0.078	0.068	0.145
9	0.290	0.284	0.574	.	0.439	.	0.043	0.033	0.075
10	0.046	0.029	0.075	0.330	0.097	0.426	0.201	0.092	0.293
11	0.011	0.064	0.075	0.022	0.009	0.031	0.0	0.041	0.041
12	0.031	0.038	0.069	0.038	0.012	0.050	0.046	0.011	0.056
13	0.058	0.145	0.208	0.152	0.038	0.191	0.047	0.011	0.058
14	0.080	0.082	0.162	0.054	0.087	0.140	0.086	0.124	0.211
15	0.053	0.124	0.177	0.0	0.0	0.0	0.0	0.018	0.018
17	0.105	0.056	0.161	0.057	0.017	0.074	0.016	0.0	0.016
18	0.023	0.026	0.048	0.101	0.0	0.101	0.037	0.129	0.166
20	0.118	0.244	0.362	0.049	0.056	0.105	0.017	0.050	0.067
21	0.141	0.096	0.237	0.064	0.057	0.121	0.362	0.0	0.362
22	0.239	0.079	0.317	0.134	0.072	0.206	0.163	0.073	0.236
23	0.086	0.121	0.207	0.024	0.038	0.062	0.075	0.007	0.082
25	0.063	0.139	0.202	0.073	0.042	0.115	0.031	0.0	0.031
26	0.069	0.067	0.136	0.095	0.085	0.180	0.030	0.052	0.082
mean	0.088	0.100[1]	0.189	0.076	0.065[1]	0.119	0.082	0.044[1]	0.126
S.D.	0.073	0.070	0.128	0.077	0.098	0.098	0.093	0.040	0.102

	ARMLEFT	ARMRIGHT	ARMS
Grand Mean	0.082	0.072	0.145
S.D.	0.080	0.076	0.113

[1] Statistically non-homogeneous (Kruskal-Wallis $\chi^2 = 10.07$, df=2, p=.0065)

NOTE: Due to rounding, ARMS does not always equal the sum of ARMLEFT and ARMRIGHT. In the table, "." refers to a missing value.

Appendix Table 3-1

DATA SUMMARY: DOSES ARE IN TOTAL ACCUMULATED MG
LEFT, RIGHT & HANDS ARE SIMPLE AVERAGES: BY DAY

DAY=1

OBS	ID	AMLEFT	AMRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
1	6	2.03	1.35	1.37	1.35	1.88	3.37	2.72	1.70	1.35	3.05	4.92	0.75	1.13
2	7	6.23	1.32	0.83	1.53	2.36	7.55	2.35	3.53	1.42	4.95	7.31	1.22	1.15
3	8	1.46	2.78	0.36	0.32	3.89	3.24	0.69	0.92	1.05	1.97	5.86	1.71	2.18
4	9	1.93	2.37	3.50	3.00	11.15	4.30	6.60	2.87	2.68	5.55	16.70	5.64	5.51
5	10	0.45	0.21	0.54	0.01	1.24	0.66	1.34	0.49	0.51	1.00	2.24	0.76	0.49
6	11	0.42	0.61	1.08	1.06	1.58	1.03	2.15	0.75	0.64	1.59	3.17	0.23	1.36
7	12	1.52	0.96	0.77	0.66	1.37	2.49	1.43	1.15	0.81	1.96	3.33	0.61	0.76
8	13	4.74	0.97	1.23	2.42	3.90	5.70	3.65	2.98	1.69	4.67	8.58	1.12	2.79
9	14	1.57	1.67	1.31	2.43	3.51	3.66	3.74	1.65	2.05	3.70	7.21	1.73	1.79
10	15	2.42	1.97	2.47	1.01	3.87	4.39	3.47	2.44	1.49	3.93	7.81	1.17	2.71
11	17	0.76	1.50	1.09	0.67	2.81	2.26	1.96	0.92	1.19	2.11	4.92	1.34	0.97
12	18	0.54	0.66	0.06	0.34	0.91	1.20	0.40	0.30	0.50	0.80	1.71	0.43	0.48
13	20	0.65	0.87	0.80	0.85	7.57	1.52	1.64	0.72	0.66	1.58	9.15	2.47	5.10
14	21	2.23	2.83	2.45	2.66	4.63	5.10	5.11	2.36	2.75	5.10	9.73	2.76	1.87
15	22	3.84	3.23	1.53	1.26	5.70	7.07	2.81	2.68	2.25	4.94	10.64	4.29	1.41
16	23	1.89	2.02	0.98	0.85	3.90	3.90	1.73	1.38	1.43	2.82	6.72	1.62	2.28
17	25	2.32	1.02	1.58	0.61	3.56	3.34	2.19	1.95	0.81	2.77	6.32	1.11	2.45
18	26	3.96	2.82	1.30	2.04	3.07	6.77	3.34	2.63	2.43	5.06	8.12	1.56	1.51

DAY=2

OBS	ID	AMLEFT	AMRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
19	6	1.54	1.64	0.96	0.70	0.62	3.58	1.67	1.45	1.17	2.62	3.44	0.55	0.27
20	7	0.17	0.20	0.21	0.24	1.19	0.37	0.45	0.19	0.22	0.41	1.60	0.22	0.96
21	8	0.23	0.18	1.18	0.92	2.64	0.41	2.09	0.70	0.55	1.25	3.89	1.43	1.16
22	9	0.67	0.80	2.53	3.01	.	1.47	5.54	1.60	1.91	5.51	.	.	8.53
23	10	2.00	1.28	1.03	0.55	7.08	3.28	1.58	1.51	0.92	2.43	9.51	5.40	1.61
24	11	0.37	0.23	0.99	1.55	0.66	0.60	2.54	0.68	0.89	1.57	2.23	0.46	0.20
25	12	1.25	0.94	0.82	0.58	1.00	2.19	1.40	1.04	0.76	1.80	2.79	0.76	0.23
26	13	1.46	0.70	1.29	0.70	3.66	2.16	2.00	1.37	0.70	2.08	5.73	2.93	0.73
27	14	1.92	1.35	2.57	0.26	3.04	3.31	2.83	2.27	0.81	3.07	6.11	1.16	1.88
28	15	0.90	1.02	0.13	0.10	0.00	1.93	0.23	0.51	0.56	1.08	1.08	0.00	0.00
29	17	1.17	1.29	0.19	0.17	1.29	2.48	0.36	0.69	0.73	1.42	2.71	0.99	0.30
30	18	0.93	0.46	0.26	0.50	1.99	1.39	0.76	0.60	0.48	1.08	2.96	1.89	0.00
31	20	2.51	0.37	0.41	2.80	2.19	2.08	3.21	1.46	1.59	3.05	5.24	1.03	1.16
32	21	0.55	0.90	0.76	0.00	2.36	1.45	0.76	0.65	0.45	1.10	3.47	1.25	1.11
33	22	0.25	0.18	1.68	1.56	3.71	0.43	3.23	0.96	0.87	1.83	5.54	2.41	1.30
34	23	1.34	1.42	0.16	0.21	1.16	2.77	0.37	0.75	0.82	1.57	2.73	0.45	0.71
35	25	1.36	0.10	2.37	0.51	2.02	2.04	2.87	2.12	0.34	2.46	4.47	1.28	0.73
36	26	1.37	0.62	1.29	0.81	4.09	2.19	2.10	1.33	0.81	2.15	6.23	2.16	1.92

DATA SUMMARY: DOSES ARE IN TOTAL ACCUMULATED MG
LEFT, RIGHT & HANDS ARE SIMPLE AVERAGES: BY DAY

DAY=3

OBS	ID	AMLEFT	AMRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
37	6	1.14	1.31	0.31	0.43	2.12	2.46	0.74	0.73	0.87	1.60	3.72	0.96	1.16
38	7	0.57	0.30	1.13	1.55	4.37	1.37	2.68	0.65	1.18	2.03	6.39	3.71	0.66
39	C	1.14	1.16	0.64	0.54	3.18	2.30	1.17	0.89	0.85	1.74	4.91	1.70	1.48
40	9	0.43	0.36	0.51	0.64	1.47	0.61	1.25	0.52	0.51	1.03	2.50	0.93	0.64
41	10	1.90	1.47	0.67	0.29	4.97	3.28	0.96	1.24	0.88	2.12	6.99	3.35	1.53
42	11	1.11	0.65	0.37	1.92	0.87	1.76	2.28	0.74	1.28	2.02	2.89	0.00	0.87
43	12	0.71	0.81	0.20	0.20	1.12	1.52	0.39	0.45	0.50	0.96	2.08	0.91	0.22
44	13	0.73	0.33	0.28	0.19	1.12	1.05	0.47	0.51	0.26	0.77	1.89	0.90	0.22
45	14	0.78	0.58	0.56	1.30	4.57	1.36	1.87	0.68	0.94	1.62	6.18	1.37	2.70
46	15	0.19	0.36	0.41	0.37	0.39	0.55	0.77	0.30	0.36	0.66	1.06	0.00	0.39
47	17	0.24	0.51	0.31	0.41	0.27	0.76	0.72	0.27	0.46	0.74	1.01	0.27	0.00
48	18	0.85	0.32	0.09	0.12	3.11	1.17	0.21	0.47	0.22	0.69	3.80	0.70	2.41
49	20	0.54	0.57	0.81	0.87	1.40	1.10	1.68	0.67	0.72	1.39	2.79	0.35	1.05
50	21	5.38	0.56	0.52	2.48	7.08	5.94	3.10	3.06	1.52	4.52	11.60	7.00	0.00
51	22	1.05	1.62	1.02	0.29	4.24	2.67	1.31	1.04	0.95	1.99	6.23	2.93	1.30
52	23	0.25	1.02	0.29	0.34	1.54	1.23	0.64	0.27	0.68	0.96	2.49	1.41	0.13
53	25	0.31	0.20	0.50	0.17	0.54	0.51	0.66	0.40	0.19	0.59	1.13	0.54	0.00
54	26	0.65	0.21	0.62	0.60	1.86	0.85	1.21	0.63	0.40	1.03	2.89	0.68	1.18

Appendix Table 4 : Overall Data And Averages (TOTAL DOSE - MG)

DATA SUMMARY: DOSES ARE IN TOTAL ACCUMULATED MG
LEFT, RIGHT & HANDS ARE SIMPLE AVERAGES

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	C.V.
ARMLEFT	53	1.579	1.472	0.000	7.080	93.229
ARMRIGHT	54	1.382	1.489	0.000	8.530	107.735
ARMS	53	2.026	2.128	0.000	11.153	75.278
AMLEFT	54	1.449	1.303	0.172	6.227	89.907
AMRIGHT	54	1.018	0.722	0.176	3.232	70.898
AM	54	2.467	1.769	0.372	7.547	71.711
PMLEFT	54	0.958	0.766	0.063	3.800	79.509
PMRIGHT	54	0.961	0.825	0.000	3.014	85.777
PM	54	1.919	1.390	0.207	6.800	72.394
LEFT	54	1.203	0.836	0.193	3.527	69.460
RIGHT	54	0.990	0.614	0.105	2.748	62.002
HANDS	54	2.193	1.355	0.412	5.549	61.767
TOTAL	53	4.995	3.131	1.009	16.702	62.691

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DATA SUMMARY: DOSES ARE IN TOTAL UG/KG: BY DAY
LEFT, RIGHT & HANDS ARE SIMPLE AVERAGES

DAY=1

OBS	ID	ANLEFT	ANRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
1	6	20.26	19.37	15.76	19.37	26.99	48.53	39.14	24.46	19.37	43.83	70.83	19.30	16.20
2	7	147.20	31.21	19.55	36.09	55.86	178.41	55.63	83.37	33.65	117.02	172.88	29.78	27.08
3	8	22.95	28.01	5.92	4.98	61.23	50.96	10.90	14.44	16.49	30.93	92.16	26.90	34.32
4	9	34.07	41.73	67.02	52.91	196.71	75.80	119.93	50.55	47.32	97.87	294.57	99.49	97.22
5	10	13.41	4.80	12.46	18.70	29.87	15.21	31.16	11.44	11.75	23.18	52.05	17.57	11.30
6	11	6.92	9.89	17.67	17.36	25.81	16.81	35.02	12.29	13.62	25.92	51.72	3.69	22.12
7	12	25.02	16.33	13.00	11.24	23.20	42.14	24.24	19.41	13.78	33.19	56.39	19.31	12.89
8	13	44.01	19.17	25.41	47.92	77.46	113.17	72.33	59.21	33.54	92.75	170.21	22.13	55.33
9	14	31.29	26.23	20.52	36.21	55.20	57.52	58.73	25.90	32.22	58.12	113.32	27.13	26.07
10	15	34.30	27.94	55.03	14.32	55.04	62.33	49.35	34.71	21.15	55.04	110.87	15.60	33.44
11	17	15.74	33.04	23.93	19.21	61.91	49.78	43.14	20.33	26.12	46.46	108.36	49.52	21.39
12	18	10.02	13.23	1.26	6.62	18.10	24.05	6.08	6.04	10.02	16.06	34.23	0.60	9.56
13	20	11.43	15.38	14.04	14.95	133.52	26.81	28.99	12.73	15.16	27.90	161.42	43.60	89.92
14	21	41.50	52.00	44.94	48.85	94.92	93.50	93.80	43.22	50.43	93.65	170.58	53.55	34.37
15	22	75.91	64.77	30.56	25.55	114.30	141.08	56.21	53.79	45.16	98.95	213.25	65.02	28.28
16	23	37.84	40.40	17.59	17.06	78.10	78.24	34.65	27.71	28.73	56.44	134.60	32.46	45.69
17	25	51.18	22.49	34.89	13.33	79.36	73.67	48.22	43.04	17.91	60.95	139.31	24.42	53.93
18	26	62.19	44.30	20.40	32.10	48.25	106.49	52.50	41.29	38.20	79.49	127.75	24.57	23.69

DAY=2

OBS	ID	AMLEFT	AMRIGHT	PHLEFT	PHRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIGHT
19	6	27.92	23.65	13.84	10.12	·11.78	51.57	23.96	20.88	16.88	37.76	49.55	7.86	3.93
20	7	4.06	4.73	5.06	5.63	28.07	9.79	10.69	4.56	5.18	9.74	37.81	5.26	22.80
21	8	3.63	2.77	18.51	14.40	41.58	6.40	32.91	11.07	8.58	19.65	61.23	23.33	16.25
22	9	11.75	14.17	44.62	53.16	.	25.93	97.78	28.19	33.66	61.85	.	.	150.45
23	10	46.41	29.64	23.93	12.03	164.29	76.05	36.66	35.12	21.23	56.35	220.65	127.03	37.26
24	11	5.93	3.78	16.15	25.25	10.77	9.76	41.40	11.07	14.52	25.58	36.35	7.54	3.23
25	12	21.12	16.00	13.97	9.80	16.88	37.12	23.77	17.55	12.90	30.44	47.32	12.94	3.94
26	13	28.89	13.93	25.60	13.99	72.57	42.82	39.58	27.24	13.96	41.20	113.77	59.06	14.51
27	14	30.72	21.29	40.47	4.05	47.81	52.08	44.52	35.63	12.67	48.30	96.11	19.31	29.50
28	15	12.84	14.51	1.78	1.42	0.00	27.35	3.20	7.31	7.97	15.27	15.27	0.00	0.00
29	17	26.24	28.37	4.26	3.73	28.46	54.61	8.00	15.25	16.05	31.30	59.77	21.89	6.57
30	18	16.65	9.13	5.30	16.02	37.84	27.78	15.32	11.48	9.57	21.55	59.38	37.84	0.00
31	20	44.25	6.55	7.29	49.38	38.66	50.79	56.67	25.77	27.96	53.73	92.39	13.22	20.54
32	21	10.05	16.57	13.92	0.00	43.30	26.61	13.92	11.98	8.28	20.27	63.62	22.95	20.40
33	22	4.93	3.70	33.58	31.16	74.25	9.63	64.77	19.26	17.44	36.70	110.95	43.20	26.05
34	23	26.93	28.54	3.21	4.17	23.30	55.47	7.37	15.07	16.35	31.42	54.72	9.02	14.20
35	25	41.07	3.91	52.15	11.13	44.41	44.99	63.28	46.61	7.52	54.13	90.54	23.26	16.15
36	26	21.60	22.68	20.34	12.68	64.17	34.48	33.02	20.97	12.70	33.75	97.92	33.92	30.25

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DATA SUMMARY: DOSES ARE IN TOTAL UG/XG: BY DAY
LEFT, RIGHT & HANDS ARE SIMPLE AVERAGES

DAY=3

OBS	ID	AMLEFT	AMRIGHT	PMLEFT	PMRIGHT	ARMS	AM	PM	LEFT	RIGHT	HANDS	TOTAL	ARMLEFT	ARMRIG
37	6	16.47	18.88	4.41	6.20	30.52	35.35	10.61	10.44	12.54	22.98	53.50	13.87	16.64
38	7	13.44	18.92	26.75	36.64	103.20	32.36	63.39	20.09	27.78	47.87	151.14	37.77	15.49
39	8	26.00	18.16	16.00	8.46	49.97	36.16	18.45	14.00	13.31	27.30	77.28	26.71	23.26
40	9	7.65	6.69	10.84	11.29	25.88	14.34	22.12	9.24	8.99	18.23	44.11	14.63	11.25
41	10	41.97	34.15	15.44	6.76	113.04	76.03	22.20	26.66	20.45	49.11	162.16	77.63	35.41
42	11	16.15	10.59	5.96	31.24	14.11	28.73	37.20	12.05	20.91	32.97	47.08	0.00	14.11
43	12	12.03	13.73	3.34	3.34	19.04	25.76	6.68	7.69	8.53	16.22	35.26	15.38	3.66
44	13	14.55	6.47	4.65	3.77	22.18	21.02	9.41	10.10	5.12	15.22	37.40	17.92	4.27
45	14	12.33	9.09	9.00	20.36	71.78	21.42	29.44	10.70	14.73	25.43	97.21	29.40	42.37
46	15	2.53	5.17	5.77	5.19	5.59	7.65	10.96	4.22	5.18	9.40	14.99	0.00	5.59
47	17	5.37	11.31	6.74	9.10	5.97	16.67	15.84	6.05	16.20	16.26	22.22	5.97	0.00
48	16	17.04	6.31	1.83	2.33	52.32	23.36	4.16	9.44	4.32	13.76	76.08	14.04	48.26
49	20	9.43	9.99	14.26	15.36	24.73	19.47	29.62	11.87	12.67	24.54	49.27	6.19	18.54
50	21	96.71	10.21	11.33	45.50	129.91	108.92	56.86	55.04	27.86	82.90	212.81	129.91	0.00
51	22	21.03	32.40	20.49	5.85	94.86	53.43	26.33	20.75	19.13	39.00	124.76	58.76	26.12
52	23	5.37	20.50	5.90	6.83	30.73	25.57	12.74	5.49	13.67	19.15	49.93	28.22	2.57
53	25	6.77	4.51	10.97	3.66	11.83	11.28	14.63	8.07	4.00	12.95	24.78	11.83	0.00
54	26	10.20	3.25	9.68	5.41	29.24	13.45	19.09	9.94	6.33	16.27	45.48	10.62	16.59

Appendix Table 6 : Overall Data and Averages (MICROGRAM/KG)

DATA SUMMARY: DOSES ARE IN TOTAL UG/KG
LEFT, RIGHT & HANDS ARE SIMPLE AVERAGES

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
ARMLEFT	53	30.255	29.920	0.000	129.910
ARMRIGHT	54	25.076	26.457	0.000	150.450
ARMS	53	52.965	41.199	0.000	196.709
AMLEFT	54	27.088	26.854	2.678	147.201
AMRIGHT	54	18.606	13.308	2.767	64.770
AM	54	45.694	35.257	6.399	178.414
PMLEFT	54	17.507	13.854	1.263	67.019
PMRIGHT	54	17.466	14.856	0.000	53.157
PM	54	34.973	25.073	3.196	119.929
LEFT	54	22.298	16.648	4.222	83.374
RIGHT	54	18.036	11.149	4.084	50.427
HANDS	54	40.334	25.892	9.403	117.022
TOTAL	53	92.892	60.676	14.991	294.575

Youth in Agriculture: Dermal Exposure to
  Vinclozolin by Strawberry Harvesters
  1982

Research performed by

University of California
Richmond, CA 94804

December 1983

Abstract

Dermal exposure to vinclozolin of 18 harvesters of strawberries
was studied on three consecutive days in June at a commercial
farm in Corvallis, Oregon. The study was designed to provide
correlations among dermal exposure, age of workers, body size or
weight of workers and productivity. Statistical analyses of the
data showed a significant correlation between exposure rate and
age and productivity. Also age appeared to correlate positively
with productivity, e.g., older workers seemed to receive higher
dermal exposures than younger ones in the same occupational setting.

edited: February 24, 1984

Youth in Agriculture

Dermal Exposure to Pesticides by Strawberry Harvesters

1982 Studies

II. Vinclozolin

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3.0 INTRODUCTION

In order to complement the 1981-studies on the assessment of pesticide exposure among strawberry pickers, an additional, detailed field study was conducted during the month of June 1982. The site of the study was the same commercial strawberry farm used for one of our studies in 1981, located near Corvallis, Oregon.

The design of the 1982-study was aimed at measuring dermal exposure to several pesticides which had been applied to this strawberry field. Since in earlier studies it had been demonstrated that the major dermal exposure to pesticides by strawberry pickers occurred on hands, forearms, and to a lesser degree on lower legs, only these three anatomical regions were monitored in this study. Observations were made on three consecutive days in the mornings and afternoons on 18 volunteers who were experienced strawberry harvesters.

The major aim of this study was to gain further insight into the mechanism of pesticide transfer from foliage and fruit to the skin of strawberry harvesters. Correlations between dermal pesticide exposure and work or physiognomic characteristics and age would be attempted. Finally, correlation between dermal exposure, age of workers, body size or weight would be tested.

This is the second report of this series and deals exclusively with dermal exposure to the fungicide vinclozolin (RONILAN). The first report of this series, submitted to EPA in

December 1983, dealt with the exposure to the insecticide
carbaryl.

4.0 EXPERIMENTAL DESIGN

4.1 Field Study

A privately owned strawberry farm near Corvallis, OR was chosen as the site of the field experiment. The dates of the study were June 22, 23, and 24, 1982. The field had been sprayed prior to the study dates with three pesticides as follows: carbaryl, 2 lbs/A, 7 June, 1982; vinclozolin, 1 lb/A, three applications each on 5,15, and 22 May 1982; endosulfan, 1 lb/A, 15 May, 1982.

Vinclozolin, or RONILAN, [3-(3,5-dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione], produced by BASF, was used on strawberries to control Botritis cinera and must be applied several times during the flowering period to achieve best results. Based on the spray history of the field, Day 1 of the study represented Day 31 post-application date, and so on. Initially, 23 harvesters volunteered to participate in the study, but only 18 workers completed the three day course.

At the beginning of each work day (between 0600 and 0800 hr), the workers were outfitted with dermal monitors, consisting of light cotton gloves for the hands and cotton patches on the forearms and lower legs. A description of these monitors has been reported previously (1982 Report to EPA, PHAP-California). Patches were worn throughout the work day (about 6 to 8 hrs) and gloves for a shorter period of time during the morning. A new set of

gloves was issued to the workers after the lunch break to be kept on until the end of the work day (about 3 hrs). The time periods during which gloves and patches were worn are found in the Appendix of the Carbaryl Report (Draft Report to EPA, December 1983).

The procedure for hand monitoring was modified on the second day of the study after it had been discovered on the first day that a large amount of dew on the strawberry foliage contributed a great deal of moisture to the gloves. This condition seems to interfere with the proper behavior of the gloves as absorptive monitors. Therefore, gloves were provided about 2 hrs after the harvesters had entered the field in the morning by which time the dew on the foliage had dried. On Day 3, the original experimental procedure was resumed.

At the completion of the monitoring period for each worker, gloves and patches were removed from each subject, stored individually in Zip-Lock type bags over dry ice, transported to the laboratory, and placed in the deep-freeze until the samples could be extracted and analyzed. Glove monitors were peeled from the hands of the workers inside-out in order to minimize field contamination.

For the purpose of measuring dislodgeable foliar residues of vinclozolin, 48 leaf disks from strawberry plants were sampled in a random design by walking across the plot diagonally and taking leaf samples from different plants at different heights. Leaf disks were collected by means of a mechanical punch which was designed so

that the disks dropped directly into a glass storage bottle. The mechanical punch was also equipped with a counter to minimize errors during sampling. The procedures for sampling, collecting and extraction of samples for the analysis of dislodgeable residues have been described in a previous report from this laboratory (Popendorf, et al. 1982).

4.2 Sample Extraction

Gloves and cotton patches were extracted with 100 mL and 30 mL of acetonitrile per sample, respectively, by shaking on a reciprocal mechanical shaker for two hours. Ten mL aliquots were filtered through 0.22 u Millipore filters and directly analyzed by gas chromatography as described below. If the concentration of vinclozolin, particularly of gloves, was too high to be within the linear range of the detector (see below), aliquots of the sample were diluted in appropriate volumes of acetonitrile.

Dislodgeable residues of pesticides on foliage and dust were extracted from leaf punches according to methods developed by Gunther et al. (1973, 1974), Iwata (1977), and Popendorf and Leffingwell (1977). The leaf punches were surface extracted with three portions, successively, of 100 mL each of 60 ppb aqueous solution of SURTEN (dioctyl sodium sulfosuccinate) for 30 min. The liquid phase was carefully decanted and extracted 3 times successively with 50 mL each of dichloromethane in a 500 mL separatory funnel. Emulsion that might form were broken up with a few drops of a saturated solution of sodium sulfate.

The combined organic extracts (bottom phases) were filtered through glass wool and a bed of anhydrous sodium sulfate and evaporated on a rotary evaporator in vacuo to about two mL. The flask was washed down with ten milliliters of acetonitrile and again evaporated down to a couple of milliliters. This procedure was repeated twice more, and the residue was finally taken up in either 10.0 or 25.0 mL of acetonitrile. Aliquots of this solution were analyzed by capillary GC, as will be described below.

To isolate and determine the weight of leaf dust, which remains in the separatory funnel at the interfacial layer and suspended in the aqueous phase, was quantitatively transferred to a pre-weighed glass filter. After drying at 110° overnight, the filter was weighed and the weight of foliar dust calculated by difference. The foliar dust is presumed to be the vehicle for the transfer of pesticides from the crop to the worker.

4.3 Analysis of Vinclozolin

Analytical grade vinclozolin (F 696) was obtained from the EPA Reference Standard Repository, Research Triangle Park, NC 27711. Acetonitrile used throughout was "Baker Resi-Analyzed", or equivalent.

There are several reports in the literature on the analysis of vinclozolin residues by High Performance Reversed Phase Liquid Chromatography (HPLC) (Cabras et al., 1982, 1983). For our purposes, however, a method was chosen capable of analyzing vinclozolin and endosulfan simultaneously; the latter pesticide

having been applied to the same strawberry plot for the control of mites, aphids, and other insects. Endosulfan isomers and the sulfate metabolite cannot be conveniently analyzed by HPLC, and gas chromatography is the method of choice.

A capillary GC method was, therefore, developed for the analysis of vinclozolin and endosulfan. A Hewlett-Packard 5880A instrument, equipped with an H-P 7672A Automatic Sampler was used. The column was a 12.5 m WCOT silica capillary column with an I.D. of 0.2 mm, coated with cross-linked dimethyl silicone (OV-1), and deactivated with siloxane. The splitless injection mode was selected, and detection was accomplished by electron capture (^{63}Ni).

Experimental conditions for the complete resolution of a mixture of vinclozolin, endosulfan I and II, and endosulfan sulfate were the following (see fig. 1):

Carrier gas (He); flow @ 15 psi; ‾ 4 mL/min.

Septum Flush; 3 mL/min.

Split Vent; 55 mL/min.

Make-up gas (5% methane, in argon); 20mL/min at the detector.

Temperature program:	Time/rise	Temperature (^{o}C)
	1 min	62
	30°/min	62 - 250
	1 min	250
	30°/min	250 - 260
	5 min	260

Under these conditions, vinclozolin had a retention time of 6.54 min.

One microliter injections of standard and sample solutions were made automatically. All samples were run in triplicate. Results were accepted when the relative standard deviation (RSD) was <5% for standards and <10% for field and laboratory samples. Standard solutions ranged from 8.7 ng/mL to 870.8 ng/mL. Over this 100-fold range, the EC response was found to be linear. Whenever the concentration of unknown was outside this range, appropriate dilutions with acetonitrile or evaporation were made.

The practical limit of detection was 8.7 ng/mL. Although concentrations of one half this level could be integrated with almost equal precision, it was not necessary to achieve a sensitivity greater than the stated value for most samples.

Recovery studies of vinclozolin for gloves, patches, and SURTEN solutions (simulated dislodgeable residue extract), as may be seen in Table 1, ranged from 70% to over 100% of added vinclozolin.

4.4 Statistical Analysis

Statistical analyses were performed using SAS, a statistical computer software program developed by Statistical Analysis Systems, Inc.

5.0 RESULTS AND DISCUSSION

5.1 Dermal Exposure

Physical characteristics (sex, age, weight, and height) and body surface, calculated by the method of Sendroy and Cecchini (1954), are shown in Table 2. Individual productivity, listed in Table 3, is expressed as crates of strawberries harvested per hour for the morning, afternoon and all-day observation periods.

Tables 4-1, -2, and -3 show exposure rates of individual workers for morning, afternoon and all day, expressed in mg/hr for left and right hands and lower-arms. Exposure rates for AM- and PM hands and lower-arms were directly calculated from dermal concentrations and hours monitored. Daily exposure rates for hands are time-weighted averages.

Lower-leg exposure concentrations were mostly nondetectable and were, therefore, not considered to contribute significantly to total dermal body exposure to vinclozolin. Since only one subject, No.7, exhibited a lower-leg exposure rate of about 10% of total on Day-1, it was decided not to include lower-leg exposure values for subsequent analyses.

Table 5 is a three-day summary of exposure rates of all 18 volunteers for six observation periods (N=108). Judging by these results, it appears that hand exposure is the major target of dermal exposure of strawberry harvesters. Mean hand exposure rate, 0.251 mg/hr, may be compared with 0.027 mg/hr for lower arms. This observation is consistent with results from previous studies on

strawberry harvesters exposed to captan (Final Report to EPA, 1982) and carbaryl (Carbaryl Report to EPA, 1983).

It also appears that vinclozolin exposure was considerably lower for the same group of workers than corresponding carbaryl exposure (0.28 mg/hr vs. 1.89 mg/hr, respectively). A probable explanation for this finding may be the fact that vinclozolin had been applied 15 days earlier than carbaryl, and lower dislodgeable vinclozolin residues were found on corresponding study dates (see below).

By statistically analyzing the date for six observation periods, hand exposures for the AM-observation period were shown to be greater than those in the afternoon, ($Z=2.157$; $N=54$; $p<0.016$). Similar results were found in the carbaryl study and may be related to dew formation on foliage during the early morning hours. This may cause glove monitors to become quickly saturated with water. In contrast to the transfer of dislodgeable residues on tree crops, as discussed by Popendorf and Leffingwell (1982), the results reported here may reflect the effect of water-saturated glove monitors which may enhance the transfer of dislodgeable residues from foliage.

By applying Duncan's Multiple Range Test, it can be shown that mean dermal exposure rates for all 18 workers were not significantly different on any of the three days of the study. One exception to this finding were afternoon exposure rates for hands, which were significantly lower on the third day than on the other

two days (0.210, 0.252, 0.125 mg/hr for Days-1,-2, and -3, respectively).

5.2 Comparison of Dermal Exposure Rates of Workers Grouped by Physical Factors

One of the primary goals of these exposure studies, sponsored jointly by EPA and DOL, was the investigation of possible differences in dermal exposure between two groups of workers, 10-11 year old (Group I) and 12 years of age and above (Group II). As may be seen in Table 2, none of the volunteers were below 12 years of age. It is possible that the cooperating grower purposely excluded volunteers from this age group. Due to the absence of 10-11 year old subjects, physical characteristics other than age had to be chosen for purposes of comparison. Body weight and body surface were selected as appropriate physiognomic properties characterizing these two age groups.

Dividing the workers into two groups according to body weight (<50 kg and >50 kg), it was shown by the application of chi-square statistics that afternoon exposure rates to hands were larger among the subject group whose weight was >50 kg (0.24 mg/hr vs. 0.12 mg/hr; see Table 5-1). Other exposure rates tested by these statistics were found not to be different. These results are consistent with those found for carbaryl exposure in the same group of workers (Carbaryl Report, 1983)

When the subjects were grouped by body surface (<1.52 m^2 and >1.52 m^2), it could be demonstrated that three types of exposure

rates were lower among the $<1.52 \ m^2$-group, hands-PM, hands-all day, and total.

There appears to be logic in dividing the group according to their physiognomic properties for testing exposure differences. For example, six out of seven subjects with smaller body weight also had smaller body surface. One exception to this rule seemed to be Subject No. 23 whose body surface was slightly larger ($1.53 \ m^2$) than the cutoff point, so that No. 23 was placed in the "bigger" group. However, the method of estimating body surface by nomograph (Sendroy and Cecchini, 1954) may not warrant making this distinction.

All 12-year old subjects belonged to the groups of "smaller" and "lighter weight" persons. (Six out of seven subjects in either group were female.) One may conclude, therefore, that younger strawberry pickers are subject to lower dermal exposure than a group of older pickers in the same occupational setting.

5.3 Correlation Between Exposure, Age, and Productivity

In previous studies on dermal exposure to captan and benomyl by strawberry harvesters (Final Report to EPA, 1982; Zweig et al., 1983), evidence was presented that exposure, productivity, and age of workers correlated in some cases. In the studies on vinclozolin reported here, additional evidence for these correlations is presented through regression analyses. Linear regressions are shown in figs. 2,3, and 4. Although the experimental data were not ideal for statistics due to uneven distribution of ages,

statistical analyses did reveal a significant correlation between
exposure rates and age (Table 7-1) and productivity (Table 7-2). A
possible interpretation of these results is that dermal exposure is
positively affected by the individual's productivity. Age also
seems to correlate positively with productivity, indicating that
older workers might be more experienced and motivated.
Consequently, the older workers seem to receive higher dermal
exposure than the younger ones in the same occupational and
environmental setting. A detailed analysis of the variability of
workers' exposure to carbaryl showed that intrapersonal variability
is larger than interpersonal variability, and, therefore, age alone
of an individual worker does not necessarily serve as a reliable
predictor of his exposure (Carbaryl Report, 1983), and no
conclusion may be drawn from the exposure rate of one individual
and his age.

6.0 DISLODGEABLE FOLIAR RESIDUES

6.1 Decline of Vinclozolin Residues

There is increasing evidence that the major source of dermal exposure to pesticides by fruit pickers is dislodgeable foliar residues of pesticides resulting from the application of pesticides to the field prior to the entry of harvesters. It was important, therefore, to study the decline of dislodgeable foliar residues of vinclozolin for a period of several weeks after the last application date. The first sampling date of strawberry leaves for vinclozolin represented Day-17 post-application and corresponded to Day-1 for carbaryl. The days on which the harvesters were monitored were Days-31, -32, and -33 post-application. A semi-log plot of vinclozolin dislodgeable residues vs. days post-application, shown in fig. 5, indicates first-order kinetics with a half-life of vinclozolin estimated at 4.3 days on strawberry foliage.

6.2 Transfer Coefficient for Strawberry Harvesters

The transfer coefficient is an expression of transfer efficiency of dislodgeable residues from foliage to the skin of the field worker or harvester. The transfer coefficient is calculated according to Equation (1):

$$(1) \qquad k_d = \frac{(dermal\ dose\ rate)}{(Dislodgeable\ foliar\ residues)}$$

(k_d has the dimensions of cm^2hr^{-1})

The transfer coefficient may be considered to represent the

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ideal area of foliage "contacted" by the worker if the residue were quantitatively removed from the foliage and deposited on his skin. In reality, much less than quantitative transfer is effected. For example, it has been shown that during harvesting of citrus, approximately one-half of parathion and paraoxon residue was removed during harvesting activity by pickers (Spear et al., 1977). Furthermore, in tree crops it is unlikely that all of the dry residue removed from the foliage will be deposited onto the person, independent of dermal absorption. Thus, the value of k_d is expected to be much smaller than the actual foliage contacted or disturbed. Theoretically, one could estimate the ideal coefficient if one could accurately determine the fraction of residue removed from the foliage during the harvesting process and the fraction deposited on the skin of the harvester.

Table 9 lists the calculated transfer coefficients from the three days of the study using mean values for dislodgeable residues and mean daily dermal dose rates for the group of workers observed. The k_d values range from about $30-50 \times 10^3 cm^2 hr^{-1}$, values which are considerably higher than those obtained in previous studies on strawberry and tree crop harvesters (Carbaryl Report, 1983; Final Report to EPA on Captan; Zweig et al., 1983) for whom the corresponding values were of the order of $5 \times 10^3 cm^2 hr^{-1}$. A larger value for k_d suggests that greater transfer efficiency exists for vinclozolin residues than, for example, those estimated for carbaryl under identical conditions. The difference between

carbaryl and vinclozolin residues may be their respective "age";
vinclozolin was applied 14 days before carbaryl, and therein might
lie the difference in the type of residue found. Based on previous
observations, it does not appear that physio-chemical properties
of a compound had a large effect on its transfer efficiency, and
one must speculate that there exist other factors which explain
this behavior.

6.3 Carbaryl-Vinclozolin Ratios

From the data presented here and those previously reported for
carbaryl (Carbaryl Report, 1983), it is possible to calculate the
ratio of carbaryl and vinclozolin existing as dislodgeable foliar
residues and dermal concentrations (dermal dose rates). The ratios
for carbaryl:vinclozolin from dislodgeable foliar residues range
from 46-98, as shown in Table 10, while the corresponding values
from dermal dose rates are considerably lower, with the possible
exception of lower-arms' on Days-1 and -3. If one were to
hypothesize that dislodgeable foliar residues represented the major
source of dermal exposure, one would have expected these two
pesticides to appear in similar proportions on leaves (dislodgeable
residues) and skin (dermal exposure). This was indeed demonstrated
in our previous study dealing the the simultaneous exposure by
strawberry harvesters to captan and benomyl (Zweig et al., 1983).
The fact that the carbaryl:vinclozolin ratios are significantly
smaller on the skin than leaves suggests two possibilities: one,
that vinclozolin dislodgeable foliar residues behave differently than

carbaryl residues and/or secondly, that there may be an additional source of vinclozolin contributing to dermal exposure (fruit or soil?), thus resulting in lower ratios. The fact, however, that vinclozolin transfer coefficients (see 6.2) were larger than "normal" supports the first view that vinclozolin dislodgeable foliar residues behave differently than most other pesticide residues which have been studied by us under field conditions.

TABLE 1

Recovery Studies on Vinclozolin

Substrate	Vinclozolin		Per Cent Recovery
	Added	Found	
	(ug)		
300 mL Surten*	239.0	196.7	82.3
300 mL Surten*	218.0	177.9	81.6
Patch #1	218.0	155.6	71.4
Patch #2	218.0	152.5	69.9
Patch #3	218.0	157.3	72.2
Patch #4	239.0	174.7	80.2
Glove #1	218.0	230.5	105.7
Glove #2	218.0	233.4	107.1

Surten* is the trade mark for sodium dioctyl sulfosuccinate surfactant. The Surten* solution for this experiment was a 60-ppb aqueous solution and was used to simulate surface extraction of dislodgeable vinclozolin residues from strawberry leaf disks.

TABLE 2

Physical Characteristics of Strawberry Harvesters

ID	Sex	Age	Weight	Height	Surface Area[1]
			kg	cm	m^2
6	F	40	69.5	168	1.77
7	F	12	42.3	163	1.52
8	F	18	63.6	175	1.78
9	F	29	56.7	164	1.58
10	F	13	43.1	149	1.35
11	F	32	61.3	175	1.72
12	F	15	59.0	160	1.62
13	F	16	50.4	173	1.56
14	M	13	63.6	178	1.76
15	M	13	70.4	168	1.78
17	F	12	45.4	157	1.42
18	F	12	49.9	163	1.52
20	M	14	56.7	180	1.70
21	F	14	54.5	165	1.59
22	F	37	49.9	152	1.46
23	F	16	49.9	165	1.53
25	M	12	45.4	160	1.43
26	M	15	63.6	183	1.84

Determined by the method of Sendroy and Ceddhini (1954).

TABLE 3

Productivity of Strawberry Harvesters (crates/hour)

ID	DAY=1			DAY=2			DAY=3			AVERAGE (3 d)
	AMPROD	IMPROD	DAYPROD	AMPROD	IMPROD	DAYPROD	AMPROD	IMPROD	DAYPROD	
6	1.47	1.33	1.17	1.01	0.42	1.03	0.95	0.68	0.93	1.04
7	0.51	0.47	0.56	0.70	1.40	0.67	0.86	1.03	0.82	0.68
8	0.64	1.00	0.85	0.99	0.92	0.97	0.95	1.23	0.91	0.91
9	0.70	1.00	0.80	1.02	0.52	1.00	0.37	1.17	1.10	0.99
10	0.35	0.63	0.92	1.17	0.22	0.75	0.70	0.46	0.67	0.78
11	0.97	1.05	1.06	1.16	1.11	1.05	0.97	0.79	0.89	1.00
12	0.90	1.15	1.05	0.33	0.41	0.98	1.00	1.37	0.93	1.00
13	0.66	1.35	0.79	0.77	0.56	0.78	0.61	0.68	0.50	0.72
14	0.90	0.88	0.84	1.09	0.67	1.08	1.02	1.43	1.00	0.97
15	0.97	0.55	0.56	0.75	0.80	0.62	1.54	0.74	0.53	0.57
17	1.00	0.92	.	0.52	0.62	0.55	1.16	0.98	0.92	0.74
18	0.66	0.72	0.63	0.52	0.25	0.42	0.95	0.30	0.74	0.60
20	2.50	0.86	1.29	0.45	0.65	0.81	1.04	0.64	1.03	1.04
21	0.65	0.47	0.54	0.67	0.50	0.56	0.37	0.64	0.71	0.60
22	0.90	0.66	.	0.51	0.86	0.77	1.01	1.03	1.01	0.89
23	1.25	0.56	1.06	1.25	1.25	0.71	1.55	1.94	1.09	0.96
25	0.50	0.84	0.80	0.57	0.62	0.60	0.70	0.90	0.65	0.70
26	0.57	.	.	0.83	0.74	0.74	0.72	0.58	0.71	0.72
Mean	0.94	0.88	0.85	0.85	0.70	0.78	0.92	0.92	0.85	0.83

Note: "." = missing value

TABLE 4-1
Vinclozolin Dose Rates for Strawberry Harvesters -- Day-1
(mg/hr)

IC	ARMLEFT	ARMRIGHT	ARMS	AMLEFT	AMRIGHT	AM	PMLEFT	PMRIGHT	PM	LEFT	RIGHT	HANDS	TOTAL
6	0.010	0.014	0.024	0.563	0.318	0.880	0.213	0.220	0.433	0.368	0.269	0.657	0.681
7	0.004	0.000	0.004	0.201	0.096	0.297	0.045	0.064	0.108	0.098	0.074	0.172	0.176
8	0.013	0.014	0.027	0.101	0.119	0.221	0.132	0.103	0.235	0.119	0.110	0.229	0.255
9	0.074	0.060	0.134	0.229	0.199	0.429	0.212	0.181	0.393	0.218	0.188	0.406	0.540
10	0.042	0.065	0.106	0.246	0.118	0.364	0.097	0.147	0.245	0.160	0.135	0.295	0.403
11	0.014	0.017	0.031	0.117	0.220	0.337	0.141	0.192	0.332	0.132	0.201	0.334	0.365
12	0.004	0.006	0.010	0.105	0.075	0.181	0.066	0.056	0.121	0.064	0.065	0.149	0.156
13	0.003	0.008	0.011	0.129	0.074	0.203	0.113	0.137	0.250	0.121	0.105	0.226	0.237
14	0.007	0.005	0.012	0.065	0.087	0.152	0.064	0.056	0.120	0.065	0.070	0.135	0.147
15	0.004	0.002	0.006	0.092	0.137	0.229	0.036	0.042	0.078	0.057	0.077	0.133	0.140
17	0.006	0.007	0.013	0.077	0.128	0.205	0.034	0.037	0.071	0.051	0.073	0.124	0.137
19	0.000	0.002	0.002	0.051	0.044	0.095	0.017	0.028	0.045	0.036	0.036	0.072	0.074
20	0.007	0.020	0.027	0.116	0.208	0.324	0.184	0.253	0.437	0.162	0.239	0.401	0.428
21	0.015	0.016	0.031	0.106	0.162	0.268	0.132	0.097	0.229	0.122	0.122	0.244	0.275
22	0.020	0.009	0.029	0.000	0.292	0.292	0.071	0.056	0.127	0.051	0.123	0.174	0.203
23	0.010	0.017	0.026	0.175	0.112	0.287	0.123	0.095	0.218	0.135	0.099	0.234	0.260
25	0.009	0.021	0.030	0.082	0.048	0.131	0.074	0.052	0.126	0.078	0.050	0.128	0.159
26	0.006	0.009	0.017	0.147	0.133	0.280	0.084	0.135	0.220	0.116	0.134	0.250	0.267
Mean	0.014	0.016	0.030	0.145	0.143	0.287	0.102	0.108	0.210	0.122	0.121	0.242	0.273
S. D.	0.018	0.018	0.035	0.121	0.078	0.171	0.059	0.068	0.123	0.081	0.065	0.140	0.157

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TABLE 4-2

Vinclozolin Dose Rates for Strawberry Harvesters -- Day-2

(mg/hr)

ID	ARMLEFT	ARMRIGHT	ARMS	AMLEFT	AMRIGHT	AM	PMLEFT	PMRIGHT	PM	LEFT	RIGHT	HANDS	TOTAL
6	0.009	0.010	0.019	0.309	0.329	0.638	0.409	0.209	0.617	0.357	0.271	0.628	0.647
7	0.001	0.009	0.010	0.027	0.102	0.129	0.022	0.036	0.058	0.024	0.061	0.085	0.095
8	0.018	0.016	0.034	0.127	0.151	0.278	0.085	0.105	0.190	0.099	0.120	0.220	0.253
9	0.044	0.067	0.111	0.238	0.214	0.452	0.124	0.158	0.282	0.159	0.175	0.334	0.446
10	0.025	0.011	0.035	0.149	0.104	0.253	0.043	0.087	0.130	0.107	0.097	0.204	0.239
11	0.003	0.003	0.006	0.081	0.076	0.157	0.066	0.120	0.186	0.073	0.097	0.171	0.177
12	0.033	0.005	0.038	0.474	0.295	0.769	0.480	0.242	0.722	0.477	0.268	0.745	0.783
13	0.081	0.067	0.148	0.248	0.184	0.432	0.321	0.147	0.468	0.285	0.165	0.450	0.598
14	0.018	0.016	0.034	0.134	0.245	0.379	0.294	0.147	0.442	0.218	0.194	0.412	0.446
15	0.008	0.015	0.023	0.121	0.108	0.228	0.041	0.060	0.100	0.082	0.084	0.166	0.189
17	0.002	0.005	0.007	0.160	0.184	0.344	0.032	0.060	0.093	0.105	0.131	0.236	0.243
18	0.013	0.002	0.014	0.078	0.042	0.120	0.015	0.032	0.046	0.057	0.039	0.096	0.110
20	0.009	0.006	0.015	0.172	0.159	0.331	0.150	0.169	0.318	0.160	0.164	0.324	0.340
21	0.011	0.022	0.033	0.105	0.159	0.265	0.077	0.003	0.080	0.087	0.057	0.144	0.177
22	0.026	0.029	0.055	0.115	0.073	0.168	0.232	0.133	0.365	0.183	0.108	0.291	0.346
23	0.005	0.006	0.011	0.418	0.518	0.936	0.023	0.025	0.048	0.220	0.272	0.492	0.503
25	0.006	0.005	0.011	0.115	0.044	0.159	0.127	0.097	0.224	0.121	0.069	0.190	0.201
26	0.009	0.013	0.022	0.050	0.026	0.077	0.118	0.052	0.171	0.078	0.037	0.115	0.137
Mean	0.018	0.017	0.035	0.173	0.167	0.341	0.148	0.105	0.253	0.161	0.134	0.295	0.329
S.D.	0.020	0.020	0.037	0.121	0.122	0.234	0.141	0.066	0.201	0.116	0.078	0.187	0.200

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TABLE 4-3

Vinclozolin Dose Rates for Strawberry Harvesters -- Day-3

(mg/hr)

ID	ARMLEFT	ARMRIGHT	ARMS	AMLEFT	AMRIGHT	AM	PMLEFT	PMRIGHT	PM	LEFT	RIGHT	HANDS	TOTAL
6	0.008	0.011	0.019	0.331	0.456	0.788	0.186	0.227	0.414	0.272	0.362	0.634	0.653
7	0.015	0.002	0.017	0.069	0.063	0.133	0.043	0.065	0.107	0.051	0.064	0.115	0.132
8	0.005	0.003	0.008	0.152	0.112	0.265	0.066	0.066	0.132	0.100	0.084	0.184	0.192
9	0.019	0.008	0.027	0.036	0.031	0.067	0.028	0.025	0.053	0.032	0.028	0.061	0.068
10	0.005	0.006	0.012	0.096	0.083	0.179	0.044	0.038	0.082	0.064	0.055	0.119	0.131
11	0.001	0.011	0.012	0.115	0.128	0.243	0.041	0.138	0.179	0.074	0.134	0.207	0.219
12	0.002	0.002	0.004	0.032	0.113	0.145	0.052	0.035	0.087	0.041	0.080	0.121	0.124
13	0.014	0.009	0.022	0.082	0.026	0.110	0.062	0.035	0.097	0.076	0.030	0.106	0.128
14	0.007	0.016	0.024	0.054	0.049	0.102	0.054	0.070	0.124	0.054	0.062	0.116	0.140
15	0.002	0.003	0.005	0.037	0.051	0.068	0.026	0.028	0.054	0.029	0.034	0.063	0.068
17	0.001	0.001	0.003	0.029	0.052	0.060	0.030	0.039	0.070	0.030	0.044	0.074	0.076
18	0.001	0.006	0.006	0.110	0.064	0.174	0.018	0.044	0.062	0.070	0.055	0.125	0.131
20	0.011	0.005	0.016	0.018	0.025	0.043	0.102	0.125	0.228	0.082	0.102	0.184	0.200
21	0.030	0.013	0.043	0.223	0.057	0.280	0.050	0.094	0.144	0.130	0.077	0.207	0.249
22	0.028	0.006	0.035	2.471	0.434	2.905	0.081	0.034	0.115	0.967	0.182	1.149	1.183
23	0.003	0.003	0.006	0.137	0.070	0.208	0.061	0.047	0.108	0.081	0.053	0.134	0.141
25	0.012	0.004	0.016	0.056	0.033	0.089	0.048	0.015	0.064	0.052	0.023	0.075	0.091
26	0.005	0.009	0.014	0.181	0.116	0.297	0.088	0.060	0.148	0.130	0.085	0.215	0.228
Mean	0.009	0.007	0.016	0.235	0.109	0.344	0.060	0.066	0.126	0.130	0.086	0.216	0.232
S.D.	0.009	0.004	0.011	0.564	0.126	0.660	0.038	0.052	0.085	0.216	0.079	0.266	0.271

TABLE 5

Summary of Dose Rates for Strawberry Harvesters (3 Days)
(mg/hr)

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
ARMLEFT	54	0.014	0.016	0.000	0.081
ARMRIGHT	54	0.013	0.016	0.000	0.067
ARMS	54	0.027	0.031	0.002	0.148
AMLEFT	54	0.184	0.336	0.000	2.471
AMRIGHT	54	0.140	0.111	0.025	0.518
AM	54	0.324	0.409	0.043	2.905
FMLEFT	54	0.103	0.096	0.015	0.480
FMRIGHT	54	0.093	0.064	0.003	0.253
FM	54	0.196	0.151	0.045	0.722
LEFT	54	0.137	0.147	0.024	0.967
RIGHT	54	0.114	0.076	0.023	0.362
HANDS	54	0.251	0.203	0.061	1.149
TOTAL	54	0.278	0.214	0.068	1.183

TABLE 6-1

Statistical Analysis of Dermal Exposure Rates for Strawberry Harvesters
Grouped by Weight -- Three Days' Observation

Variable	N	Dermal Exposure Rate mg/hr	Type	Kruskall Wallis x^2	p
>50 kg	33	0.03	Lower arms	2.36	0.12
<50 kg	21	0.02			
>50 kg	33	0.30	Hands,AM	1.08	0.3
<50 kg	21	0.36			
>50 kg	33	0.24	Hands,PM*	11.19	0.0008
<50 kg	21	0.12			
>50 kg	33	0.27	Hands,all day**	3.44	0.06
<50 kg	21	0.22			
>50 kg	33	0.30	Total**	3.71	0.05
<50 kg	21	0.24			

*significant

**time-weighted average

TABLE 6-2

Statistical Analysis of Dermal Exposure Rates of Strawberry Harvesters

Grouped by Body Surface -- Three Days' Observation

Variable	N	Dermal Exposure Rate mg/hr	Type	Kruskall Wallis x^2	p
>1.52 m^2	36	0.23	Hands,PM**	9.06	0.0026
<1.52 m^2	18	0.12			
>1.52 m^2	36	0.27	Hands,all day*	5.26	0.0218
<1.52 m^2	18	0.21			
>1.52 m^2	36	0.30	Total*	5.43	0.0198
<1.52 m2	18	0.23			

*significant

**time-weighted average

TABLE 7-1

Correlation Between Dermal Exposure Rates of Vinclozolin and Age of

Strawberry Harvesters

Type of Exposure	Pearson Correlation Coefficient	p	Spearman Correlation Coefficient	p
Left hand*	0.48	0.003	0.50	0.0001
Right hand*	0.56	0.0001	0.57	0.0001
Hands, AM	0.46	0.0005	0.46	0.0005
Hands, PM	0.42	0.0016	0.53	0.0001
Hands, all day*	0.55	0.0001	0.57	0.0001
Arms	0.21	0.13	0.37	0.0056
Total*	0.55	0.0001	0.58	0.0001

*Time-weighted averages for hands

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TABLE 7-2

Correlation between Dermal Exposure Rates and

Productivity of Strawberry Harvesters

Type of Exposure	Pearson Correlation Coefficient	p
Left hand*	0.31	0.0268
Right hand*	0.44	0.0011
Hands, AM	0.23	0.0987
Hands, PM	0.47	0.0005
Hands, all day*	0.39	0.0046
Arms	0.14	0.32
Total*	0.39	0.0046

*Time-weighted average for hands

TABLE 8

Decline of Dislodgeable Residues of Vinclozolin on Strawberry Leaves

Days Post-Application*	N	Dislodgeable Residues (Geometric Means) ng/cm^2
17	2	91.2
19	3	41.7
23	1	18.2
30	2	7.41
31	2	8.91
32	2	5.37
33	2	5.24

*1 lb/A each on May 5,15, and 22 May, 1982;

first sampling date: June 8, 1983

TABLE 9

Transfer Coefficients for Vinclozolin for Strawberry Harvesters

Day of Study	Days Post-Application	k_d $(cm^2 hr^{-1})$
1	31	30.0×10^3
2	32	58.8×10^3
3	33	44.6×10^3
Mean		44.5×10^3
Standard Deviation		14.4×10^3

TABLE 10

Carbaryl:Vinclozolin Ratios for Dislodgeable Foliar Residues and Dermal Exposure Rates

	Dislodgeable Residue ug/cm$_2$			Dermal Exposure mg/hr		
	Carbaryl	Vinclozolin	C/V	Carbaryl	Vinclozolin	C/V
Day-1	0.61	0.009	67			
Hands				1.99	0.242	8.2
Arms				0.66	0.030	22
Total				2.65	0.262	9.7
Day-2	0.55	0.0056	98			
Hands				1.20	0.295	4
Arms				0.41	0.035	12
Total				1.61	0.330	4.9
Day-3	0.24	0.0052	46			
Hands				1.02	0.216	4.7
Arms				0.43	0.016	26
Total				1.45	0.232	6.3

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Section No. 16
Revision No. 0
Date: February 29, 1984

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LITERATURE CITATIONS

Cabras, P., Paolo, P., Meloni, M., Pirisi, F.M. J. Agric. Food Chem. 1982, 30, 569-572.

Cabras, P., Paolo, D., Meloni, M., Pirisi, F.M., and Pirisi, R. J. Chromatogr. 1983, 256, 176-181.

Gunther, F.A., Westlake, W.E., Barkley, J.H., Winterlin, W., Langbehn, L. Bull. Environm. Contam. Toxicol. 1973, 9, 243-249.

Gunther, F.A., Barkley, J.H., Westlake, W.E. Bull. Environm. Contam. Toxicol. 1974, 12, 641-644.

Iwata, Y., Spear, R.C., Knaak, J.B., Foster, R.J. Bull. Environm. Contam. Toxicol. 1977, 18, 649-653.

Popendorf, W.J. and Leffingwell, J.T. Bull. Environm. Contam. Toxico. 1977, 18, 787-788.

Popendorf, W.J., Leffingwell, J.T., McLean, H.R., Zweig, G., and Witt, J.M. Youth in Agriculture. Pesticide Exposure by Strawberry Pickers. Captan. 1981-Studies. PHAP-University of Calif.-Berkeley, Final Report to OPTS, EPA, September, 1982.

Sendroy, J., Jr.and Cecchini, L.P. J. Appl. Physiol. 1954, 7, 1-12.

Spear, R.C., Popendorf, W.J., Spencer, W.F. and Milby, T.H. J. Occup. Med. 1977, 19, 411-414.

Zweig, G., Gao, Ru-yu, and Popendorf, W. J. Agric. and Food Chem. 1983, 31, 1109-1113.

Zweig, G., Gao, Ru-yu, Witt, J.M., Popendorf, W., and Bogen, K. Youth in Agriculture. Dermal Exposure to Pesticides by Strawberry Harvesters. 1982-Studies. I. Carbaryl. PHAP University of Calif.-Berkeley, Draft Report Submitted to OPTS, EPA, December, 1983.

FIGURE 1

Capillary GLC of mixture of standards of vinclozolin (retention time: 6.53 min); endosulfan I (7.44 min); endosulfan II (7.80 min); endosulfan sulfate (8.16 min); experimental dtails described in text.

FIGURE 2

Linear regression of exposure rates versus age of strawberry
harvesters exposed to vinclozolin.

(VINCLOZOLIN) EXPOSURE VS. AGE

EXPOSURE RATE (mg/hr)

□ 2 POINTS

y = 0.0132X + 0.0326

r = 0.82
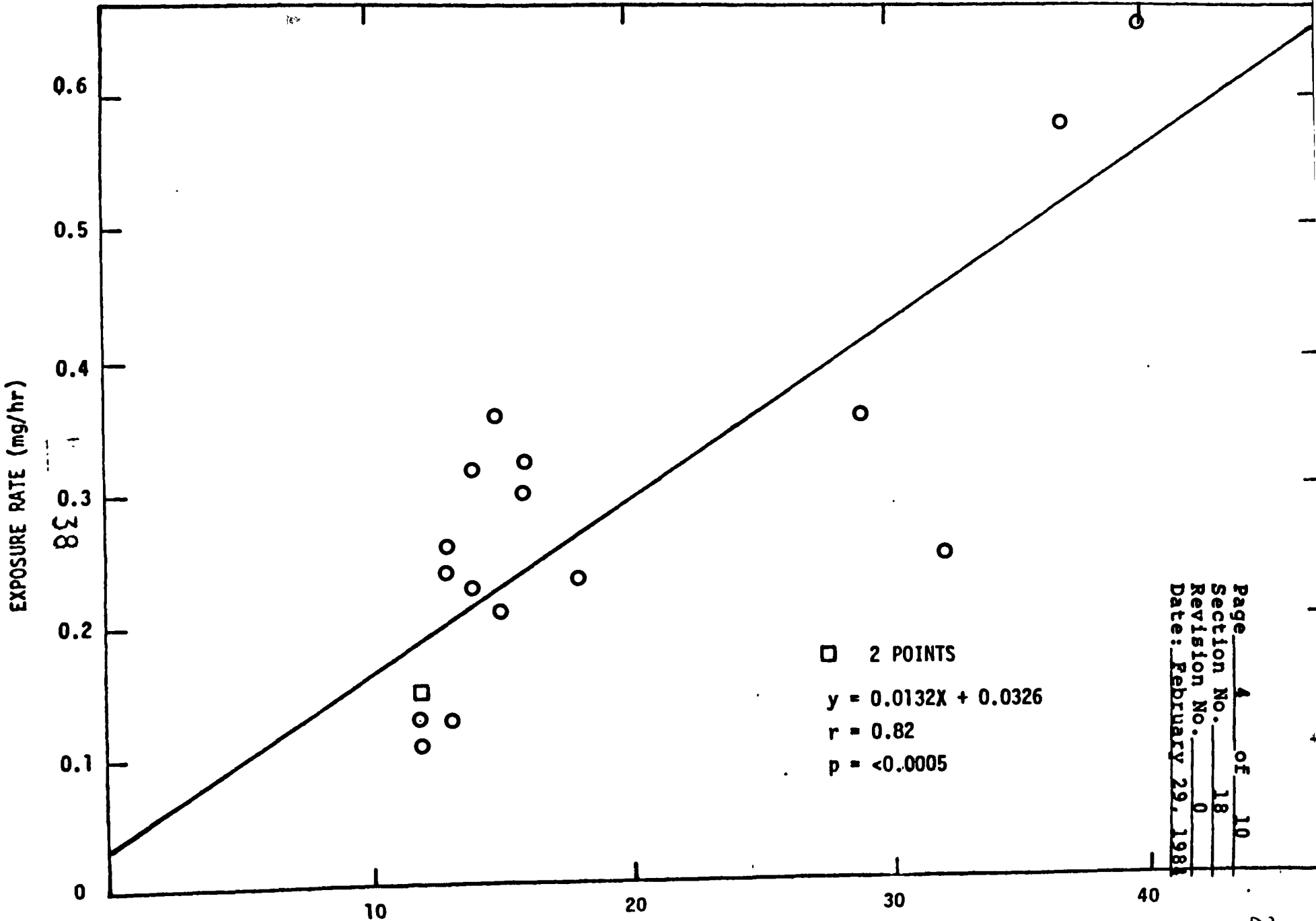
p = <0.0005

FIGURE 3

Linear regression of exposure versus productivity of strawberry

harvesters exposed to vinclozolin.

EXPOSURE VS. PRODUCTIVITY
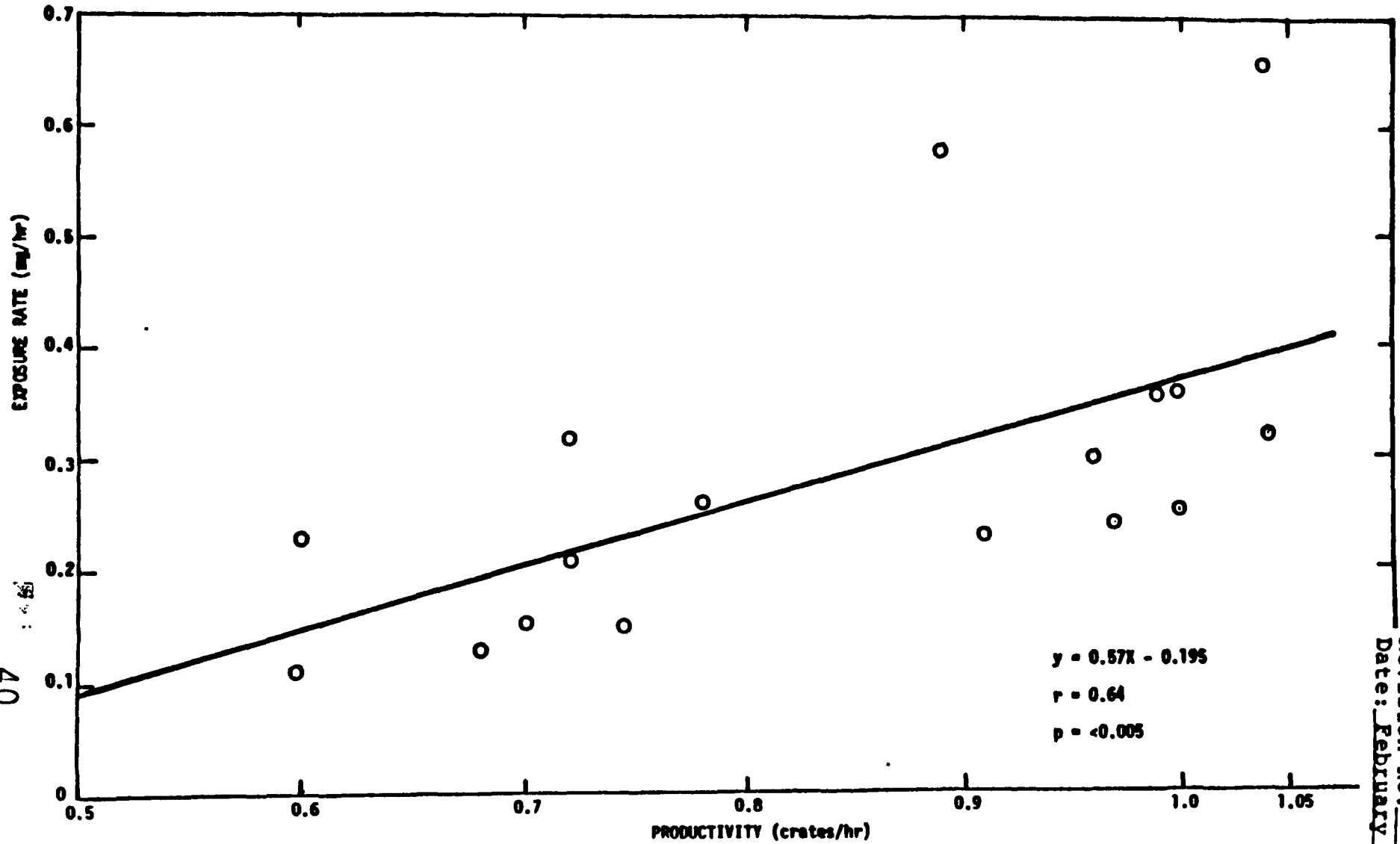
$y = 0.57X - 0.19S$

$r = 0.64$

$p = <0.005$

FIGURE 4

Linear regression of productivity of strawberry harvesters

versus age

AGE - PRODUCTIVITY

$y = .01X + 0.645$

$r = 0.55$
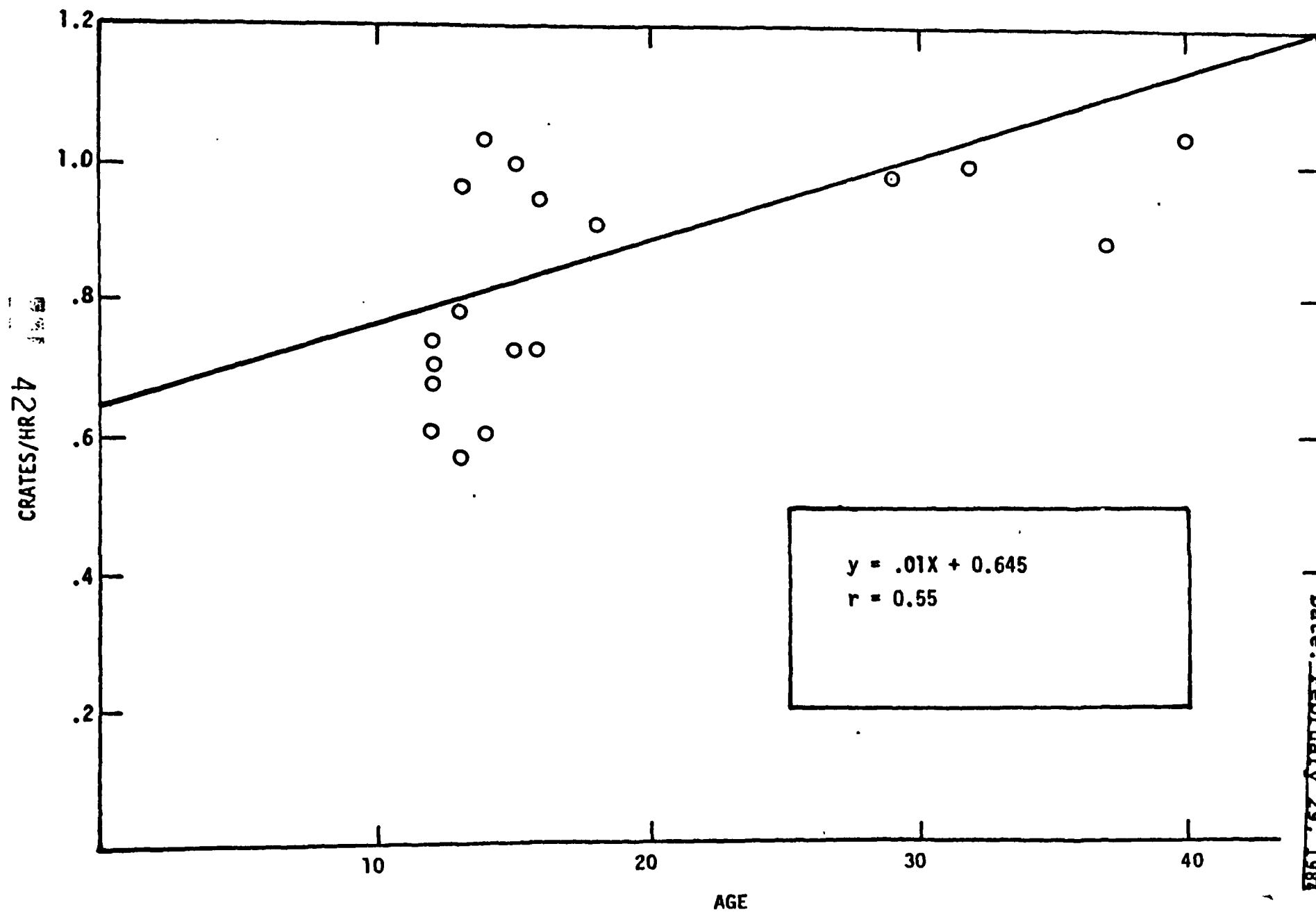
FIGURE 5

Semi-log plot of decline of dislodgeable vinclozolin foliar

residues on strawberry plants; vertical bars are confidence

intervals; r=-0.96.

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DISLODGEABLE RESIDUE (ng/cm²)

DAY POST-APPLICATION

図2.5

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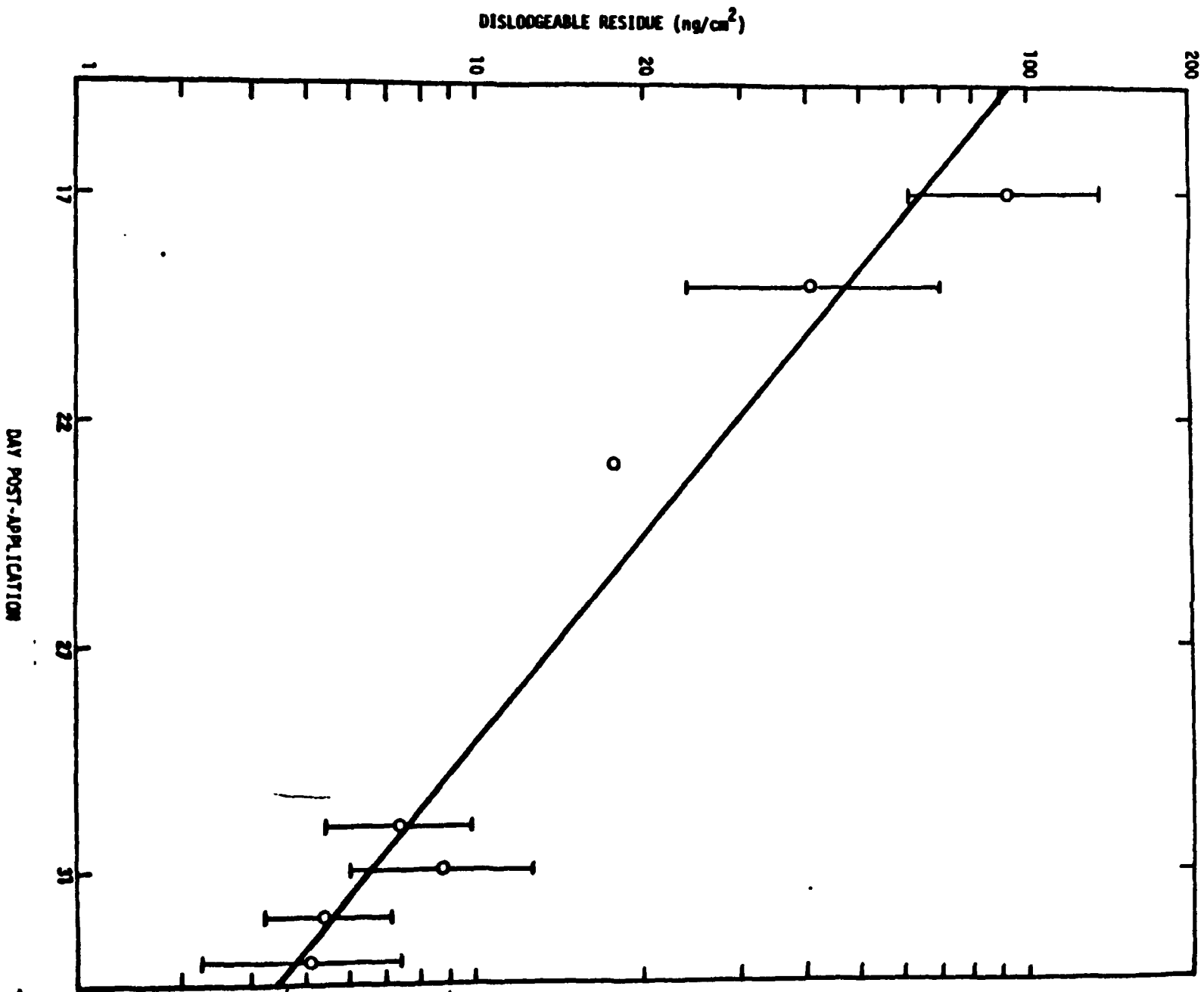
Simultaneous Dermal Exposure to Captan
and Benomyl by Strawberry Harvesters
1983

Research performed by

University of California
Richmond, CA 94804

Abstract

Ten strawberry harvesters were monitored during work-
ing hours for dermal exposure due to captan [3a,4,7,7a-
tetrahydro-N-(trichloromethanesulfenyl) phthalimide] and
benomyl [methyl 1-[(butylamino) carbonyl]-1H-benzimidazol-
2-ylcarbamate]. The average dermal exposure was found to be
39.01 mg/hr/person for captan and 5.39 mg/hr/person for
benomyl. The ratio of the dermal concentration of captan
and benomyl was found to be similar to the ratio for
dislodgeable foliar residues of the same two pesticides
from strawberry plants in the same plot. Productivity, as
measured by the quantity of fruit picked, and dermal expos-
ure of individuals to benomyl correlate positively. The
study was designed to measure left- and right handed dermal
exposure and to determine dextral preference among
strawberry pickers.

The determination of dermal exposure to pesticides by harvesters of fruit and field crops forms the basis for establishing reentry intervals. These intervals are designed to permit agricultural field workers to reenter pesticide-treated plots without suffering any ill effects. The regulation of organophosphorus insecticide residues for farmworker protection has been recently discussed by Popendorf and Leffingwell (1982). Most of the previous attempts to correlate dermal human exposure with dislodgeable foliar pesticide residues have dealt with a single pesticide (e. g. Popendorf, 1980). A field study has now been conducted in which strawberry harvesters were monitored in a plot that had been treated with two fungicides, captan and benomyl, to control mainly botrytis and powdery mildew. The major aim of the experiment was to answer a key question: Does the same proportional relationship exist between two pesticides occurring as dislodgeable foliar residues and dermal deposit?

EXPERIMENTAL SECTION

Description of Field Study. A cooperative strawberry farm located in the Pajaro Valley, near Salinas, California, was chosen as the site. The date of the study was May 19, 1982. The monitoring was conducted during the morning (0800 - 1000 hours) when the temperature ranged between 53 $^\circ$F and 66 $^\circ$F, and the wind was recorded at less than 7.4 km/hr. Ten harvesters who volunteered for this study were provided with light cotton gloves, used in photographic darkrooms, marked with indelible numbers to identify each subject and the letters "R" and "L" to designate the right and left hand.

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Each volunteer was also provided with dermal dosimeters fastened
to the outer side of the forearm, 6-in. above the wrist, with
surgical tape. This dosimeter consisted of a 12-ply 3x3 in
surgical gauze placed into a slightly larger glacine-paper
envelope with a circular 60-mm diam hole facing the outside (away
from the skin) and a piece of polyethylene film placed on the
other side of the gauze nearer the skin to serve as a moisture
barrier. In this way, 28 cm^2 of the gauze pad was exposed to the
environment. The workers were not required to wear any special
protective clothing other than those normally worn early in the
morning, like slacks and long-sleeve shirts. Subjects were
measured for height and weight; age, sex and manual preference
were recorded.

Subjects went about their normal work, picking
strawberries in a bending or squatting position. For the comfort
of the workers, the gloves and forearm dosimeters were removed
from the subjects after about two hours and stored in plastic
bags, packed with "dry-ice" during transport and kept in freezers
until the extraction and analyses could be performed.
Productivity for each subject was recorded as "number of crates
harvested" during the monitoring period.

Forty-eight strawberry leaf disks for dislodgeable
residue analyses were taken from different plants diagonal-
ly across the strawberry plot with a mechanical leaf punch.
This tool is equipped with a 3-cm diam circular die and
attached with a screw cap to a 4-oz wide-mouth glass jar.
Details of this and other sampling techniques are described

by Popendorf, et al.(1982b).

Information obtained from the commercial pesticide applicator showed that the latest application prior to the study took place on May 15, 1982 (4 days prior to the study) and consisted of the following given as active ingredient (a.i.):   1.5 gal EC dicofol (2.4 lb a.i.); 1 lb benomyl; 4 lb captan.

Materials and Analytical Instrumentation. Analytical-grade captan, benomyl, and carbendazim (methyl 1H-benzimidazol-2-ylcarbamate) were obtained from the EPA Reference Standard Repository, Research.Triangle Park, NC 27711; carbendazim was also obtained from duPont Nemours & Co. All solvents used throughout were HPLC-Grade ("Baker Analyzed" or equivalent). Water for HPLC solvents was passed through a Milli-Q Water Purification System. Mobile phases for HPLC were degassed by filtration through Millipore FHUP filters and stirring under a water-pulled vacuum for 30 min.

A Tracor-222 Gas Chromatography Apparatus, equipped with a ^{63}Ni-EC detector and Hewlett-Packard electronic integrator (HP 3390A) was used for captan analysis. The chromatographic column was a 3 ft × 2 mm (i.d.) glass column packed with OV-10 (10%) on Supelcoport (80/100 mesh).

For the analysis of benomyl and carbendazim the following HPLC apparatus was used: Waters Model 6000A Solvent Delivery System; WISP Automatic Sample Processor; Model 450 Variable Wave Length Detector; Water Data Module;

RP-18 Spheri 5 Brownlee Labs. bonded reversed-phase column

(25 cmx 2 mm i.d.). A Bausch & Lomb Spectronic 2000 record-

ing spectrophotometer was employed for confirmatory analy-

sis of benomyl and carbendazim.

Extraction. Gauze patches were individually extracted with

50 to 60 mL of acetonitrile by placing the sample and solvent

into a 125-mL wide-mouth LPE bottle fitted with a screw cap and

shaking the contents on a mechanical platform for one hour.

Gloves were extracted in a similar manner by using 100 mL of

solvent and 500 mL-plastic bottles.The solvent layer was decanted

and passed through a Millipore BD (0.6 μm) filter. Aliquots of

the filtrate were analyzed for captan and benomyl by GLC and

HPLC, respectively. In order to maintain the linearity of the

electron-capture detector for captan analysis, up to 20-fold

dilutions of extracts containing high concentrations of this

pesticide were necessary.

Dislodgeable foliar pesticide residues and dust were

isolated from leaf punches according to methods developed by

Gunther (1973,1974), Iwata (1977) and Popendorf and Leffingwell

(1977). Leaf punches were surface-extracted with 100 mL of a 60 -

ppb aqueous solution of dioctyl sodium sulfosuccinate by agita-

tion on a reciprocal-action mechanical shaker for 30 min. The

liquid phase was carefully separated from the plant tissue and

extracted three times successively with 50 mL each of dichlorome-

thane in a 500-mL separatory funnel. If an emulsion formed, the

addition of a few mLs of sat. aqueous Na SO was usually
                                         2 4

sufficient to separate the phases. The combined organic extracts

(bottom phase) were filtered through glass wool and a bed of anh.

Na$_2$SO$_4$ and evaporated in vacuo to complete dryness. The residue

was finally taken up in 10.0 mL of acetonitrile. Aliquots of this

solution were directly analyzed for captan and benomyl as will be

described below.

Leaf dust, originally washed off with the surfactant,

remained in the interfacial solvent-water layer in the separatory

funnel and was quantitatively transferred after the last solvent-

extraction to a pre-weighed glass filter. After drying at 110°

overnight, the filter was weighed again, and the weight of the

foliar dust calculated by difference.

Analysis of Captan and Benomyl One to 5 μL of the

final extract or appropriate dilutions thereof, were ana-

lyzed for captan by gas-liquid chromatography. Chromatogra-

phic conditions were the following: argon-methane carrier

gas flow rate -- 65 mL/min; column temperature -- 210°.

Under these conditions, captan eluted as a sharp peak at

1.27 min. No interfering peaks were observed in any of the

field samples. Quantification was performed by area-integr-

ation using an electronic integrator and an external stand-

ard calibration curve. Results were reported as μg/sample

for patches and gloves and μg/cm^2 leaf surface or μg/mg of

dust for dislodgeable residues.

The analytical method for benomyl is based on the

spontaneous conversion of benomyl to carbendazim in

acetonitrile and subsequent analysis of carbendazim by HPLC

(Zweig and Gao, 1983). Twenty-five microliters of the final

extracts was analyzed by reversed-phase HPLC on a C-18

bonded column using as mobile phases acetonitrile-water in

the proportions of 65:35 or 50:50, v/v and a solvent flow

rate of 1.3 or 1.5 mL/min, respectively. Benomyl and

carbendazim were detected at 286 nm. The elution time for

carbendazim with both mobile phases was found to be 3.4

min. The retention times for benomyl, stabilized by the

addition of n-butylisocyanate (Chiba, 1977), were 7.8 and

15.8 for the two mobile phases, respectively. Quantifica-

tion was accomplished by an electronic integrator, using

the external standard method. The minimum detectable quan-

tity for both compounds as limited by instrumental noise

and detector sensitivity was found to be 5 ng.

[Important note. All extracts must be kept at room tempera-

ture for 3 hrs or 40° for 1 hr prior to the analysis. The purpose

of this waiting period is to permit the quantitative conversion

of benomyl to carbendazim in acetonitrile, which is fully

discussed by Zweig and Gao (1983).]

All results are reported as benomyl. If carbendazim was

chosen as external standard, the molecular weight conversion

factor of 1.52 was applied.

Estimation of Dermal Exposure   To estimate dermal

exposure on the forearm, the following calculations were

made: The concentration of pesticide on the patch was

multiplied by 645/28, 28 cm^2 being the exposed surface area

of the patch and 645 cm^2 the surface area of the forearm of

the 50-percentile man (Popendorf, 1982). This was further
corrected for individual body surface differing from that
of the 50-percentile man, 1.92 m^2, by estimating individual
body surface from a body weight-height nomograph (Sendroy
and Cecchini, 1954). Because gloves cover the entire ex-
posed area of the hands, total manual exposure was estim-
ated without transformations. All exposure data were
normalized for an hourly exposure rate.

Recovery Studies for Captan and Benomyl. Control
samples of patches, gloves, and strawberry leaves were
spiked with known amounts of captan, benomyl, and
carbendazim. For recovery purposes, benomyl was stabilized
by the addition of excess n-butylisocyanate (Chiba, 1977).
Strawberry leaves from a non-treated field were not
available when benomyl-carbendazim recovery studies were
conducted, and, therefore, a dilute aqueous solution of
dioctyl sodium sulfosuccinate served as surrogate for "dis-
lodgeable foliar residue samples". All spiked samples were
processed by the same procedures as described above under
"Extraction" and analyzed by appropriate instrumental
methods, GLC or HPLC. As shown in Table I, recoveries were
almost quantitative for all compounds studied.

Confirmation of Carbendazim Residues. The identity of
suspected carbendazim residues from field samples was con-
firmed by two independent methods: The solvent extract of a
field sample (left-handed glove, Subject No. 2) was chroma-
tographed by HPLC and the eluant collected at the previous-
ly determined retention time of carbendazim.The uv-scan of

this solution was identical to the spectrum of authentic

carbendazim with characteristic absorption peaks at 286.1

nm and 280.0 nm and a shoulder at 294.1 nm. The uv-spectrum

of this solution containing n-butylisocyanate (final concn. 10^3

ppm) was identical to one of authentic benomyl with absorption

peaks at 292.6 nm and 286.1 nm and the absence of the absorption

maximum at 280 nm, belonging to carbendazim.

A second confirmatory method involved the demonstra-

tion of quantitative conversion of suspected carbendazim to

benomyl following the addition of excess n-butylisocyanate. The

extracts of two representative field samples (gloves belonging to

Subject No. 7) were first analyzed for carbendazim by HPLC and,

after the addition of n-butylisocyanate, for benomyl. The reten-

tion times for carbendazim and converted benomyl from the field

samples were identical with those of reference standards. As

shown in Table II, quantitative conversion of carbendazim to

benomyl had taken place, demonstrating that carbendazim was

indeed the compound isolated from field samples.

RESULTS AND DISCUSSION

Dermal Exposure to Benomyl and Captan. The ten

volunteers for this study (7 male and 3 females) were

experienced strawberry pickers and ranged in age from 19 to

55 years of age (Table III). Pickers 1 an 2 were most

productive as judged by the number of crates picked per

hour. Each crate consisted of twelve 1-pint baskets with a

total net weight of fruit of about 5 kg.

Popendorf et al.(1982,a,b) and Everhart and Holt (1982) have shown that the major dermal exposure of strawberry harvesters to captan and benomyl occurred on hands and lower forearms. Dermal body exposure could, therefore, be estimated by monitoring only these two anatomical regions, hands and forearms. This assumption may not be valid for harvesters of other crops, like tree-grown fruits, where Popendorf (1980) observed a more uniform total body exposure. Row crops, like strawberries, are hand-picked from a stooped or squatting position which determines the dermal distribution found by Popendorf (1982,a,b) and Everhart and Holt (1982).

Forearm exposure was estimated from the gauze dosimeter placed in a position where greatest exposure from contact with plant foliage would most likely be expected, i.e. the region of the forearm above the wrist. Using the concept of the 50-percentile man and the proportional surface allocation for each anatomical region, an estimate to that particular region (forearm) was made, notwithstanding the possibility of non-uniform pesticide distribution, leading to possible error in the final estimate.

Table III shows that dermal exposure by the ten subjects studied ranged from 1.2 mg/hr to 15.5 mg/hr for benomyl and 13.2 mg/hr to 51.3 mg/hr for captan. Corresponding means were calculated to be 5.39 mg/hr/person (86.4%) and 39.01 mg/hr/person (38.0%), respectively, with the percent relative standard deviations in parentheses. Subject No. 1 exhibited an inexplicably high left-handed

captan exposure (see Table IV). However, using Grubbs'
procedure (1969), this value could be excluded as an out-
lier and substituted with the experimental value for the
right-handed exposure. Further justification for this
adjustment were the equal exposure of benomyl to both hands
(Table V) and similar ratios for left- and right forearm
exposures for captan (3.2) and benomyl (3.9).

The higher dermal captan exposure compared to benomyl
exposure was probably due to the higher rate of captan
application (4 lbs/A and 1 lb/A, respectively), with both
pesticides being applied at the same time. This explanation
is further supported by the finding of much higher dislod-
geable residue levels for captan than those found for
benomyl (Table VI).

Benomyl exposures at 4-days' post-application found in this
study were similar to those reported by Everhart and Holt (1982).
They found an average dermal exposure of 5.9 mg/hr/person among
three strawberry pickers who worked in the field 24 hrs after the
last application of benomyl. Benomyl was at the same rate as
that reported for this study (1 lb/A). According to Baude, et
al. (1973), foliar benomyl residues appear to be stable over
several days after application, e.g. apple leaves were found to
retain 91% of the originally applied benomyl 7 days after the
last application.

Dislodgeable Foliar Residues. Table VI shows the
results from the analysis of dislodgeable foliar residues
of captan and benomyl sampled the same day as the study.

The ratio of average dislodgeable residues of captan and benomyl is 6.1. The corresponding ratio for dermal exposure is 7.2 (see Table III). These two ratios are similar, suggesting that dislodgeable foliar residues of several pesticides are transferred from foliage in the same proportion to the exposed skin surface of field workers. Popendorf and Leffingwell (1982) and Popendorf et al. (1982,a,b) have already shown that a positive correlation between dislodgeable foliar residues and dermal concentrations of pesticides exists.

Using the data from Tables III and VI, transfer coefficients(k_d) for captan and benomyl were be calculated and found to be 8.57×10^3 cm^2/hr and 7.19×10^3 cm^2/hr, respectively. ("k_d" is defined as the ratio of dermal concentration to dislodgeable foliar residue and assumes the units of area over time). The transfer coefficients from this study are similar to those reported by Popendorf and Leffingwell (1982c) for citrus and peach harvesters exposed to organophosphorus insecticides. Converting the k_d's to minutes (143 and 120 cm^2/min), it would appear that strawberry harvesters are contacting a small foliar surface thereby receiving maximum pesticide exposure. This reason-ing is based on the unlikely situation that foliar pesti-cide residues are transfered quantitatively to skin.

In prior studies by this laboratory (Popendorf, et al., 1982a,b), surface captan residues of about 1 ppm were found on strawberries, and these residues may, therefore, be a contributory factor of dermal exposure, especially to hands of fruit harvesters. The relative contribution to dermal exposure from foliar dislodgeable residues and surface residues from fruit

remains.to be the subject of a future study.

Comparison of Left- and Right-Handed Exposure. Since
left- and right-handed gloves were individually analyzed,
it was possible, therefore, to compare dermal pesticide
exposure of each worker on his left and right hand. At
least eight out of these ten workers professed to be right-
handed, and the remaining two workers did not express a
preference. As may be seen in Tables IV and V, it appears
that Subject 5 exhibits right-handed preference as shown by
the data for both captan and benomyl. In addition, Subjects
3, 6 , and 10 also showed right-handed preference, based on
the data from one of the pesticides. The remaining subjects
appear to be ambidextrous in picking strawberries as manif-
ested by hand exposure data. These findings suggest that
analyses of chemical exposure on the left and right hand
might be a suitable method for conducting time-motion stud-
ies of farm workers harvesting row crops.

Productivity and Exposure. A positive correlation was
found between productivity, expressed as crates harvested
per hour, and dermal exposure of benomyl per hour (fig.1)
(r = 0.812; p = 0.0043) which might explain why workers
with the greatest productivity (Subjects 1 and 2) receive
the highest benomyl exposure (Table III). The worker who
picks a large amount of fruit may be subject to more skin
contact with fruit and foliage bearing dislodgeable
pesticide residues than the worker who is less productive.

A similar correlation between productivity and dermal
exposure to captan was not found.

REMARKS

The toxicological consequence of dermal exposure to
pesticides by crop harvesters remains uncertain until
percutaneous absorption rates for these pesticides have
been determined. Although there are few compounds which
are quantitatively absorbed through the skin, a conserva-
tive estimate of body dose may be made by assuming 100%-
absorption of the dermal dose. In the absence of the
experimentally derived data, this hypothetical dose may
serve as a first basis for estimating potential toxicological
hazard to crop harvesters.

Another uncertainty, as illustrated by the present
study, is the estimation of daily exposure based on a rela-
tively short observation period (less than two hours). It
has been observed in this and previous studies (Popendorf, et
al., 1982 a,b) that gloves became quickly saturated with fruit
juice and dew, especially in the early morning hours when most of
our observations were made. It seems reasonable to assume that
once gloves have become moisture-laden, the absorptive capacity
of the cotton cloth might be impeded. The techniques for measur-
ing average dermal exposure during a workday may, therefore, not
represent actual dermal exposure. This concern has prompted the
initiation of a series of studies by this laboratory investigat-
ing, comparing, and improving presently used techniques for mea-
suring dermal exposure to pesticides (Noel, et al., 1983).

Literature Cited

Baude, F.J.; Gardiner, J.A.; Han,J.C.Y. J. Agric. Food Chem. 1973, 21, 1084-90.

Chiba, M. J. Agric. Food Chem. 1977, 25, 368-73.

Everhart,L.P.; Holt,R.F. J. Agric. Food Chem. 1982, 30,222-7.

Grubbs, F.E. Technometrics 1969,11, 1-21.

Gunther, F.A.;Westlake, W.E.; Barkley, J.H.; Winterlin, W.; Langbehn,L.Bull. Environ. Contam. Toxicol. 1973, 9, 243-9.

Gunther, F.A.; Barkley,J.H.; Westlake,W.E. Bull. Environ. Contam. Toxicol. 1974, 12, 641-4.

Iwata, Y.;Spear,R.C.; Knaak,J.B.;Foster,R.J.Bull. Environ. Contam. Toxicol. 1977,18, 649-53.

Noel, M.E.; Zweig, G.; Popendorf, W.J. "Abstracts of Paper", 185th National Meeting of the American Chemical Society. Seattle, WA, March, 1983; American Chemical Society, Washington, D.C. CHAS 27.

Popendorf,W.J. Amer. Ind. Hyg. J. 1980, 41, 652-9.

Popendorf, W.J.; Leffingwell, J.T. Bull. Environ. Contam. Toxicol. 1977, 18, 787-8.

Popendorf, W.J.; Leffingwell, J.T. Residue Reviews 1982, 82,125-201.

Popendorf,W.J.;Leffingwell,J.T.;Zweig,G."Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, MO, September, 1982; American Chemical Society, Washington, D.C. CHSA 33.

Popendorf, W.J.;Leffingwell,J.T.; McLean,H.R.,;Zweig, G.;

Witt, J.M. "Youth in Agriculture"--Festicide Exposure to
Strawberry Pickers: 1981-Studies", Final Report submitted
to Office of Pesticide Programs, EPA, Washington,D.C.
(Sept.1982b).

Sendroy, J., Jr.; Cecchini, L.P. *J. Appl. Physiol.* 1954, *7*,
1-12.

Zweig, G.; Gao, Ru-yu. Accepted by *Anal. Chem.* 1983; see
also "Abstracts of Papers",185th National Meeting of the
American Chemical Society, Seattle, WA, 1983;American
Chemical Society, Washington, D.C.; PEST 29.

Legends to Figures

Figure 1:   Linear regression curve of "productivity"   vs.   total

dermal dose of benomyl for ten strawberry harvesters.

Table I

Summary of Recovery Studies for Carbendazim, Benomyl, and

Captan

Sample	Compound	Added	Found	Per cent Recovery
		μg		
Gauze pad (60 mL)[a]	carbendazim	51.0	49.5	97.0
Gloves (100 mL)	carbendazim	102.0	97.5	95.6
Gloves (100 mL)	carbendazim	204.0	194.3	95.3
DOSSS[b] (100 mL)	carbendazim	160.0	152.9	95.6
DOSSS (100 mL)	carbendazim	160.0	153.3	95.8
DOSSS (100 mL)	carbendazim	160.0	151.7	94.8
Gauze pad (50 mL)	benomyl[c]	127.5	126.6	99.3
Gauze pad (50 mL)	benomyl	127.5	125.0	98.0
Gauze pad (50 mL)	benomyl	255.0	252.2	98.9
Gauze pad (50 mL)	benomyl	255.0	250.0	98.0
Gauze pad (60 mL)	captan	27.5	30.2	103.3
Gloves (100 mL)	captan	27.5	31.6	108.4
Leaf disks #1	captan	5.5	5.3	95.6
Leaf disks #2	captan	2.8	2.7	96.4

[a] volume of extract

[b] aqueous solution of 0.06 ppm dioctyl sodium sulfosuccinate

[c] To a standard solution of benomyl in acetonitrile (50.0 mg/100 mL)
was added n-butylisocyanate to a final concentration of 10^3 ppm.

Table II

Confirmation of Carbendazim and Benomyl Residues

Sample	Carbendazim[a]		Benomyl[b]		Per cent Recovery
	Found		Theory	Found	
	ng			ng	
Left glove (Sub.No. 7)	115.2		158.9	162.7	102.6
Right glove (Sub.No. 7)	137.1		189.4	189.0	100.0

[a] Sample extracted with 60 mL of acetonitrile; diluted 1:5 with solvent; 25-uL aliquots analyzed in duplicate by HPLC.

[b] To 20.0 mL of diluted extract, 0.2 mL of 10^4 ppm solution of n-butylisocyanate was added; 25-µL aliquots analyzed by HPLC in duplicates.

Table III

Hand- and Lower Arm Dermal Exposure by Strawberry Harvesters

Subject No.	Sex	Age	Productivity (crates/hr)	Exposure (mg/hr) Captan	Benomyl
1	M	36	7.36	52 (180.9) [a]	15.5
2	M	45	7.36	37.4	12.1
3	M	29	5.45	35.0	4.2
4	M	19	5.38	49.8	2.8
5	F	55	3.00	13.2	1.2
6	M	22	3.40	25.0	1.9
7	M	30	4.00	51.3	4.2
8	M	23	3.25	62.1	4.9
9	F	51	4.65	28.9	2.7
10	F	20	2.96	35.1	4.4
			Mean	39.01	5.39
			rel.std.dev.	(38.0%)	(86.4%)

Captan/Benlate = 7.23

[a] The experimental figure has been deleted as an outlier according to the procedure of Grubbs (1969) and substituted by an estimate of 52 mg/hr. See also footnote, Table IV.

Table IV

Left   and   Right   Hand and Forearm Exposure to   Captan

by   Strawberry   Harvesters

| Worker No. | Dermal Exposure (mg/hr/person) | | | |
| | Forearm | | Hands | |
	left	right	left	right
1	15.22	4.82	16.14	16.14
			(144.79)[a]	
2	13.81	4.55	8.96	10.00
3	3.05	2.59	3.39	25.94
4	0.31	1.18	22.69	25.62
5	0.50	3.81	2.75	6.10
6	0.68	0.64	12.14	11.57
7	4.13	3.60	20.32	23.20
8	1.75	2.18	27.32	30.81
9	0.95	0.24	8.67	19.06
10	0.95	2.49	16.67	15.04

[a] This figure is deleted according to procedure by Grubbs (1969) for outlying observations and is replaced by value for right-hand exposure, assuming ambidexterity of Worker No. 1.

Table V

Left and Right Hand and Forearm Exposure to Benomyl

by Strawberry Harvesters

Worker No.	Dermal Exposure (mg/hr/person)			
	Forearm		Hands	
	left	right	left	right
1	1.25	0.32	6.93	6.96
2	1.16	0.31	5.30	5.23
3	0.42	0.18	1.66	1.94
4	0.0	0.06	1.36	1.38
5	0.0	0.21	0.30	0.67
6	0.07	0.04	0.83	0.97
7	0.28	0.29	1.65	2.00
8	0.19	0.17	2.04	2.46
9	0.07	0.04	0.88	1.67
10	0.09	0.21	1.13	2.94

Table VI

Dislodgeable Foliar Residues From Strawberry Plants

Sample No.	Captan		Benomyl	
	$\mu g/cm^2$	$\mu g/mg$ dust	$\mu g/cm^2$	$\mu g/mg$ dust
1	4.21	10.4	0.73	1.79
2	4.89	13.9	0.78	2.19
Mean	4.55	12.2	0.75	1.99

Captan/Benomyl = 6.06
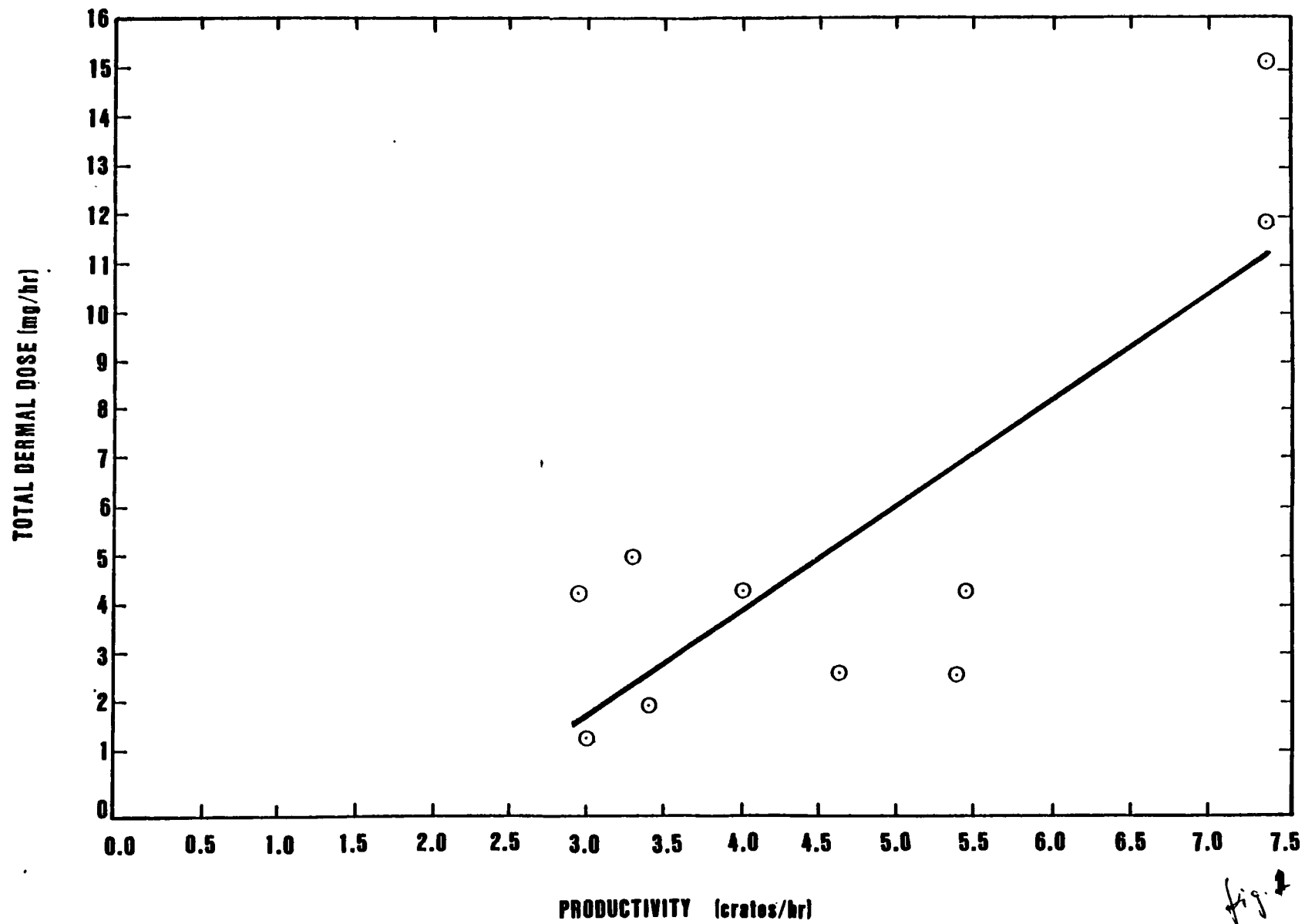
fig. 4

The Relationship between Dermal Pesticide
   Exposure by Fruit Harvesters and Dislodgeable
   Foliar Residues 1981-1983

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THE RELATIONSHIP BETWEEN DERMAL PESTICIDE EXPOSURE BY

FRUIT HARVESTERS AND DISLODGEABLE FOLIAR RESIDUES

Key Words: Pesticides, captan, vinclozolin, methiocarb,

carbaryl, Dermal Exposure, Strawberry Harvesters,

Blueberry Harvesters, Dislodgeable Foliar Residues

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ABSTRACT

Dermal pesticide exposure rates, expressed in mg/hr, by strawberry and blueberry harvesters and dislodgeable foliar pesticide residues were determined in 7 separate field experiments during 1981 - 1983 in California and Oregon. The pesticides which were studied included captan, vinclozolin, carbaryl, and methiocarb. A positive correlation between these two parameters was found and compared with literature values involving different

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pesticides and tree crops. The ratio between dermal exposure rate and dislodgeable foliar residues, the units of which are area/time, may have a possible use as an empirical factor for a first approximation of dermal exposure rates by fruit harvesters without the involvement of human subjects.

INTRODUCTION

In a recent publication, Popendorf and Leffingwell (1982) proposed a technique for the estimation of reentry intervals for harvesters of citrus and peach crops exposed to cholinergic organophosphorus insecticides. Their technique was based on dermal toxicity and decay of the foliar dislodgeable residues of parent pesticide and toxic metabolites. Nigg, et al., (1984) also have suggested the use of an empirical factor and foliar residue levels to estimate total body exposure by citrus workers.

This concept has now been extended to study workers harvesting row and bush crops (strawberries and blueberries, respectively). From the results of these recent field experiments, we are proposing to estimate dermal pesticide exposure of crop harvesters by using a similar empirical factor experimentally obtained from dermal exposure rates and dislodgeable foliar residues on different crops for various pesticides.

MATERIALS AND METHODS

Field Studies — Overview

Field studies on total dermal exposure were first conducted with strawberry harvesters exposed to the fungicide captan

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(N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide). Later experiments involved strawberry harvesters exposed simultaneously to the fungicide vinclozolin [3-(3,5-dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione] and the insecticide carbaryl (1-naphthyl-N-methylcarbamate) and blueberry harvesters exposed to methiocarb [4-(methylthio)-3,5-xylyl-methylcarbamate] used as a bird repellent. Some of the latter studies were simplified by limiting the number of personal monitoring sites without sacrificing the accuracy for the estimation of total dermal exposure.

The studies reported here took place during the harvesting seasons of 1981 - 1983 at several locations in California and Oregon. Details on sites, study dates, pesticides applied, dosage, crops, and meteorological information may be found in TABLE 1.

The experimental plan was to recruit for each study at least twenty fruit harvesters to include males, females, adults and children (10 - 11 years old) to be monitored for dermal exposure to pesticides during regular working ours and under normal working conditions, resulting in minimal interference in their assigned duties. Due to the sparser harvest of strawberries in August, there were fewer subjects for Studies 4 and 5 (see TABLE 1).

Dermal Exposure

Monitoring devices for dermal exposure consisted of 12 - ply, 3 x 3 in. surgical gauze pads. A polyethylene moisture barrier was placed on the side of the pad facing the skin of the

TABLE 1

Summary of Field Studies

Study No.[a]	Date	Crop	Compound	Dosage[b] (kg/ha)	Days[c] Post Appl.	No. of Workers	Weather °C	Ppt
1	5/9/81	Strawberries	Captan	2.5	13	19	23	0
2	6/22/81	Strawberries	Captan	2.8	26	23	16-19	~4mm
3	7/21/81	Strawberries	Captan	2.2	4	15	12-24	0
4	8/21/81	Strawberries	Captan	2.2	3	6	18-21	0
5	8/21/81	Strawberries	Captan	1.1	48	10	18-21	0
6	6/22 - 24/81	Strawberries	Carbaryl	1.1	15,16,17[d]	18	12-32	0
6a	6/22 - 24/81	Strawberries	Vinclozolin	1.1	31,32,33	18	12-32	0
7	7/24 - 28/83	Blueberries	Methiocarb	1.65	3,4,6	25	18-21	[e]

[a] 1 = Cooperative farm near Salinas,CA

   2 = Private farm near Corvallis, OR

   3-5 = Cooperative farms near Salinas, OR

   6 = Private farm near Corvallis, OR

   7 = Private farm near Salem, OR

[b] Dosage of active ingredient (a.i)

[c] Days after last treatment.

[d] Observations were made on each day.

[e] Heavy rainfall on Day-5, post-application.

subject. The container of the monitor is a hand-folded glossy envelope with a circular hole 60 mm in diam. on the side facing away from the skin, thus exposing 28 cm^2 of the gauze pad.

Patch monitors are placed at various body sites, the head (fastened to a head band or brim of a cap); chest, back, upper arms (stapled to a tightly fitting cotton T-shirt); lower arms and lower legs (fastened to skin with surgical tape). Light-weight cotton gloves, similar to those worn in photographic darkrooms and electronic assembly plants serve as hand monitors.

The subjects were not required to wear special clothing; their garments usually consisted of denim jeans and long-sleeved cotton shirts. On hot days, male workers might remove their shirts but continued to wear the specially supplied T-shirts outfitted with monitoring patches. The cotton gloves did not seem to impede the work efficiency of the harvesters and offered no unusual discomfort. Dermal monitors were worn throughout the workday with the exception of gloves, which were removed earlier in Studies 6 and 6a because they became saturated with moisture and fruit juice. The exact time of monitoring body or hand monitors was recorded for each subject.

Dislodgeable Foliar Residues

Foliar samples consisted of 3 cm diam. leaf disks collected with a mechanical punch first described by Smith and Little (1954). The device is fashioned from a parallel-action paper punch modified by the installation of a 3 cm diameter metal punch and die. Each stroke of the punch cuts a leaf disk and pushes it

into a 4 oz wide-mouth glass jar which is directly attached to the punch and at the same time serves as convenient sample storage container. A resettable counter activated by each stroke of the device records the number of leaf disks collected.

Samples were collected from plants on a random diagonal line across the study fields in which the subjects were harvesting fruit. For each 48-leaf disk sample, foliage was randomly collected from the outer and inner canopy of the plants.

Soil Samples

Soil samples were taken in a similar pattern as that described for leaf disks, by sampling along diagonal lines across the plot of land which was being studied. Samples were taken every 8 to 10 rows until six replicates had been collected. The soil sampling device consisted of a 10 x 8 x 8 cm metal frame which, when pressed into the soil, outlined an 80 cm^2 area. A flat, rectangular shaped metal shovel with a 1-cm high rim that just fitted inside the metal form, was then inserted into the soil, pushed forward until a soil surface layer of the same area could be scooped up.

Preparation of Samples and Analysis

All samples taken in the field were kept frozen over dry-ice or in a deep-freeze until they could be extracted prior to analysis. Dermal monitors and gloves were extracted with 30 and 100 mL of a suitable solvent, respectively, (e.g. toluene, methanol, or acetonitrile) by agitation on a reciprocal shaker. If the final analysis was to be performed by high performance

liquid chromatography (HPLC), toluene could not be used as an extracting solvent due to interference with the UV detector. These solutions had to be filtered through Durapore (0.45 µm) filters.

Dislodgeable foliar residues were washed from the leaf disks with a 60 ppb aqueous solution of dioctyl sodium sulfosuccinate (SURTEN) and subsequently extracted into dichloromethane via liquid-liquid extraction (Gunther, et al., 1973; Iwata, et al., 1977). With a rotary evaporator, the dichloromethane was converted to the solvent of choice for chromatography (toluene for gas chromatography and acetonitrile for HPLC). Results are expressed in weight (µg or ng) per area. The area is one side of the 3 cm diam. disk, namely 7.1 cm^2.

Soil samples were sifted through a #10 sieve to remove gravel and plant debris and dried in vacuo at room temperature overnight. The sample was weighed and then exhaustively extracted in a Soxhlet apparatus for 4 hrs with an azeotropic mixture of acetone-hexane (59:41, v/v). As with the dichloromethane above, the acetone-hexane was converted to the solvent suitable for the particular analytical technique. Results are reported as ppm of pesticide in air-dried (less than 0.5% moisture) soil.

Analysis of Pesticide Residues

Captan residues were analyzed by GC on a packed column TRACOR 222 GC under the following operating conditions:

Carrier Gas: 5% Argon in methane

Carrier Flow: 65 mL/min.

Inlet Temperature: 220°C.

Column: 0.9 m x 2 mm ID Pyrex packed with 10% OV-1

silicone coated on 80/100 mesh SUPELCOPORT

Column Temperature: 210°C.

Detector: [63]Ni electron capture

Makeup Gas: Argon-methane, 35 mL/min.

Detector Temperature: 275°C.

Under these conditions, captan eluted at 1.27 min. Quantification was performed automatically by area-integration (H-P 3390A) and expressed as micro- or milligrams/sample. Recoveries of added captan ranged from 96 to 103% (Zweig, 1983).

Vinclozolin residues have been analyzed previously by HPLC (Cabras, et al., 1982, 1983). An improved capillary GC method was developed for the analysis of vinclozolin, the two isomers of endosulfan (6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide) and endosulfan sulfate and was employed for the analyses of vinclozolin field samples generated in Study 6b. The instrument used was a Hewlett-Packard 5880A equipped with an H-P 7672 Automatic Sampler and Level Four Computer and Terminal (automatic integrator). The column was a 12.5 m WCOT silica capillary column (0.2 mm, i.d.) coated with OV-1 silicone and deactivated with siloxane. The splitless injection mode and a [63]Ni electron capture detector (ECD) were employed. Experimental conditions for the complete resolution of

a mixture of vinclozolin, endosulfan I and II, and endosulfan sulfate were the following.

Carrier gas (He); flow @ 15 psi; -4 mL/min.

Septum Flush; 3 mL/min.

Split Vent; 55 mL/min.

Make-up gas (5% methane in argon); 20 mL/min. at the detector.

Temperature program:	Time/rise	Temperature ($^{\circ}$C)
	1 min.	62
	30°/min.	62 - 250
	1 min.	250
	30°/min.	250 - 260
	5 min.	260

Under these conditions, vinclozolin had a retention time of 6.53 min. (see FIGURE 1).

One microliter aliquots of standard and sample solutions were automatically injected. All samples were run in triplicate. Results were accepted when the relative standard deviation (RSD) was <5% for standards and <10% for field and laboratory samples. Standard solutions ranged from 8.7 ng/mL to 870.8 ng/mL. Over this 100-fold range, the ECD response was found to be linear. Whenever the concentration of unknown was outside this range, the sample was concentrated in vacuo or diluted with appropriate volumes of acetonitrile. The practical limit of detection was 4.3 - 8.7 ng/mL.
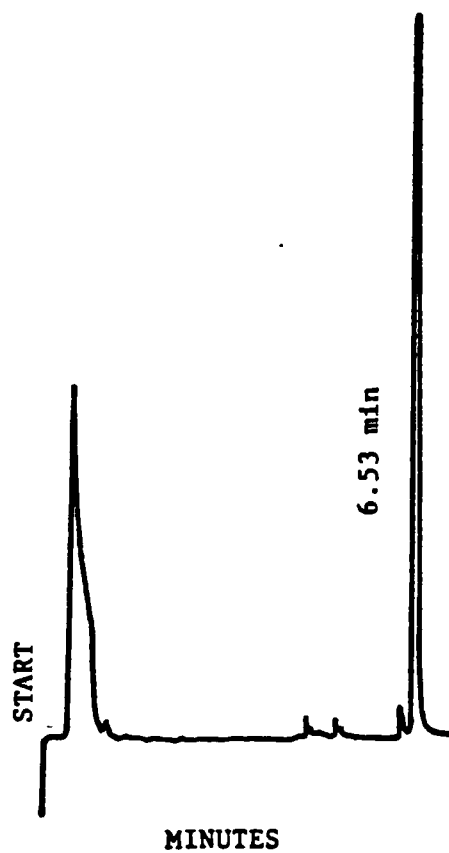
FIGURE 1

Capillary Gas Chromatography of Vinclozolin Standard (experimental details in text).

Recovery studies of vinclozolin for gloves, patches, and SURTEN solutions (simulated dislodgeable residue extracts) ranged from 70% to over 100% of added vinclozolin.

Carbaryl and methiocarb residues were analyzed by reverse-phase HPLC using a Waters 6000A Solvent Delivery System, WISP Automatic Sample Processor, Waters Data Module and Automatic Integrator, and a Model 4530 Variable Wave Length Detector. A μBondapak C-18 reverse-phase column (25 cm x 2 mm i.d.) was capable of separating each of these compounds without appreciable interference from extraneous materials originating in the field. The mobile phase was a mixture of acetonitrile and water, and the optimum chromatographic conditions for each compound are listed in TABLE 2.

Calculation of Dermal Dose

Calculation of dose rate per person is made by the following equation:

$$mg/hr = \frac{(\mu g \text{ Pesticides}) \times [\text{Surface Area of Body Part } (cm^2)]}{[\text{Patch Area } (cm^2)] \times Hr \times 1000}$$

where "Hr" is hours monitored, and "μg Pesticide" is obtained from chemical analyses. Surface area of body parts is calculated according to Popendorf and Leffingwell (1982) using the 50-percentile man and adjusting the individual total body surface from a nomograph linking body weight and height with body surface (Sendroy and Cecchini, 1954). "Patch area" is 28 cm^2 as explained above. Hand exposure rates are obtained from pesticide concentrations on gloves, normalized for "hours worn," because

TABLE 2

Conditions for HPLC Analysis of Several Pesticides
(μBONDAPAK C-18 Reverse-Phase Column)

Pesticide	Acetonitrile: Water	Solvent Flow (mL/min)	Detection (nm)	Ret. Time (min)	% Recovery
Benomyl[a]	50:50	1.5	286	15.8	98.0 – 99.3[b]
Carbendazim	50:50	1.5	286	3.5	87.0 – 100.4[b]
Carbaryl	40:60	2.0	230	4.6	85.3 – 106.7[c]
1-Naphthol	40:60	2.0	230	5.1	98.9 – 106.5[c]
Methiocarb	65:35	0.8	265	6.3	88.2 – 109.1

[a]benomyl in acetonitrile is stabilized by the addition of 1000:1 (w/w) 1-butylisocyanate
(Chiba, 1977).

[b]Zweig and Gao, 1983.

[c]Zweig, et al., 1985.

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gloves, unlike patches, cover the entire exposure surface area.

RESULTS AND DISCUSSION

Dermal Exposure to Captan

As may be seen in TABLE 3, the exposure rates of strawberry harvesters in Studies 1 - 5, ranged from 4.70 mg/hr to 17.41 mg/hr or, normalized to body weight, 0.082 mg/kg/hr to 0.31 mg/kg/hr. These results compare favorably with those obtained in previous studies on dermal exposure by strawberry harvesters (Zweig, et al., 1983; Winterlin, et al., 1984). Dermal exposure rates of four subjects who were engaged in weeding (Study 3) were much higher than for harvesters in any of the studies. We observed that the four weeders were stirring up a considerable amount of dust during their work activities indicating that dust

TABLE 3

Mean Dermal Captan Exposure
by Strawberry Harvesters and Weeders

Expt.No.	Days Post Appl.	Subjects Occup.	Nos.	Dermal Exposure mg/hr	mg/kg b.w./hr
1	13	Pickers	20	6.50(5.08)	0.108(0.079)
2	26	Pickers	23	4.70(4.11)	0.082(0.077)
3	4	Pickers	15	17.41(14.53)	0.310(0.200)
3	4	Weeders	4	94.13(118.4)	1.784(2.177)
4	3	Pickers	6	16.37(3.78)	0.411(0.118)
5	48	Pickers	10	5.88(3.70)	0.104(0.072)

rather than foliar contact and transfer was the source of their dermal exposure. This assumption is based on the finding that soil samples at or near the weeding site contained 6.29 ppm extractable captan residues.

TABLE 4

Decay of Captan Soil Residues in Strawberry Fields
(Studies 1 and 3)

Days Since Last Application[a]	Date (1981)	Captan Residues ppm
2	April 28	3.47
2	April 28	1.58
8	May 4	3.40
9	May 5	0
13	May 9[b]	8.63
13	May 9	2.89
4	July 21[c]	6.29
10	July 27	3.77

[a]Pesticide treatment, captan 2.2 - 2.5 kg active ingredient (a.i.)/ha on April 15 - 18, April 23, April 26, May 10, May 17; 1.7 kg/ha on May 31; 2.2 kg/ha on June 7 and July 17.
[b,c]Study dates for Studies 1 and 3, respectively.

As may be seen in TABLE 4, captan soil residues appear to be stable for at least 13 days post application. The literature on the decline of captan in soils of various types is in conflict. Munnecke (1958) claimed that fungicidal activity of captan in

soil remained almost unchanged for 65 days. Kluge (1969) confirmed this finding by demonstrating that the biological activity of captan did not decrease appreciably during the first six weeks in two different soils at pH 7.4 and 5.1. On the other hand, Griffith and Mathews (1969), using bioassays, showed a rapid decline of captan within four days after it had been mixed with the soil. On glass beads, the fungicidal activity was almost quantitatively retained after 21 days. These results suggest that microbiological degradation in soil plays a major role in the dissipation of this compound, and that different soils may harbor different microbiological populations.

The agricultural practice of strawberry picking is a hand operation in which the harvester squats, kneels, and sometimes sits between the rows of strawberry plants. When berries are picked for the fresh fruit market, the picker will grab the fruit at the stem about 2 cm from the calix and twist the fruit off the stem with a fast wrist action. The experienced picker can perform this operation equally well with both hands.

When fruit is picked for canning or processing, it is handled in a different manner. The harvester will pick the fruit with one hand and pluck the stem off the berry with the other. Strawberries harvested in Oregon (Field Study 2) were picked mostly for canning, while in California during the early season (Field Studies 1 and 3), for the fresh fruit market. Due to these work practices, it is possible that the harvesters receive varying concentrations of pesticides on different parts of the

TABLE 5

Anatomical Distribution of Dermal Exposure
to Captan by Strawberry Harvesters

Body Part	Percent of Total Dermal Exposure[a]					
Study	1	2	3	4	5	Average
Head+Neck	0.65	2.92	1.90	0.32	3.66	1.89
Back+Shoulders	1.37	3.36	2.81	0.39	3.26	2.24
Chest+Stomach	1.17	1.15	1.78	0.25	3.68	1.61
Lower Legs	3.30	6.96	10.33	0.95	1.93	4.69
Upper Arms	0.59	4.82	2.46	0.24	1.47	1.92
Lower arms	7.20	13.28	21.17	10.18	9.93	12.35
Hands	85.73	67.52	59.55	87.69	76.07	75.31

[a]Weighted average.

body. The distribution of whole-body dose rates found in the first five studies in which the major anatomical regions of the subjects were monitored, may be seen in TABLE 5. Harvesters consistently had the highest exposure on hands (60 - 86%), lower arms (7 - 21%), and lower legs (1 - 10%), compared to other parts of the body. A possible explanation for captan residues found on the lower legs of the workers is that dew during the early morning hours caused the lower pants legs to become water soaked and contaminated with dislodgeable pesticide residues. When the fields are dry, dust may also move up the pants' legs and deposit on the skin.

The dermal distribution of captan among the four weeders as

shown in TABLE 6, demonstrated a different, but not totally
unexpected distribution pattern of captan exposure. The highest
dermal exposures were not found on hands, but on the chest, head
and neck, and lower arms. The variability of the anatomical
distribution, however, was too large to make the type of general-
ization that was made in the case of strawberry harvesters.

TABLE 6

Anatomical Distribution of Dermal Exposure to Captan by Weeders

Body Part		Percent of Total Dermal Exposure[a]			
	Subject	1	2	3	4
Head+Neck		1.53	78.80	35.07	2.65
Back+Shoulders		3.32	0.13	0.18	1.62
Chest+Stomach		56.38	4.18	2.74	84.89
Lower Legs		10.97	0.97	0.10	6.51
Upper Arms		9.43	7.69	2.09	0.47
Lower arms		3.57	0.54	58.99	1.21
Hands		14.79	7.67	0.81	2.65

[a]Average.

Dermal Exposure to Carbaryl

On the basis of the results from Studies 1 - 5, it was
decided that in subsequent experiments with strawberry
harvesters, the study should be limited to three anatomical
regions for the estimation of total body exposure of harvesters,
namely hands, lower arms, and lower legs.

A summary of the simultaneous exposure to carbaryl and vinclozolin may be found in TABLE 7. Detailed results on carbaryl exposure are reported elsewhere (Zweig, et al., 1984, 1985). Because dermal exposure on lower legs was found to be less than 4% of total exposure, with the exception of one worker out of 18, our following conclusions were based solely on hand and lower arm exposures. Exposure rates on the first day of the study were greater than on the next two days. It was observed that morning dew and relative humidity on Day-1 were considerably higher than on either of the other two days of the study. Pesticide exposures on Days-1 and -3 in the morning were also found to be higher than in the afternoon. It was concluded that high humidity may have a positive effect on pesticide transfer from foliage or adherence to the cloth monitors. Two recent investigations have been suggestive that dermal exposure obtained from cotton gloves may yield higher values than would be obtained from hand rinses (Noel, et al., 1983; Davis, et al., 1983). Both monitoring methods, however, have their limitations as discussed by Popendorf (1985); a comparison of rinse and glove monitors with "true" values must await further research for validation. Examining TABLES 3 and 7, it is seen that carbaryl dermal exposure rates are lower than, but of the same order of magnitude as those found for captan.

Dermal Exposure to Vinclozolin

TABLE 8 also has a summary of exposure rates for vinclozolin for six observation periods in Field Study 6b. Lower leg

TABLE 7

Mean Dermal Exposure by Strawberry Harvesters
to Carbaryl

Day of Study	Time of Day	Body Part	Dermal Exposure (mg/hr)
1	AM	Hands	3.01(1.70)
1	PM	Hands	1.42(0.80)
1	All Day	Lower Arms	0.66(0.41)
1	All Day	Hands+Arms	2.65(1.14)
2	AM	Hands	1.23(0.62)
2	PM	Hands	1.12(0.73)
2	All Day	Lower Arms	0.41(0.27)
2	All Day	Hands+Arms	1.55(0.61)
3	AM	Hands	1.47(0.82)
3	PM	Hands	1.09(0.71)
3	All Day	Lower Arms	0.43(0.30)
3	All Day	Hands+Arms	1.45 (0.69)
Means	AM	Hands	1.90(1.38)
Means	PM	Hands	1.09(0.71)
Means	All Day	Lower Arms	0.50(0.35)
Means	All Day	Hands+Arms	1.89(1.00)

[a]Data from Zweig, et al., (1984, 1985).

exposure concentrations were, again, mostly nondetectable and could be considered to contribute insignificantly to total dermal exposure to vinclozolin. Only one subject exhibited a lower leg exposure rate of about 10% of the total, and then only on Day-1. Judging from these results, it appears that hand exposure is the major target of dermal exposure among strawberry harvesters. The mean hand exposure rate, 0.251 mg/hr, may be compared with 0.027 mg/hr for lower arms. This observation is consistent with results on strawberry harvesters exposed to captan and carbaryl.

Quantitatively, however, it appears that vinclozolin exposure was considerably lower for the same group of workers than corresponding carbaryl exposures (0.28 mg/hr vs 1.89 ng/hr, respectively). A probable explanation for this finding may be the fact that vinclozolin had been applied 14 days earlier than carbaryl, and that lower dislodgeable vinclozolin residues were found (see TABLE 11).

Hand exposure rates for vinclozolin in the morning observation periods were shown to be greater than those found in the afternoon ($Z = 2.157$; $N = 54$; $p < 0.016$; large N, unequal variances). Similar results were reported in the carbaryl study (Zweig, et al., 1984) and are probably related to to the presence of dew on foliage during the early morning hours, which caused glove monitors to become quickly saturated with water. These findings are in contrast to the transfer of dislodgeable residues on tree crops, as discussed by Popendorf and Leffingwell (1982).

TABLE 8

Mean Dermal Exposure by Strawberry Harvesters to Vinclozolin

Day of Study	Time of Day	Body Part	Dermal Exposure (mg/hr)
1	AM	Hands	0.29(0.17)
1	PM	Hands	0.21(0.12)
1	All Day	Lower Arms	0.03(0.04)
1	All Day	Hands+Arms	0.27(0.16)
2	AM	Hands	0.34(0.23)
2	PM	Hands	0.25(0.20)
2	All Day	Lower Arms	0.04(0.04)
2	All Day	Hands+Arms	0.33(0.20)
3	AM	Hands	0.34(0.66)
3	PM	Hands	0.13(0.09)
3	All Day	Lower Arms	0.02(0.01)
3	All Day	Hands+Arms	0.23 (0.27
Means	AM	Hands	0.32(0.41)
Means	PM	Hands	0.20(0.15)
Means	All Day	Lower Arms	0.03(0.03)
Means	All Day	Hands+Arms	0.28(0.21)

By the use of Duncan's Multiple Range Test, it can be demonstrated that mean dermal exposure rates for all 18 workers were not significantly different on any of the three days of the study. The exceptions to this finding were the afternoon exposure rates for hands, which were significantly lower on the third day than on either of the other two days.

Dermal Exposure to Methiocarb

As is seen in TABLE 9, anatomical distribution of methiocarb exposure by blueberry pickers is quite different than was observed for strawberry harvesters, namely that body parts other than hands and lower arms showed considerable amounts of pesticide residues. The blueberries cultivated on the farm chosen for Study 7 is a variety that grows on bushes four to six feet high, and the chance of total body contact by harvesters with foliage and concomitant pesticide residues was much greater than that experienced during harvesting strawberries growing close to the ground. Hand exposure on Day-4 post application was significantly higher than on Day-5; a heavy rainfall on the later day presumably washed significant amounts of pesticide residues from the foliage and possibly from the body and glove monitors, which had become soaked. The overall total exposure rate for methiocarb was comparable with that observed among strawberry harvesters exposed to carbaryl.

Dislodgeable Foliar Residues

Dislodgeable foliar residues of pesticides may consist of pesticide residues absorbed or adsorbed onto foliage or dust

TABLE 9

Anatomical Distribution of Dermal Exposure
to Methiocarb by Blueberry Harvesters

Days Post Application	4		5	
	Dermal Exposure			
Body Part	mg/hr	%	mg/hr	%
	N = 12		N = 6	
Head+Neck	0.28(0.19)	7.4	0.13(0.05)	6.2
Back+Shoulders	0.13(0.05)	3.4	0.19(0.09)	8.8
Chest+Stomach	0.23(0.09)	6.0	0.23(0.07)	10.6
Lower Legs	0.23(0.10)	6.0	0.34(0.08)	15.9
Upper Arms	0.22(0.13)	5.8	0.20(0.07)	9.7
Lower arms	0.64(0.49)	16.8	0.74(0.72)	34.6
Hands	2.05(1.29)	53.9	0.31(0.09)	14.3
Total	3.80(1.96)	—	2.14(0.85)	—

particles which are residing on the leaf surface. Fractions of these residues may be transferred to the skin or clothing of field workers either by direct contact with foliage or by fall-out of dust aerosols resuspended by work activities. An earlier study by Zweig, et al., (1983) demonstrated that the ratio of two pesticides, captan and benomyl, present as a dislodgeable residue, was similar to the ratio found on gloves and patch monitors worn by strawberry harvesters. This was taken as evidence that the dislodgeable foliar residue was being transferred from leaf surfaces to the workers either partially or entirely.

In order to determine the dislodgeable residues on the day(s) when field workers were monitored for dermal exposure, it was important to study the decline of the foliar residues for several day or even weeks prior to the beginning of a study. FIGURES 2, 3 and 4 depict the decline of dislodgeable residues of captan and vinclozolin on strawberry foliage and methiocarb on blueberry foliage. All plots are semi-log and fall on straight lines, indicating first-order kinetics for the decay of these pesticides. Similar conclusions have been propounded for dislodgeable foliar residue declines of carbaryl on strawberry leaves (Zweig, et al., 1984, 1985). From the slopes of these plots, the half-lives of these compounds existing as dislodgeable residues can be calculated (TABLE 10).

TABLE 10

Half-Lives of Some Pesticides Present
as Dislodgeable Foliar Residues

Pesticide	Crop	Half-Life (days)	Reference
Captan	Strawberries	7.1	Field Expt. 2
Carbaryl	Strawberries	4.1	Zweig, et al., 1984
Vinclozolin	Strawberries	4.0	Field Expt. 6b
Methiocarb	Blueberries	1.7	Field Expt. 7
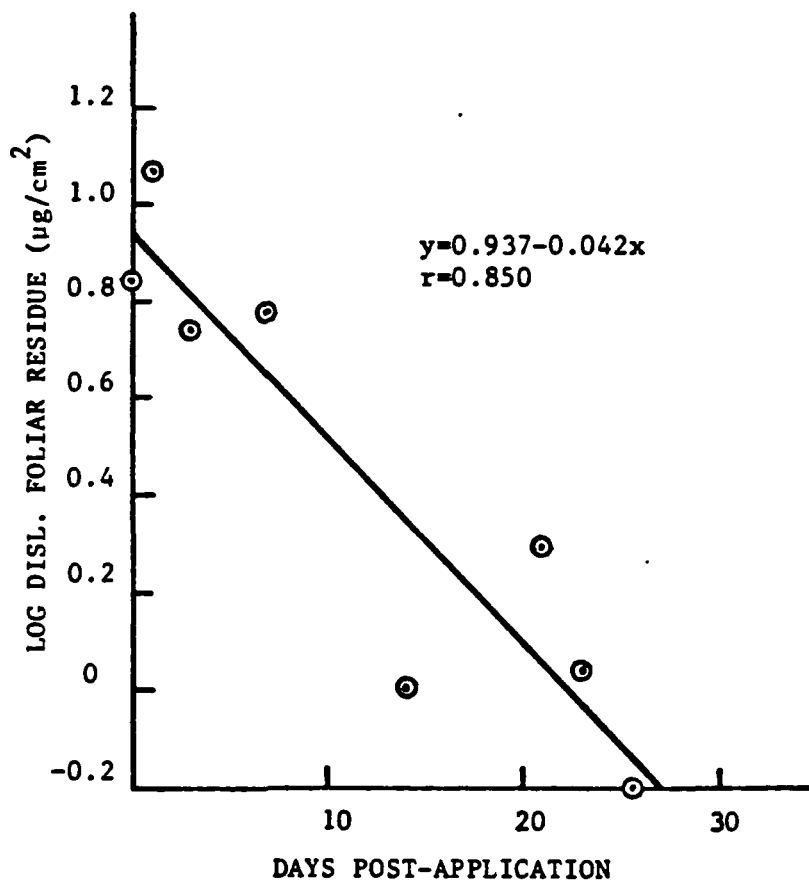
FIGURE 2

Decline of Captan Dislodgeable Residues from Strawberry Foliage (Field Study 2); log Dislodgeable Residue vs. Days, Post-Application. Each plot is the geometric means of 2-4 replicates; this also refers to FIGURES 3 and 4.
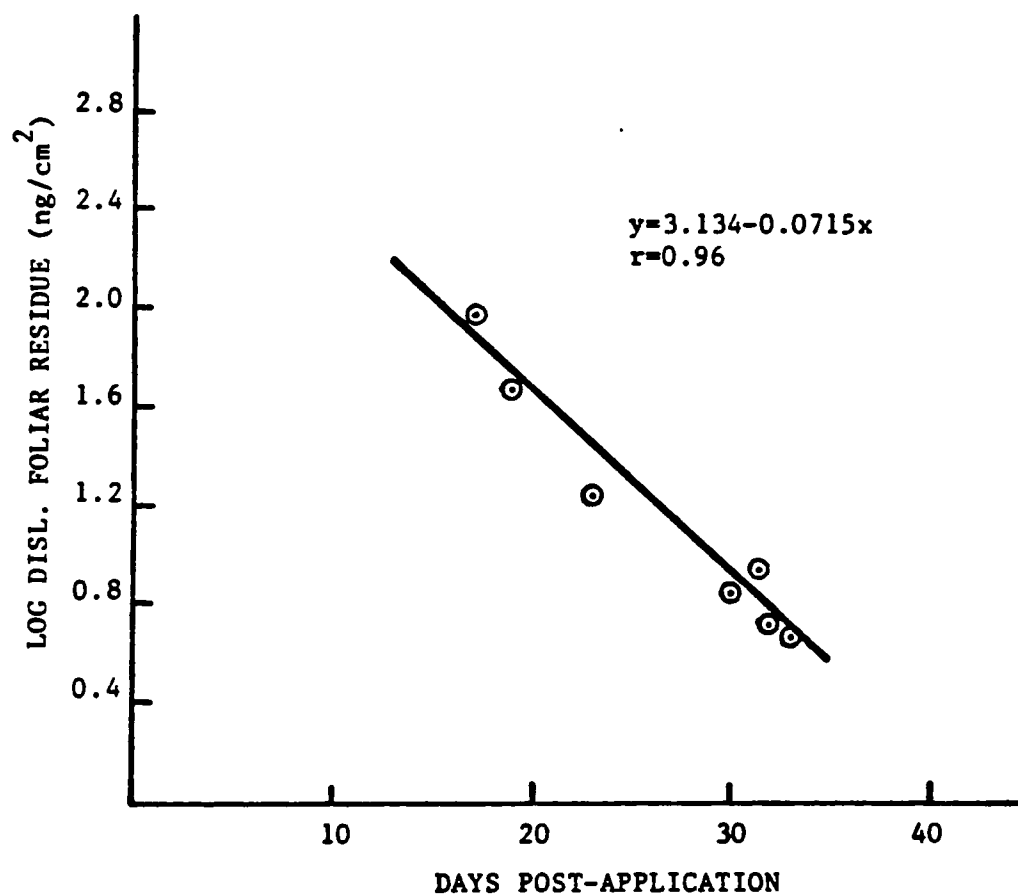
FIGURE 3

Decline of Vinclozolin Dislodgeable Residues from Strawberry Foliage (Field Study 6b); note units of DFR are in ng/cm^2.

Popendorf and Leffingwell (1982) have reviewed the results of their field work on the exposure by citrus and peach harvesters to organophosphorous insecticides. They concluded that log-log regression analyses were essentially linear between dislodgeable foliar residues and dermal dose rates. We have now extended these regression analyses to include the results for strawberry and blueberry harvesters exposed to captan, benomyl, vinclozolin, carbaryl and methiocarb. The anatomical distribution of dermal exposure to pesticide by field workers harvesting row or bush crops may be quite different than that of harvesters of tree crops, probably due to the operation of different exposure mechanisms. Nevertheless, the regressions of 43 separate observations fell on the same straight line (FIGURE 5), and the ratios of dermal exposures and dislodgeable foliar residues were essentially within an order of magnitude (TABLE 11). The mean value of 43 observations [16 from these studies and 23 from Popendorf and Leffingwell (1983)] was 7.84×10^3 (S.D. 12.2×10^3). The ratios for vinclozolin appeared to be significantly higher than the values for carbaryl observed simultaneously. Since the vinclozolin residues were two weeks older than the concomitant carbaryl residues (see above) and considerably lower than all the others listed in TABLE 11, it could be speculated that the anomalous ratio derived for vinclozolin is related to aging of its residues.
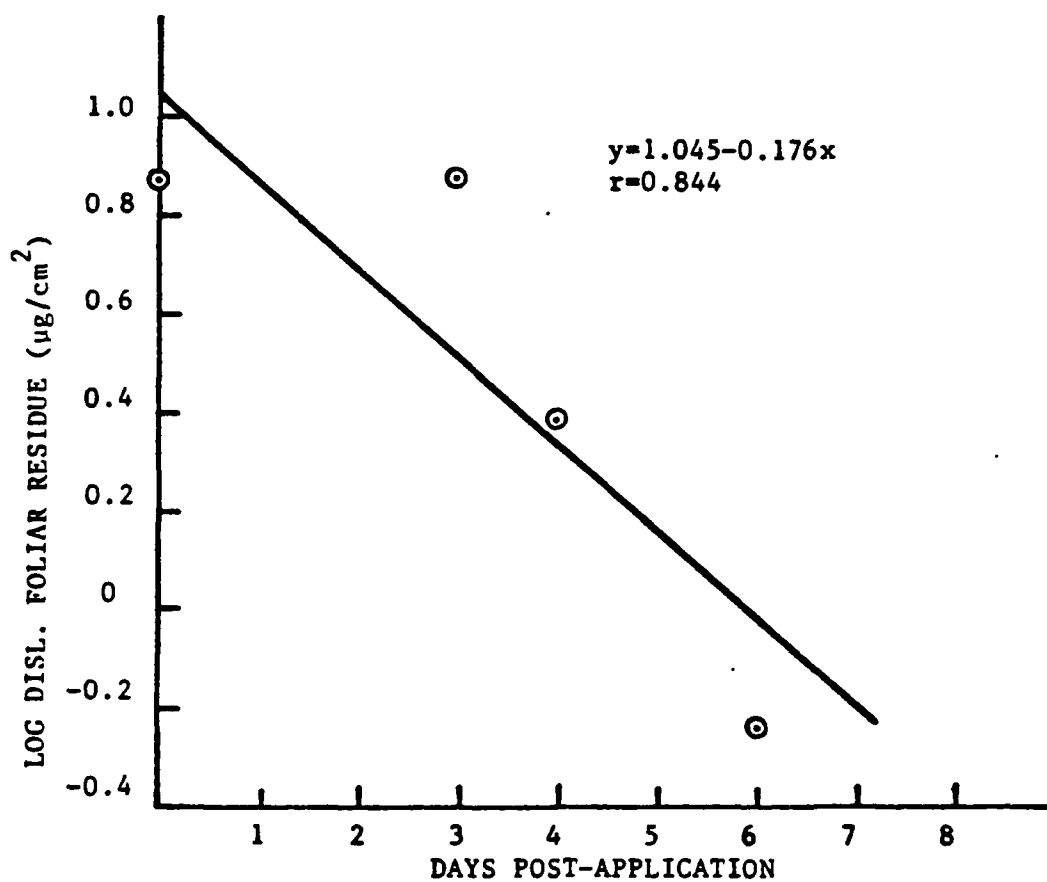
FIGURE 4

Decline of Methiocarb Dislodgeable Residues from Blueberry Foliage (Field Study 7).

28
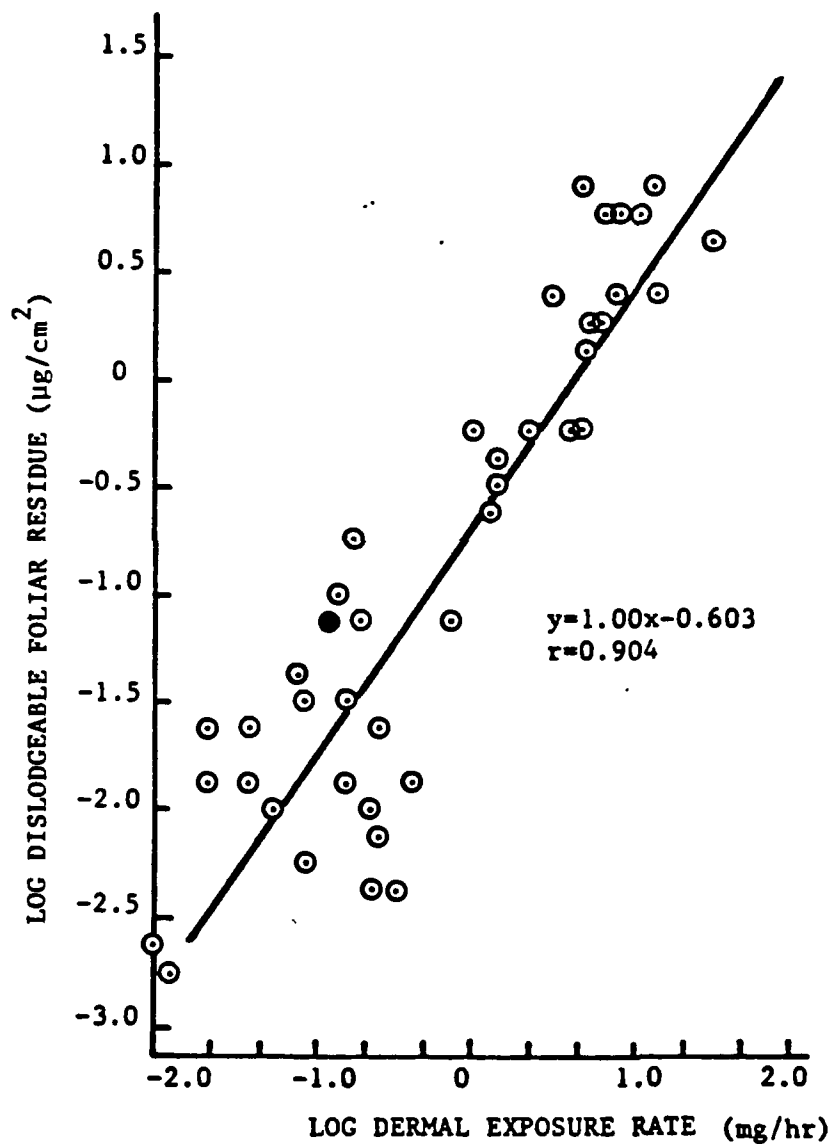
FIGURE 5

Regression Line of Ratios Between Dermal Exposure Rates and
Dislodgeable Foliar Residues of Various Pesticides and Crops;
data are from this report and Popendorf and Leffingwell (1982).
● =2 points with same coordinates.

TABLE 11

Ratio Between Dermal Dose Rate and Dislodgeable Foliar Residues

Study No. or Lit. Citation	Pesticide	Crop	Dermal Dose Rate (mg/hr)	Dislodgeable Foliar Residue ($\mu g/cm^2$)	Ratio $\times 10^{-3}$
Study 1	Captan	Strawberries	6.50	2.36	2.754
Study 2	Captan	Strawberries	4.70	0.71	6.620
Study 3	Captan	Strawberries	17.41	7.76	2.244
Study 4	Captan	Strawberries	16.37	2.74	5.974
Study 5	Captan	Strawberries	5.88	1.72	3.418
Study 6a	Carbaryl	Strawberries	2.65	0.61	4.344
Study 6a	Carbaryl	Strawberries	1.55	0.55	2.818
Study 6a	Carbaryl	Strawberries	1.45	0.24	6.042
Study 6b	Vinclozolin	Strawberries	0.273	0.00891	30.64
Study 6b	Vinclozolin	Strawberries	0.329	0.00537	61.27
Study 6b	Vinclozolin	Strawberries	0.232	0.00524	44.27
Study 7	Methiocarb	Blueberries	6.037	7.83	0.771
Study 7	Methiocarb	Blueberries	3.80	2.42	1.570
Study 7	Methiocarb	Blueberries	1.06	0.59	1.802
Zweig,1983	Captan	Strawberries	39.01	4.55	8.574
Zweig,1983	Benomyl	Strawberries	5.39	0.75	7.187

The units of this ratio are area per time (viz. cm^2hr^{-1}), but the significance of this relationship is not clearly understood. The "area" expression may represent the foliar surface with which the field worker actually comes into contact, or it may be the hypothetical area of the foliage given quantitative transfer of the dislodgeable residue on its surface.

We subscribe to the concept put forth by Popendorf and Leffingwell (1982) and Nigg, et al., (1984) to use this ratio as an empirical factor for the estimation of dermal exposure by field workers without involving the workers, themselves, but measuring, instead, the dislodgeable foliar residues in the particular combination of pesticide and crop under consideration. The fact that this factor is relatively constant for a variety of crops as diverse as citrus and strawberries and holds for different pesticides, suggests that a constant fraction of dislodgeable residues is transferred to the skin or clothing of personnel during manual activities in treated fields. Nigg, et al., (1984) have recommended that an empirical constant of 10^4 be used to to make this estimate, but these researchers calculate dislodgeable residues on the basis of two leaf surfaces. In our work, only a single leaf surface (projected area) is considered, making the value of our ratio about one-half that derived by Nigg's group. As recently stated by Zweig (1984), a rough first approximation of dermal exposure rate for fruit harvesters based on dislodgeable foliar residues (DFR) may be calculated using the following

expression:

Dermal Exposure Rate (mg hr^{-1}) $\approx$ 5 x 10^3 x DFR

This simple transformation suggests a method for obtaining exposure rates of fruit harvesters in order to establish safe reentry periods without involvement of human subjects. Experiments are needed on additional crop/pesticide combinations to further validate the use of this factor.

REFERENCES

Cabras, P., Paolo, P., Meloni, M., Pirisi, F.M., J. Agric. Food Chem., 30, 569 - 572 (1982).

Cabras, P., Paolo, D., Meloni, M., Pirisi, F.M., and Pirisi, R., J. Chromatogr., 256, 176 - 181 (1983).

Davis, J.E., Stevens, E.R., Staiff, D.C., Bull. Environm. Contam. Toxicol., 31, 631 - 638 (1983).

Griffith, R.L. and Mathews, S., Ann. Appl. Biol., 64, 113 - 118 (1969).

Gunther, F.A., Westlake, W.E.,Barkley, J.H., Winterlin, W. and Langbehn, L., Bull. Environ. Contam. Toxicol., 9, 243 -249 (1973).

Gunther, F.A., Barkley, J.H. and Westlake, W.E., Bull. Environ. Contam. Toxicol., 12, 641 - 644 (1974).

Iwata, Y., Spear, R.C., Knaak, J.B. and Foster, R.J., Bull. Environ. Contam. Toxicol., 18, 649 - 655 (1977).

Kluge, E., Arch. Pflanzenschutz, 5, 263 - 271 (1969).

Munnecke, D.E., Phytopahtology, 48, 581 - 585 (1958).

Nigg, H.N., Stamper, J.H., and Queen, R. M., Amer. Ind. Hyg. Assoc. J., 45, 182 - 186 (1984).

Noel, M.E., Zweig, G., and Popendorf, W.J., Abstr. Papers, 185th Nat.Meeting Amer. Chem. Soc., CHAS 27 (1983).

Popendorf, W.J. and Leffingwell, J.T., Residue Reviews, 82, 125 - 201 (1982).

Popendorf, W., Accepted for publication in "Proc. Symposium on Risk Assessment of Agricultural Field Workers Due to Pesticide Dermal Exposure," Amer. Chem. Soc., Washington, D.C. (Scheduled in 1985).

Sendroy, J., Jr., Cecchini, L.P., J. Appl. Physiol., 7, 1 - 12 (1954).

Smith, G.L., and Little, D.E., Cal. Agric., 8, #6, 13 (1954).

Winterlin, W.L., Kilgore, W.W., Mourer, C.R., and Schoen, S.R., J. Agric. Food Chem., 32, 664 - 672 (1984).

Zweig, G., Gao, Ru-Yu, and Popendorf, W., J. Agric. Food Chem., 31, 1109 - 1113 (1983).

Zweig, G., Gao, Ru-Yu, Witt, J.M., Popendorf, W., and Bogen, K. Accepted for publication in J. Agric. Food Chem. (1984) and "Proc. Symposium on Risk Assessment of Agricultural Field Workers Due to Pesticide Dermal Exposure," Amer. Chem. Soc., Washington, D.C. (Scheduled in 1985).

Reentry Simulation Study, Phase I and Phase II

Research performed by

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REENTRY SIMULATION STUDY, PHASE I

by
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Phase I of this study consisted of retrieval of reported foliar residue data, chemical toxicity and crop related parameters for selected organophosphate pesticides, calculation of cholinesterase inhibition corresponding to the residues and recommend appropriate reentry intervals based on a Unified Field Model.

Phase II conducts computer simulation studies testing the effect of both mean residue hazard (dACHE) and its variability upon harvesters health status in order to define an appropriate criteria (daily inhibition of cholinesterase or %dACHE) for recommending reentry intervals.

INTRODUCTION: ·

"Reentry interval" is the term given to the time period (usually days)

necessary for a pesticide residue to become safe for a subsequent activity.

The activity of interest in this report is harvesting (although any similar

activity with prolonged, substantial contact with the foliage or other

repository of the residue would be covered within this context). The

pesticides of interest are those currently regulated by either the U.S.

Environmental Protection Agency (EPA) or the state of California and a

small number of OPs which are not currently regulated by either agency;

these chemicals are predominantly organophosphate pesticides (OPs) many of

which have been historically associated with sporadic incidents of

harvester acute poisonings (Quinby and Lemmon, 1958; Milby et al, 1964;

Spear et al 1975; Spear et al, 1977; and Gunther et al, 1977).

The precedent for this review and synthesis was a report submitted to

the EPA in 1981 entitled "A Model for Farmworker Protection from

Organophosphate Pesticide Residues"; an only slightly modified version of

this report was subsequently published in Residue Reviews (Popendorf and

Leffingwell, 1982). These documents outlined a concept and model for

unifying the aspects of pesticide application, pesticide decay, exposure to

the residue during harvest, dose dermal deposition and absorption, and the

harvester's biological response (this submodel was specific to the

inhibition of the neural enzyme acetyl cholinesterase (AChE)), respectfully

called the Unified Field Model by its author. A subsequent publication

(Popendorf, 1984) outlined some useful applications for the model, further

examples, and some of its limitations.

Of particular interest in these reports were two needs, (1) to examine

the necessity for and adequacy of current reentry intervals in comparison to intervals using the Unified Field Model and reported residue, toxicologic, and exposure data, and (2) to establish an appropriate criterion for setting the reentry interval based on an allowable change in AChE (dAChE) given the natural variability in residues and exposure patterns intrinsic to real agricultural practices. Therefore, two phases of this study were undertaken: (Phase I) to assemble all reported foliar residue data for the pesticides of interest with the necessary chemical toxicity and crop related parameters, to calculate the cholinesterase inhibition corresponding to these residues, and to recommend appropriate reentry intervals based on the Unified Field Model, and (Phase II) to conduct computer simulation studies testing the effect of both the mean residue hazard (dAChE) and its variability upon harvesters health status in order to define an appropriate criterion (daily inhibition of cholinesterase or % dAChE) for recommending reentry intervals.

While these two phases of the study are related, much of each of them could be and was conducted separately. Unfortunately, they were not well synchronized in time, and this draft report of Phase I was completed without benefit of input from Phase II. The particular point at which such input will be important is when selecting the % dAChE criterion for an assumed 8-hour harvesting workday. Due to time constraints, a draft report was prepared using a criterion of 4% as guided by the earlier reports by Popendorf and Leffingwell (1982), discussed in the Results section, and presented in Table IV.

METHOD:

The data base for the study was developed through a computerized literature search initially conducted in October 1981 (supervised by Norma Kobzina at the University of California, Berkeley, Natural Resources Library). A subsequent search was conducted in April 1984 (by E. Rumsey at the University of Iowa, Health Sciences Library). Four data bases were used:

1) CHEMLINE (Chemical Dictionary online) which supplied synonyms and registry numbers for various chemicals, and also named data bases (files) within the National Library of Medicine Computer System (MEDLARS) where articles on the chemicals were listed.

2) TOXLINE (Toxicology Information online) which contains an indexed file of abstracts relating to human and animal toxicity studies. This data base is also part of MEDLARS.

3) AGRICOLA (Bibliography of Agriculture)

and 4) BIOSIS (Biological Abstracts) are both owned by the Dialog Information Retrieval Service, and lists by title the articles related to agriculture and life sciences, respectively.

The object of the literature search was to find articles containing decay data on dislodgeable foliar residues of organophosphate pesticides currently subject to either EPA and/or CDFA reentry restrictions. The first step was to obtain a list of chemicals and their synonyms and registry numbers through CHEMLINE. These names and numbers were then used to search TOXLINE, AGRICOLA, and BIOSIS using selected keywords. At that time it appeared that some registry numbers had more than one chemical assigned to them (mixtures); as a result, several chemicals were listed in the literature search which were not organophosphates.

There were some differences in the cross-referenced keywords used within the various bibliographic data base searches because of their unique structures and features. TOXLINE was searched for each of the chemicals listed in Table I when used with the words in list (a) of Table II. For AGRICOLA and BIOSIS the list of chemicals was cross-referenced twice, once when used with those words in lists (a) and (b) of Table II, and the other when used with list (a) but without list (c), i.e. with no mention of soil/soils. The period of time encompassed by each literature search is listed in Table III.

From the printout of references selected through the TOXLINE, AGRICOLA, and BIOSIS searches, those articles whose titles were clearly unrelated to the objective of the study were deleted. All references even possibly applicable to the study were located and further screened to those that did indeed meet the following criteria:

1) Article contained data on <u>dislodgeable foliar residue decay</u>, as opposed to dislodgeable fruit residues, penetrated residues, soil residues or total residues. In cases where authors used organic solvents for removal of residue (as opposed to the more established "dislodgeable" method using an aqueous solution) but still claimed that the data represented <u>dislodgeable</u> foliar residues, this data was included in the data base but the extraction solvent was noted.

2) Residue data were available at more than one point in time as part of either a table or plot. Decay data with less than two points in time were not used for this study, although the articles are included in a secondary bibliography.

A standardized data sheet (Appendix A) was used to record the experimental parameters and methodology of each study, the actual data set was copied, attached to the data sheet, and filed. A bibliography of the selected references for the study is enclosed (Appendix B) along with references which may be useful in related studies.

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Information from the standardized data sheets and the original data
sets were entered into the computer in the format shown in Appendix D.
Each set of decay data, given in days post application and residue levels,
is preceded by the corresponding ID number and coded variables. Where only
a graph of data was provided, residue and interval values were determined
by measurement of the graph. If only an equation was given in the original
reference, values were interpolated from the equation for days 1, 2, 5, 10,
20, and 30 (days -) post application (as permitted by the duration of the
reported data) and inserted into the residue data file.

Other application, environmental, and sampling factors were determined
from each report where possible and included within the library file as
explained in Appendix C. Among these factors are:

- location (by country or state or area within large states)

- crop (see also Appendix E)

- formulation (WP, EC, etc)

- application rate (lb active ingredient/acre)

- pesticide dilution (gal water/acre)

- primary extraction solvent (generally water with
  surfactant)

- reporting procedure within publication (e.g. 1 or 2 sides
  of leaf, units, graphical results only)

- application date

Computer library data files were established for other model variable such
as pesticide toxicities (LD_{50}) as shown in Appendix D and crop dosing
coefficients (k_d) as shown in Appendix E.

These residue data were then used with the other above library data
files and unified field reentry model to assess the anticholinesterase
potential of reported residues. Two approaches to interpret these data

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were explored. The first approach relied upon a generalized pesticide decay model coefficient-fitting program (Appendix F) in order to interpolate between and extrapolate from scattered sampling intervals as reported in the literature to intervals preset by EPA or California and/or to intervals corresponding to "acceptable" cholinesterase inhibitions. This approach found only moderate success because the algorithm was not efficient at establishing the best fit for the twelve coefficients without assuming certain "simplifying" constraints on the coefficients (which can effectively reduce the number of coefficients); much operator interaction was required to establish the range of these coefficients and the appropriate constraints for each chemical.

A second approach was not as elegant in that no decay model was used to interpolate between or extrapolate from reported intervals. This second program (Appendix G) merely uses the crop and chemical coefficient library with other elements of the unified field model to tabulate the resulting residues in consistent units ($\mu g/cm^2$, 1-sided) and health effects (percent AChE inhibited). Several further simplifying assumptions were made within the Unified Field Model as follows when used with the second approach:

1) Harvest practices for a particular crop in different studies or regions are assumed to be not significantly different. Therefore, a single crop dose coefficient, k_d, was used for those crops which have an established k_d. When necessary and possible, crops without a k_d are given the k_d of a similar crop (e.g. peaches and plums, see Appendix E).

2) To estimate the dose rate for crops without an established k_d and without a similar crop (e.g. apples) a default crop k_d equal to 5000 cm^2/hr was assumed.

3) The enzyme coefficient K_e was fixed at 6.0 (ref. Popendorf & Leffingwell, 1982).

4) Harvester mass (weight) was assumed to be 70 kg.

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5)   The ratio of ppm to ng/cm^2 was assumed to be the same for all studies of a particular crop, e.g. 1 ppm = 25 ng/cm^2 as established by Leffingwell et al (1975) for grapes, see Appendix E.

Although several variables affect the decay process, only one reentry interval is currently established for each combination of pesticide except in California for certain crops. Hence, to estimate a safe reentry interval for the majority of harvest settings the data has been analyzed only by pesticide. The remaining variables are noted but are not listed separately. Differences between manually harvested crops have so far been found to differ mainly by application rate; machine harvesting or non-harvesting practices may certainly cause differences in the residue-dose relationships not otherwise reflected in Appendix E. Future comparisons might be done, for instance, among states or regions to examine the feasibility of separate reentry intervals for different parts of the country, dependent on the area's climate; however, the available data base currently appears too limited in most cases to be used for comparisons between such other variables.

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Table I.

Chemicals with currently assigned reentry intervals specified by either the U.S. Environmental Protection Agency[a] (EPA), the California Department of Food and Agriculture[b] (CDFA), or both. Asterisk (*) indicates chemicals for which residue data was reported (see also Appendix E, chemical coefficients).

CHEMICAL NAME (see footnote g)	CAS #	RTECS #	EPA[a] (aoc)[c]	CDFA[b] Cit	P&N	G	A
Pesticides Regulated by EPA Only							
* Azodrin	6923-224	TC43750	2				
* Metasystox-R	301-122	TG14200	2				
Pesticides Regulated by EPA and California Intervals							
Bidrin [Dicrotophos]	141-662	TC38500	2				
* Carbophenothion (Trithion)	786-196	TD52500	2	14	14	14	-
Demeton (Systox)	8065-483	TF31500	2	5	7	7	-
Endrin	72-208	ID15750	2				
EPN	2104-645	TB19250	1(2)[c]	14	14	14	14
* Ethion	563-122	TE45500	1(2)[c]	30	14	14	-
* Ethyl Parathion [Parathion-ethyl]	56-382	TF45500	2	30[d] 45[e] 60[f]	21	21	14
* Guthion [Azinphosmethyl]	86-500	TE19250	1	30	14	21	14
* Methyl Parathion [Parathion-methyl]	298-000	TG01750	2	-	21	14	14
Pesticides Regulated by California Intervals Only							
* Dialifor (Torak)	10311-849	TD51650		-	-	75	-
Diazinon	333-415	TF33250		5	5	5	-
* Dimecron (Phosphamidon)	13171-216	TC28000	(2)[c]	14	-	-	-
* Dimethoate (Cygon)	60-515	TE17500	-	4	-	4	-
* Dioxathion (Delnav)	78-342	TE33500	(1)[c]	30	30	30	-

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CHEMICAL NAME (see footnote g)	CAS #	RTECS #	EPA[a] (aoc)[c]	INTERVAL CDFA[b] Cit	P&N	G	A
Disufoton (Di-syston)	298-044	TD92750	(2)[c]				
* Endosulfan (Thiodan)	115-297	RB92750	(2)[c]				
Imidan	732-116	TE22750	(2)[c]	–	5	5	–
* Malathion	121-755	WM84000		1	1	1	–
* Methidathion (Supracide)	950-378	TE21000	(2)	30	–	–	–
Methomyl (Lannate, Nudrin)	16752-775	AK29750	(1)[c]	2	2	2	–
* Mevinphos (Phosdrin)	7786-347	GQ52500	(2)[c]	4	4	4	–
Naled (Dibrom)	300-765	TB94500		1	1	1	–
Phorate (Thimet)	298-022	TD94500	(2)[c]				
* Phosalone (Zolone)	2310-170	TD51750	(1)	7	7	7	–
Sulphur	7704-349	WS42500		1	1	1	–
TEPP	107-493	UX68250	(2)[c]	4	4	–	–

Footnotes:

a 40CFR 170.3 Worker Protection Standards for Agricultural Pesticides. Federal Register 39:16888-16891, Friday, May 10 (1974), which apply to all crops for which registered.

b 3 Cal Adm Code. Chp 4, Section 2479. California Regulations include a 48 hour interval for a somewhat different list of chemicals applied to any crop than are listed by EPA (see footnote c). In addition, a list is included of reentry intervals by specific crop abbreviated as follows:

  Cit = citrus
  P&N = peaches and nectarines
  G = grapes
  A = apples
  aoc = all other crops, see footnote c below

c Numbers in parentheses indicate reentry intervals for "all other crops" in California which differ from EPA intervals.

d For application mixtures of not more than 2 lb AI/100 Gal and rates not more than 8 lb AIA.

e For application mixtures of not more than 2 lb AI/100 Gal but rates more than 8 lb AIA.

f For application mixtures of more than 2 lb AI/100 Gal.

g Chemical names in [ ] indicates name as listed in California; chemical names in ( ) indicates a second name in California listing.

Table II: Keyword lists searched with "pesticides" from Table I

(a)	(b)	(c)
degradation	crop	not soil
deterioration	foliar	not soils
dissipation	leafy	
persistence	leaves	
residues		
volatilization		

Table III: Period of time encompassed by each literature search

	from	initially to	finally to
CHEMLINE	1966	Sept 1981	Jan 1984
TOXLINE	Jan 1975	Sept 1981	Jan 1984
AGRICOLA	Jan 1970	Sept 1981	Jan 1984
BIOSIS	Jan 1977	Sept 1981	Jan 1984

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The numeric results of the Phase I studies of the potential impact of reported residue data is tabulated in Appendix H. In an effort to focus the attention of this review on the many different chemicals regulated by reentry intervals and to provide a visual overview of Appendix H, the cholinesterase inhibition (% delta-AChE, abbreviated dAChE in the computer programs and hereafter) potentially resulting from harvester exposure to residues of the various chemicals at reported days-postapplication are plotted in Figures 1 through 20, listed alphabetically. These values will often be referred to as measures of "residue hazard" herein.

The most striking first impression of these plots is the variability of those with many studies. This variability stems from both the initial residues as well as their decay rates. Before discussing further each of these plots and their significance, the general issue of variability of application conditions and initial residue level affecting nearly all chemicals will be addressed.

Among the more prominent variables affecting initial deposition are application rate, mixture concentration, crop, and method of application. The "ideal" uniform deposition of 1-lb of chemical applied to a flat 1-acre plot of land (or foliage) can be calculated to be 11 ug/cm². Different crops and crop spacing will result in different amounts (cm²) of foliage per acre; for instance, Turrell (1961) measured the number and size of leaves on orange trees of different ages, from which it can be calculated that the area of citrus foliage will vary from about 1.5 to 4 times the land area of the grove. Thus, if the 1-lb application were uniformly distributed upon only the foliage of a citrus grove, the initial deposition would be between 3 and 7 µg/cm². Crops with more or less foliage per acre would be expected to have a less or more density of initial residue, respectively.

All initial depositions included in Appendix H for which application rate was reported in the literature, are summarized in Figure 21 as a function of application rate (AIA, lb active ingredient per acre). Subsets of these values are summarized in Figures 22-25 for citrus, peaches, grapes, and cotton, respectively. For 1-lb applications these initial depositions range from 0.1 to 7 $\mu g/cm^2$. There is a general tendency in Figure 21 for the deposition to increase with increasing rates of application, but a number of other factors affect this pattern. For instance, high rates of application are most often associated with lower mixture concentrations, high gallons of water per acre, more thorough crop coverage, and higher rates of runoff; all mitigating toward lower levels of initial deposition. The additional affects of crop planting practices, foliage anatomy, and application methods increase the apparent variability.

Attempts to control for these other factors were considered but found not appropriate at this time in comparison to application rate, and even application rate is not a good predictor in all cases. For instance, when attempting to isolate the influence of application, rate on deposition (the slope of the X-Y regression indicated in Figures 22-25), it became apparent that only for some crops can a reasonable quantitative relationship be found. It appears (from admittedly sketchy data) that initial residues on grapes and peaches increase respectively by 1.9 and 3.3 $\mu g/cm^2$ per pound of additional material applied; cotton may have a slope right in this region (circa 3 $\mu g/cm^2$ per lb/acre) but there is too little range in its application rates to tell. Citrus residues, on the other hand, increase in a highly variable manner with a mean near 0.75 $\mu g/cm^2$ per pound; selecting citrus applications further by chemical did not improve the scatter.

Incorporating application rate into future reentry regulations may be a viable consideration. To date the only chemical so regulated is parathion on citrus in California. At first glance this regulation seems ironic based on the relatively poor correlation between application rate and hazard for citrus (Figure 9) in comparison to the relatively straight forward application-deposition association for most other crops. It is this author's considered opinion (based on experience and the pattern of decay characterized in Figure 22) that the reason reentry intervals for parathion on citrus are based on application rate, was the result more of the coincidental typical application of parathion at high application rates during seasonal weather patterns conducive to the formation of persistent, high hazard residues, than of the only somewhat higher initial residues, per se. Further consideration of incorporating application rate into other crop-pesticide combinations seems prudent but would require more information concerning label application recommendations and restrictions.

In the final analysis, the reentry hazard interpretations summarized in Table IV were made on the data as reported, incorporating agricultural practices implicitly as reflected in the residues reported. The one exception to this rule was the residues reported by Gehrich et al (1976, ref. #12). Their study was specifically commissioned to examine the residue levels and decay patterns among different pesticides, seasons, crops, and regions following equal applications at the maximum rates possible. It is a landmark report, but the conditions studied are not necessarily representative of common agricultural practices in all cases. Therefore, Figures 1 - 20 were interpreted in Table IV on the basis of three factors:

(1) the initial mean dAChE as estimated by the Unified
     Field Model from all reports; thus the initial dAChE
     reflects both the inherent toxicity of the parent-
     pesticide (and any reported metabolites) as well
     as application conditions. Both the typical hazard
     (mode) and maximum hazard were considered.

(2) the half-life of the cholinesterase inhibition
     hazards estimated from the pattern of decay.
     Note that in Table IV the half-life is sometimes
     preceded by "ca" to indicate "circa" when the decay
     pattern does not appear to fit an exponential model;
     in this case an effective half-life is listed
     corresponding to the rate of decay in the 1 to 10%
     dAChE per day region.

(3) optional reentry intervals determined by the days
     necessary for the dAChE 8-hour workday to fall below
     4%. Two versions of this reentry interval are listed:
     one is the time for the typical residue (mode) to
     fall below the 4% criterion (combining factors 1 and
     2, above), the second is the time for the maximum
     reported residue to decay below the 4% criterion.

1. Azinphosmethyl (Guthion) has been quite well studied with fourteen

references cited covering 4 crops. The initial residue depositions span

nearly two orders of magnitude. It is not unexpected that studies of

relatively low residues may not have been pursued for as long a time as

studies of higher residues; thus, residues appear to become more consistent

at longer intervals post-application. Thereafter, residue hazards appear

to decay exponentially rather slowly, with a half-life of about 3 weeks.

The presence of its oxon was reported in only one study (Iwata, 1980); in

this one case the initial deposition, its hazard, and its half-life all

appear to be outliers, but not more than 25% of the dAChE hazard at any

point is attributable to its oxon. The recommended reentry interval of 16

to 23 days is consistent with California's standard but much longer than

EPA's 1 day.

2. Carbaryl (Sevin) residues were only marginally reported, but its very low acute toxicity (not to mention its less cumulative dAChE effect as a carbamate) result in maximum dAChE hazards of <0.1%. Neither agency has current reentry requirements for this pesticide and no additional requirements are suggested by this data.

3. Carbophenothion (Trithion) residues have been reported only modestly. Its typical initial dAChE hazard was near 4%; its maximum initial residue hazard did not exceed 10% and was below 4% in 2 days except when applied at unusually high rates (studies by Gehrich et al (12) were applied at 8 lb/acre to match high parathion applications, an apparently uncommon practice with Trithion). Given the apparent agricultural usage (application rates) of this pesticide, the recommended reentry interval of 0 to 2 days is consistent with EPA's current standard and much less than the California requirement of 14 days; On the other hand,if the pesticide were used at or near 8 lb AIA, this data would suggest reentry requirements near 60 days.

4. Chlorthiophos has not been well reported in the literature. The only citation does not report initial depositions, but dAChE responses in excess of 15% per day are expected. It may decay in a biphasic pattern (fast then slow) and in the one report required about 7 weeks for the hazard to decay below the 4% criterion. Reentry intervals for this pesticide are not currently required by either agency but are highly suggested by these data.

5. Dialifor (Torak) residues have again been reported only modestly, despite the fact that the chemical has been implicated in at least one

harvester residue poisoning incident (Winterlin, 1982 (ref. 83) and in California is regulated by a 75 reentry interval. Reported residues indicate initial hazards range generally from 3 to 10% and decay at a moderate rate. A second set of hazard predictions were made for dialifor assuming a 10-fold increase in the toxicity of its oxon versus the parent; this assumption affected very long-term residues several fold, but their cholinesterase responses were still projected to be circa only 1% per day. In order to explain the poisoning incidents on the basis of these residues, either the incorrect portions of the field were sampled, not all the residue was detected, the dosing coefficient for grape harvesters is significantly higher than for peach or citrus harvesters, or the toxicity of the oxon is very much greater than expected. Even the highest residues reported were below the 4% dAChE criterion within 15 days. EPA currently requires no reentry for this pesticide, but the data only supports a recommendation in the range of 4 to 15 days.

6. Dimethoate (Cygon) residues appear to represent a low hazard under all use conditions reported. Its highest initial hazard is projected to represent a 1% dAChE per day response and its half-life is 9 days. No further requirement is recommended for this pesticide (California currently requires a 4 day interval on citrus and grapes).

7. Dioxathion (Delnav) presents a modestly low (1 - 10% dAChE per day) but unusually long residue hazard (a half-life near 48 days). Thus, the typical initial residue hazard would just comply with the 4% per day criterion but the maximum residue reported would require approximately 70 days to reach this criterion. A final recommendation concerning the

adequacy of any reentry interval for this chemical would require more information on use and exposure patterns, and on any chronic noncholinergic health effects associated with the chemical.

8. Ethion residues have been studied and reported in a reasonable number of studies. In most of these studies one or more of its oxons have been reported, but no acute dermal toxicologic information was found for either its monoxon or its dioxon. Therefore, two interpretations (Figures 8 and 8a and Table IV entries) were made: (1) assuming all metabolites have toxicities equal to the parent pesticide, and (2) assuming its monoxon is ten-fold more toxic than the parent (in the range of the oxons of azinphosmethyl (30x), ethyl parathion (10x), methidathion (3x), and phosalone (5x)) and its dioxon is twenty-fold more toxic (based on the number of active sites). Inclusion of the assumed oxon toxicity increased the typical initial hazard from about 1.5% to 6%, neither of which is capable of causing an acute clinical poisoning. This inclusion also increased the hazard's half-life from 10 to 16 days, respectively. However, the maximum residue hazards for this chemical when applied at high rates in the range of 40%. The reentry intervals corresponding to the typical or maximum residues (other than by Gehrich et al (1976) range from 9 to 23 days, intervals considerably higher than the current EPA standard (1 day) but very much in the range of the current 14 to 30 day California requirement.

9. Ethyl Parathion residues are no doubt the best reported organophosphate pesticide. At the same time the amount of data makes their interpretation difficult. As an aid in interpretation, a number of sub-Figure 9's are

included in this report, each one isolating the residue hazards by region
(i.e. California, Texas, Arizona, Washington, and Florida). The apparent
lack of consistency of the residue hazards, particularly between regions
but also within some regions is notable. But also of particular note is
the similarity among the residues reported by Gehrich et al for similar
applications within four of these regions. Thus, most (but not all) of the
apparent differences among regions appears attributable to and to different
application rates and initial deposits on different crops (parathion
application rates on most crops other than citrus (and even on citrus in
Florida) are 1-1 lb/acre or less. Secondarily, the half-lives of the
residue hazard from more common agricultural applications seem to differ
among the regions and to vary inversely with moisture (rainfall) associated
with the various regions. The suggested reentry intervals (see Table IV)
closely parallel those currently regulated in California but often greatly
exceed those currently set by EPA (2 days).

10. Malathion has one of the lowest acute toxicities of the pesticides
studied. Its residues have not been reported often, but its residue hazard
is well below 0.1% dAChE under all conditions reported. Thus, no further
reentry requirement is recommended based on acute toxicity.

11. Methyl Parathion residues have been reported on a fairly wide range of
crops; it should be pointed out, however, that lacking other experimental
information, the default dosing coefficient of 5000 cm^2/hr was assumed for
exposures in cotton. Considerable variability is apparent in the rate of
hazard decay, more clearly varying inversely with moisture and possibly

with application rate. The presence of its oxon was reported in about 20%

of the studies, but only under the high application conditions reported by

Gehrich et al did the oxon eventually become the predominant residue

hazard. Thus, the assumed toxicity of the oxon was rarely important to the

overall dAChE hazard, but in the high application rate condition the two

optional toxicity assumptions caused the recommended reentry interval to

range from 17 to 27 days. The highest other residue hazard was on apples

and fell below the 4% criterion after 8 days. The generally low

application rates kept typical initial hazards in the range of 6%

(depending upon the onon toxicity assumption), and its half-life ranged

from 1 - 2 days depending upon the crop and climate. Thus, various

recommended reentry intervals could be made for this chemical ranging from

1 to 8 days depending upon crop, region, and application rate. The longer

intervals are consistent with California's standards of 14 and 21 days;

only the shortest is consistent with EPA's but it is not inclusive of all

non-California conditions reported.

12. Methidathion (Supracide) residues were well studied in a small number

of reports. Application rates in the two citrus growing regions were quite

comparable, but the initial residue hazards were strongly affected by

sometimes quite different application mixture concentrations (ranging from

a nominal 3 to 6 lb/1000 gal/acre tested in both regions, up to 6 lb/100

gal/acre tested only in California). Decay patterns were biphasic but did

not differ widely either among or within studies. Only in the relatively

dry region was the oxon consistently found in significant quantities. The

recommended reentry times differ among the studies from none to 30 days

primarily because of the initial deposits and secondarily because of oxon

formation. These values are generally consistent with California (which requires either 30 days on citrus or 2 days on all other crops) while EPA has no current reentry interval for this pesticide.

13. Mevinphos (Phosdrin) residues were very sparsely reported. Because of their high toxicity, initial hazards were often quite high, typically circa 25% dAChE, but their very short half-life under the conditions reported results in recommended reentry intervals similar to California regulations of 2 to 4 days (EPA has no additional requirements for this chemical).

14. Monocrotophos (Azodrin) residues were only reported in a few studies. The inherent toxicity of its initial deposition is sufficient to present modest dAChE hazards at the outset (typically 8%). Estimates of its half-life are limited by the short span of reported studies but appear to be circa 2.5 days. Thus, its recommended reentry intervals of 3 - 5 days is about double the EPA standard (California has no additional requirements for this chemical).

15. Oxydemeton (Metasystox-R) residues have been reported hardly at all. The one report listed two widely divergent studies. The initial deposits of this otherwise moderately toxic pesticide were quite low, creating a maximum dAChE hazard of 1.5%. EPA currently regulates a 2 day reentry interval. Based on this limited data, no further reentry interval can be recommended.

16. Phenthoate again has been only weakly reported. It has a fairly low toxicity, and its highest residue hazard was only 2% (but on the second

day, the earliest reported in that particular study). This pesticide is currently regulated by neither EPA nor California and would appear to satisfy the 4% criterion without additional requirements.

17. Phosalone (Zolone) residues have been modestly studied. Both the parent and its oxon have fairly low toxicity, resulting in typical (and consistent) initial depositions hazards of only 1.5%. EPA has no reentry requirement for this pesticide, but California requires 7 days for several fruit crops. Despite its long half-life of about 11 days, there appears to be little justification for adding additional reentry requirements for this chemical.

18. Phosphamidon (Dimecron) residues have been studied a fair number of times, but nearly all of these studies have reported the data in units of ppm on crops for which conversion to $\mu g/cm^2$ was not possible. In the one study interpretable, its initial dAChE hazard was projected (back from the earliest sample of 2 days) to be about 10%, with a half-life of about 3.5 days. Thus, recommended reentry intervals are in the range of 4 - 5 days, twice the current California standard (EPA has no current requirement for this pesticide).

19. Phosmet (Imidan) residues have been studied in 3 cases. Its initial depositions were in the expected range, but its low acute toxicity resulted in a negligible dAChE hazard (<0.1%) in all cases.

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20. Trichlorfon (like phosmet) has been only weakly reported, has somewhat high initial depositions, but its maximum dAChE hazard was just under 1% with a 1.5 day half-life. Reentry intervals are not currently required by either agency and no further requirements are justified by this data.

Table IV. Summary of reentry parameters extracted from reported residue dAChE hazard analysis via the Unified Field Model. Initial dAChE was estimated from all reports; thus it reflects both inherent toxicity as well as application conditions. The half-life is estimated from the pattern of decay and is preceded by "ca" [circa] when the decay pattern does not appear to be exponential. Recommended reentry intervals are the days necessary for the initial dAChE hazard (inhibition expected from 8-hours working exposure) to fall below 4%; values are listed based both on the typical residue (mode) as well as on the maximum residue reported.

Fig. #	Pesticide Name	Initial typical dAChE	Est. 1/2 Life days	Days until dAChE=4% mode	max
1	Azinphosmethyl (Guthion)	2.5%	23.	na	16
2	Carbaryl (Sevin)	<0.1	ca 2.	na	na
3	Carbophenothion (Trithion)	0.9%	7.6	na	ca 2
4	Chlorthiophos	>15. %	19.	36	36
5	Dialifor (Torak)	5. %	12.	4	15
5a	Dialifor (Torak) *	5. % *	12. *	4 *	14 *
6	Dimethoate (Cygon)	0.6%	9.	na	na
7	Dioxathion (Delnav)	4. %	ca 48.	na	70
8	Ethion	1.5%	10.	na	15
8a	Ethion *	6. % *	16. *	9 *	23 *
9	Ethyl Parathion	18. %	10.	22	60
9a	Ethyl Parathion (AZ,citrus)	(90) %	12.	54	60
9b	Ethyl Parathion (CA)	60. %	7.	27	60
9c	Ethyl Parathion (TX)	(90) %	7.	21	21
9c	Ethyl Parathion (FL,dry)	15. %	7.	14	ca 45
9c	Ethyl Parathion (WA)	10. %	4.	5	21
9c	Ethyl Parathion (AZ,cotton)	20. %	2.	5	8
9c	Ethyl Parathion (FL,wet)	5. %	2.	1	5
10	Malathion	<0.1%	ca 1.	na	na
11	Methyl Parathion	2. %	2.	na	8
11	[high appl. rate]	(60) %	4	16	17
11a	Methyl Parathion *	4. % *	3. *	na *	8 *
11a	[high appl. rate] *	(62) % *	6. *	24 *	27 *
12	Methidathion (conc.,CA)	15. %	ca 4.	8	30
12	Methidathion (dilute,CA)	4. %	ca 4.	na	ca 12
12	Methidathion (dilute,FL)	2. %	ca 2.	na	na
13	Mevinphos (Phosdrin)	25. %	0.8	2	3
14	Monocrotophos (Azodrin)	8. %	2.3	3	5
15	Oxydemeton (Metasystox-R)	1.5%	ca 6.	na	na
16	Phenthoate	2.5%	ca 3.	na	2
17	Phosalone (Zolone)	1.5%	11.	na	na
18	Phosphamidon (Dimecron)	10. %	ca 3.6	5	4
19	Phosmet (Imidan)	0.1%	6.	na	na
20	Trichlorfon	1. %	1.4	na	na

CONCLUSION:

A review of the reported foliar residue data has revealed a number of deficiencies in the reentry intervals currently regulated by both the EPA and California, as well as some dificiencies in the available information necessary to recommend better reentry intervals. One of the most fundamental deficiencies is the basic criterion of cholinesterase inhibition allowed during a workday, on the basis of either acute or chronic inhibion. The former is known to have been associated with harvester clinical poisoning (e.g. Spear et al, 1977); the latter is hypothesized to be a potential problem (milby et al, 1964). For the purposes of this report, an allowable daily inhibition of 4% was assumed.

Based on this criterion and the available data, EPA reentry intervals for eight pesticides appear inadequate in comparison to the Unified Field Model assessment (not within the range of the optional recommendations in Table IV); four are marginal (within the low range of the optional recommendations in Table IV); eight are adequate; and none may be excessive. A similar balance for California indicates three are inadequate; five are marginal; eight are adequate; and four appear excessive.

These conclusions are based on a considerable amount of residue data not equally distributed among all pesticides listed, nor has the model been confirmed in all the conditions examined. However, the model has been developed under realistic field tests, most of its premises have been confirmed in a limited number of tests, and its recommendations appear to parallel experience and regulations in California where pesticide use and decay conditions may have been most severe. The conclusions definitely suggest that improved levels of protection are needed in other regions.

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Table V. A comparison between the current reentry intervals regulated by the EPA and by California (as listed in Table I) with recommendations based on the Unified Field Model with a 4% daily inhibition threshold (Table IV).

		EPA	California
1	Azinphosmethyl (Guthion)	Marginal	Adequate
2	Carbaryl (Sevin)	Adequate	Adequate
3	Carbophenothion (Trithion)	Adequate	Excessive
4	Chlorthiophos	Inadequate	Inadequate
5	Dialifor (Torak)	Inadequate	Marginal
6	Dimethoate (Cygon)	Adequate	Excessive
7	Dioxathion (Delnav)	Inadequate	Marginal
8	Ethion	Marginal	Adequate
9	Ethyl Parathion	Inadequate	Marginal
10	Malathion	Adequate	Adequate
11	Methyl Parathion	Marginal	Adequate
12	Methidathion (Supracide)	Inadequate	Marginal
13	Mevinphos (Phosdrin)	Inadequate	Adequate
14	Monocrotophos (Azodrin)	Adequate	Inadequate
15	Oxydemeton (Metasystox-R)	Adequate	Marginal
16	Phenthoate	Inadequate	Inadequate
17	Phosalone (Zolone)	Marginal	Excessive
18	Phosphamidon (Dimecron)	Inadequate	Excessive
19	Phosmet (Imidan)	Adequate	Adequate
20	Trichlorfon	Adequate	Adequate

TEXT REFERENCES:

California Administrative Code: Title 3 (Agriculture), Article 23 (Pesticide Worker Safety), Parts 2479 Field Worker Safety. Sacramento CA, (Rev. Jan 1979).

EPA: Reinstatement of certain existing standards. Fed. Reg. 39: 16888 (10 May 1974).

Gunther, F.A., et al: The citrus reentry problem: Research on its causes and effects, and approaches to its minimization. Residue Reviews 67:1 (1977).

Milby, T.H., F. Ottoboni, and H. Mitchell: Parathion residue poisoning among orchard workers. J.Amer.Med.Assoc. 189: 351, (1964).

Popendorf, W.J. and J.T. Leffingwell: Regulating OP pesticide residues for farmworker protection. Residue Reviews 82: 125 (1982).

Quinby, G.E., and A.B. Lemmon: Parathion residues as a cause of poisoning in crop workers. J.Amer. Med. Assoc. 166:740 (1958).

Spear, R.C., T.H. Milby, and D.I. Jenkins: Pesticide residues and field workers. Env.Sci.Technol. 9:308 (1975).

Spear, R.C., W.J. Popendorf, J.T. Leffingwell, and T.H. Milby: Worker poisoning due to paraoxon residue. J. Occup.Med. 19:411 (1977).

Turrell, F.M.: Growth in the photosymthesis area of citrus. Bot.Gaz. 122: 284 (1961).
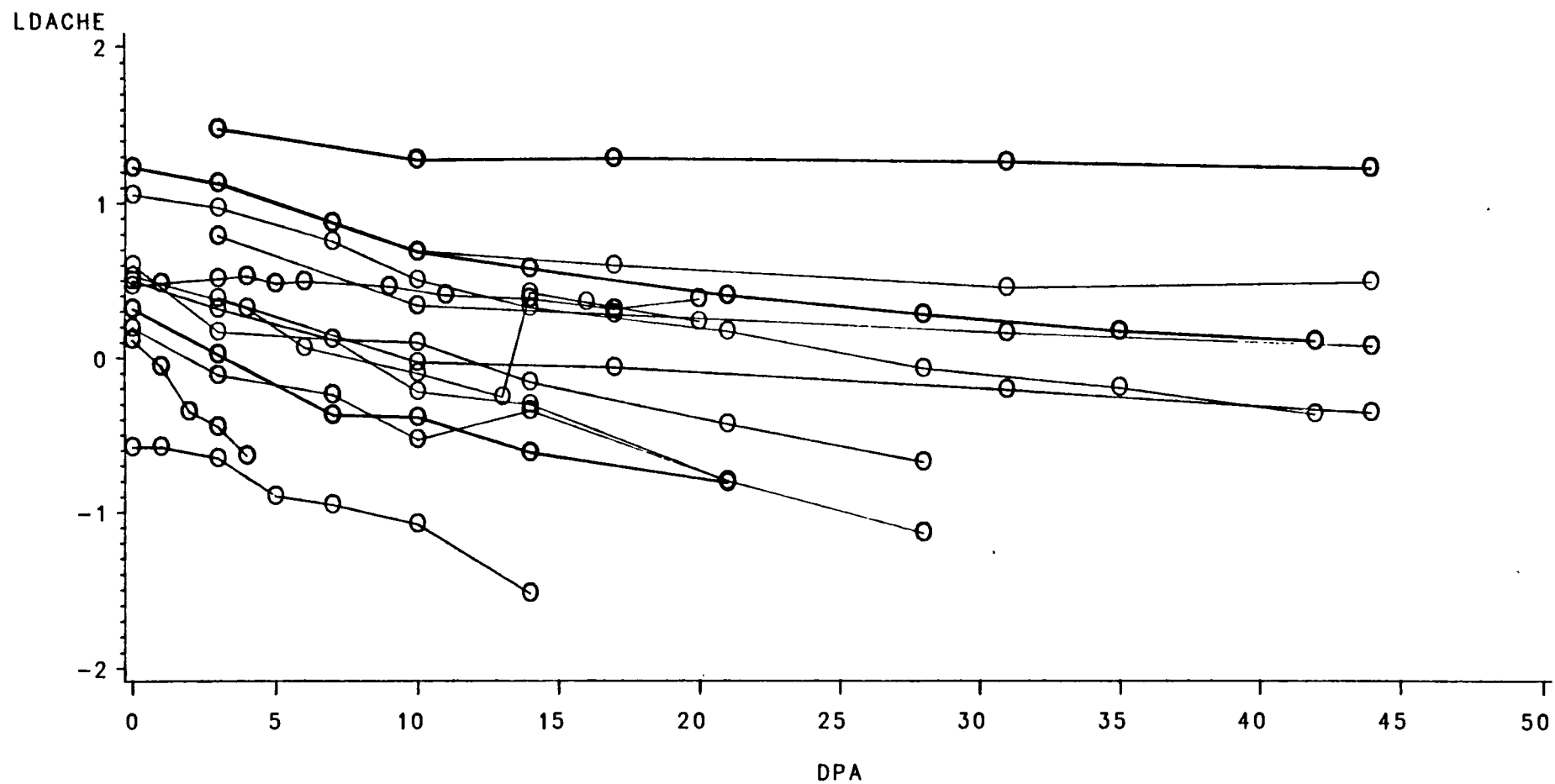
Figure 1. Plot of residual hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Azinphosmethyl (Guthion).
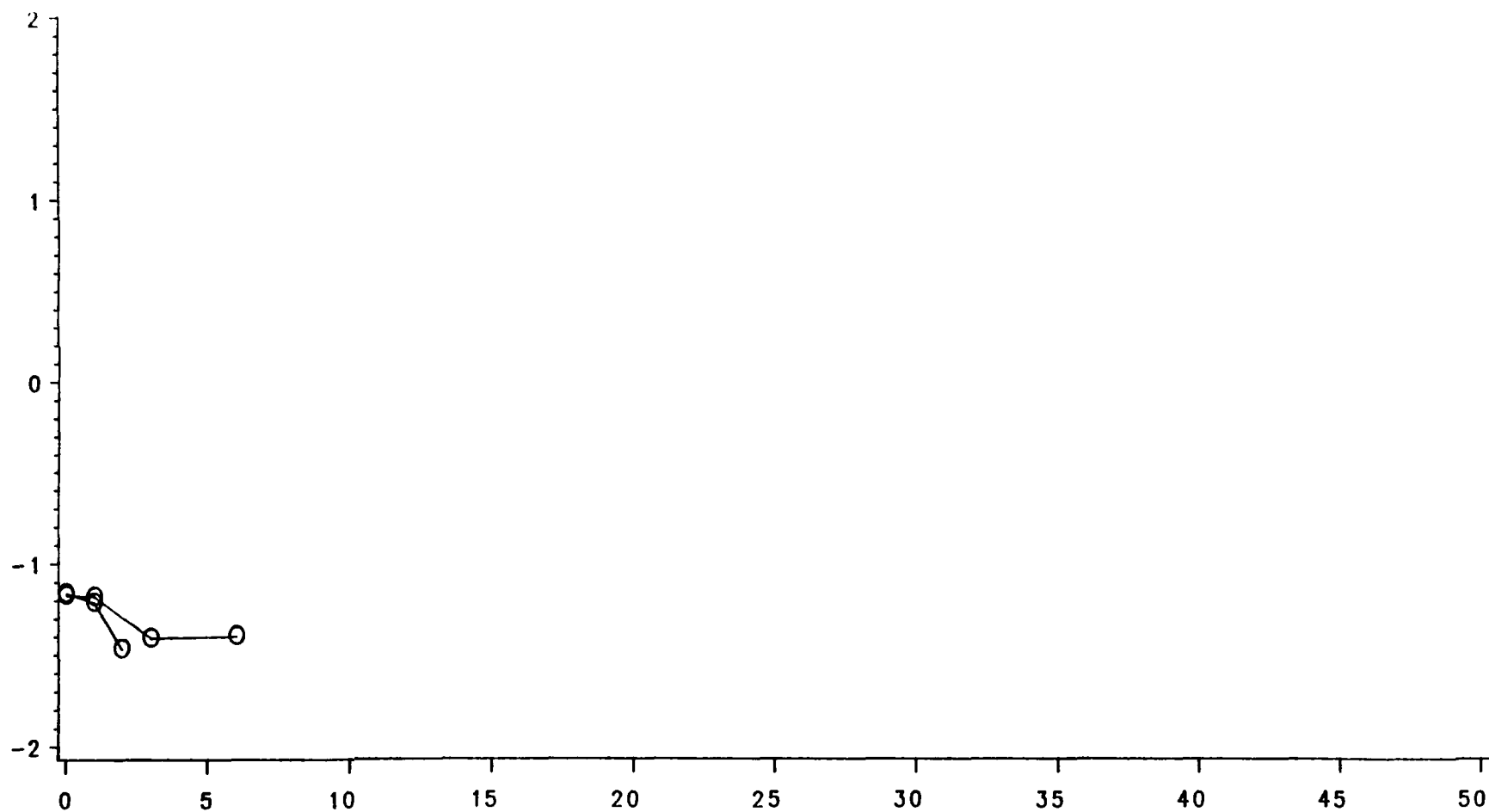
Figure 2. Plot of residue hazard (common logarithm of % dAChE) as a function
of time (days post-application, DPA) for Carbaryl (Sevin).
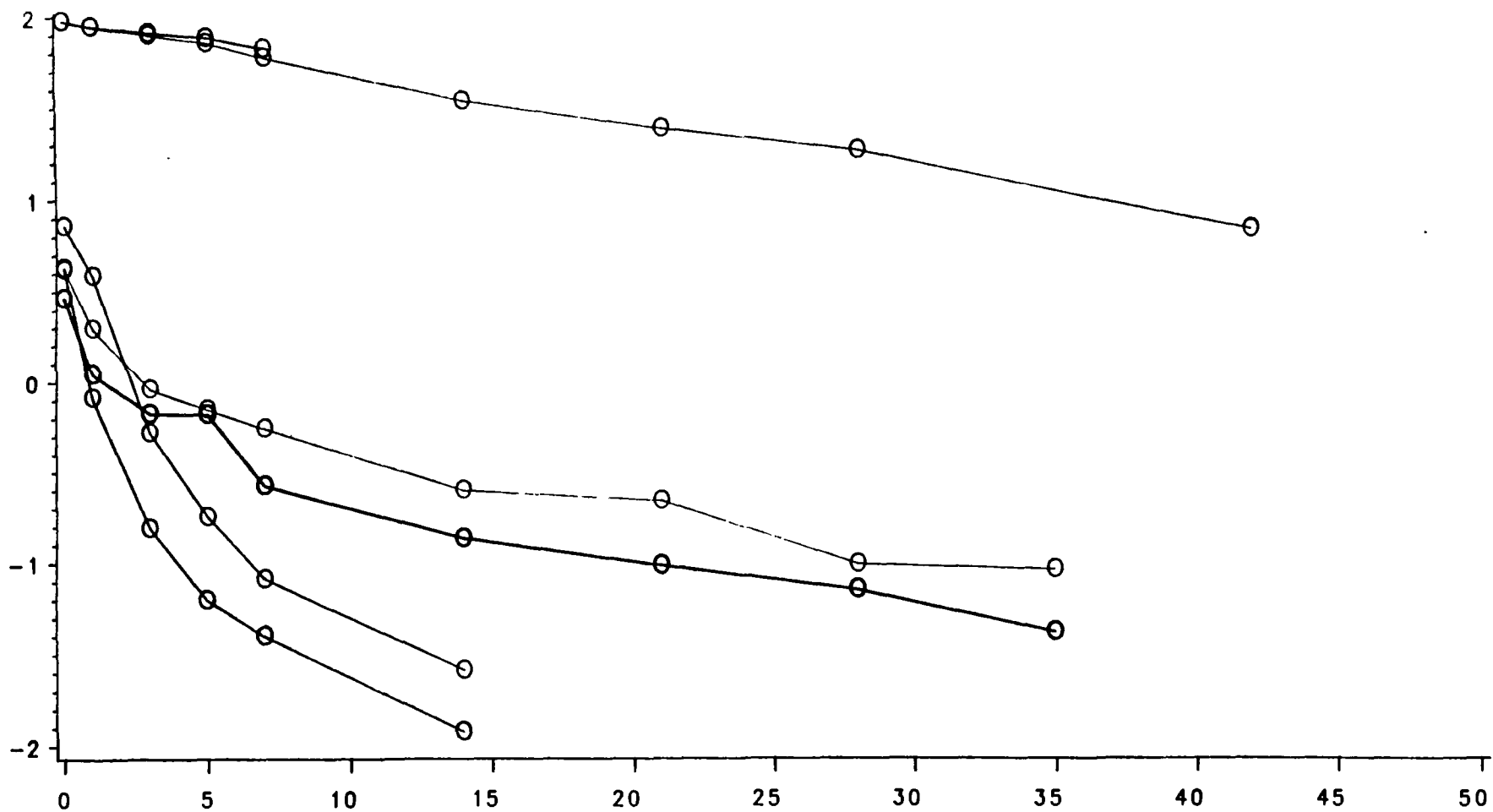
Figure 3. Plot of residue hazard (common logarithm of % dAChE) as a function
of time (days post-application, DPA) for Carbophenothion (Trithion).
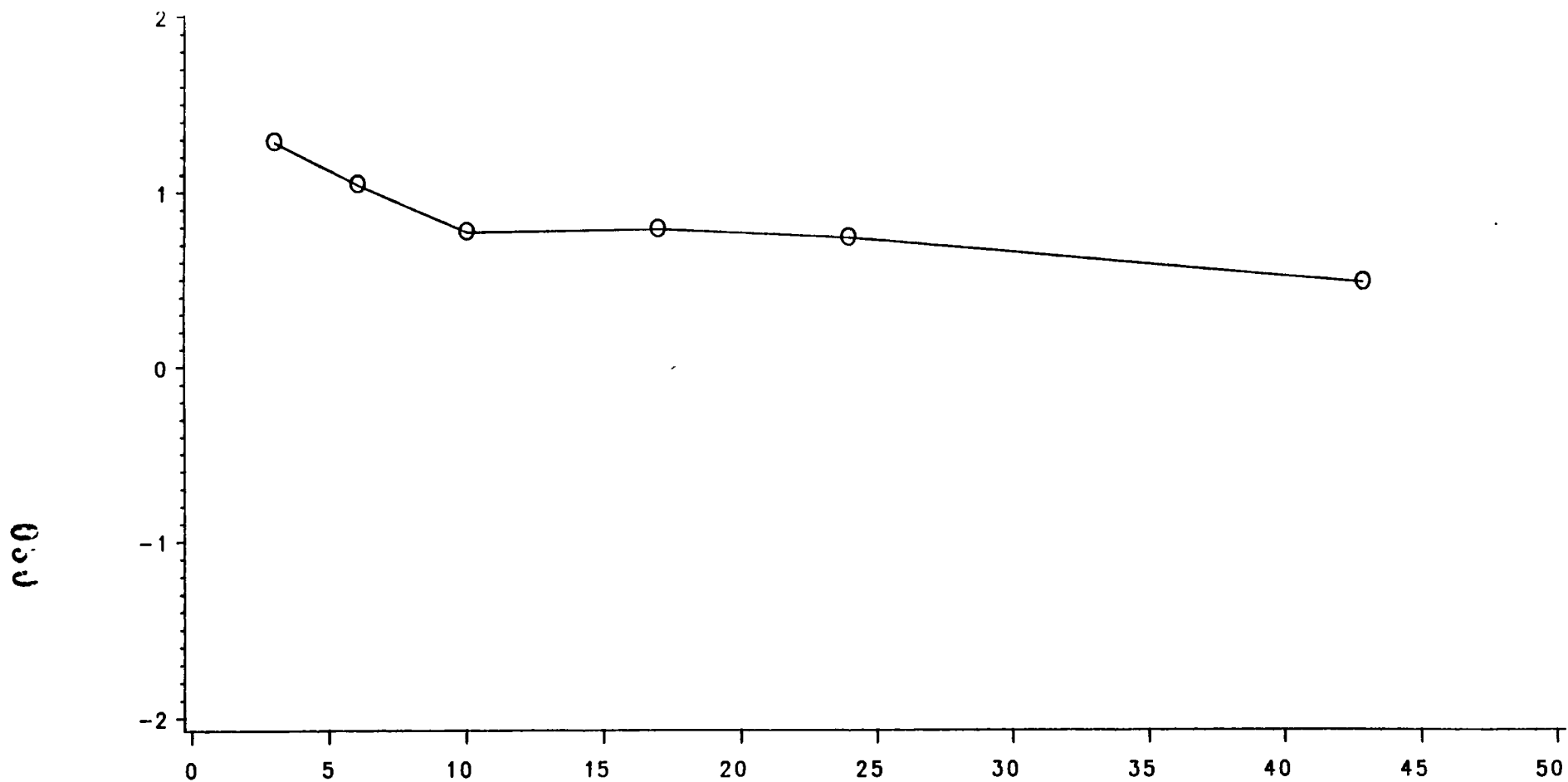
Figure 4. Plot of residue hazard (common logarithm of 7 dAChE) as a function
of time (days post-application, DPA) for Chlorthiophos.
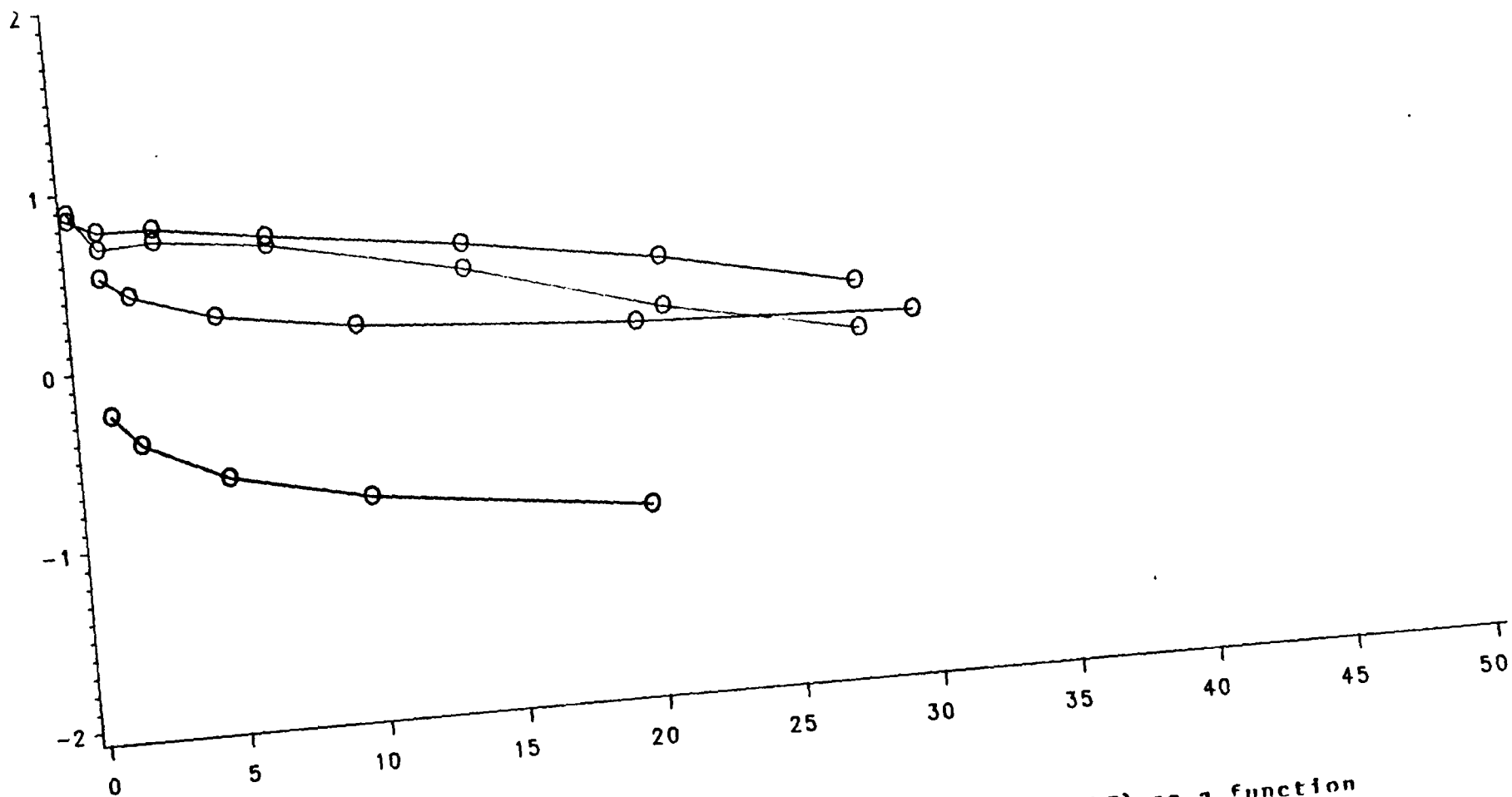
Figure 5. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Dialifor (Torak).

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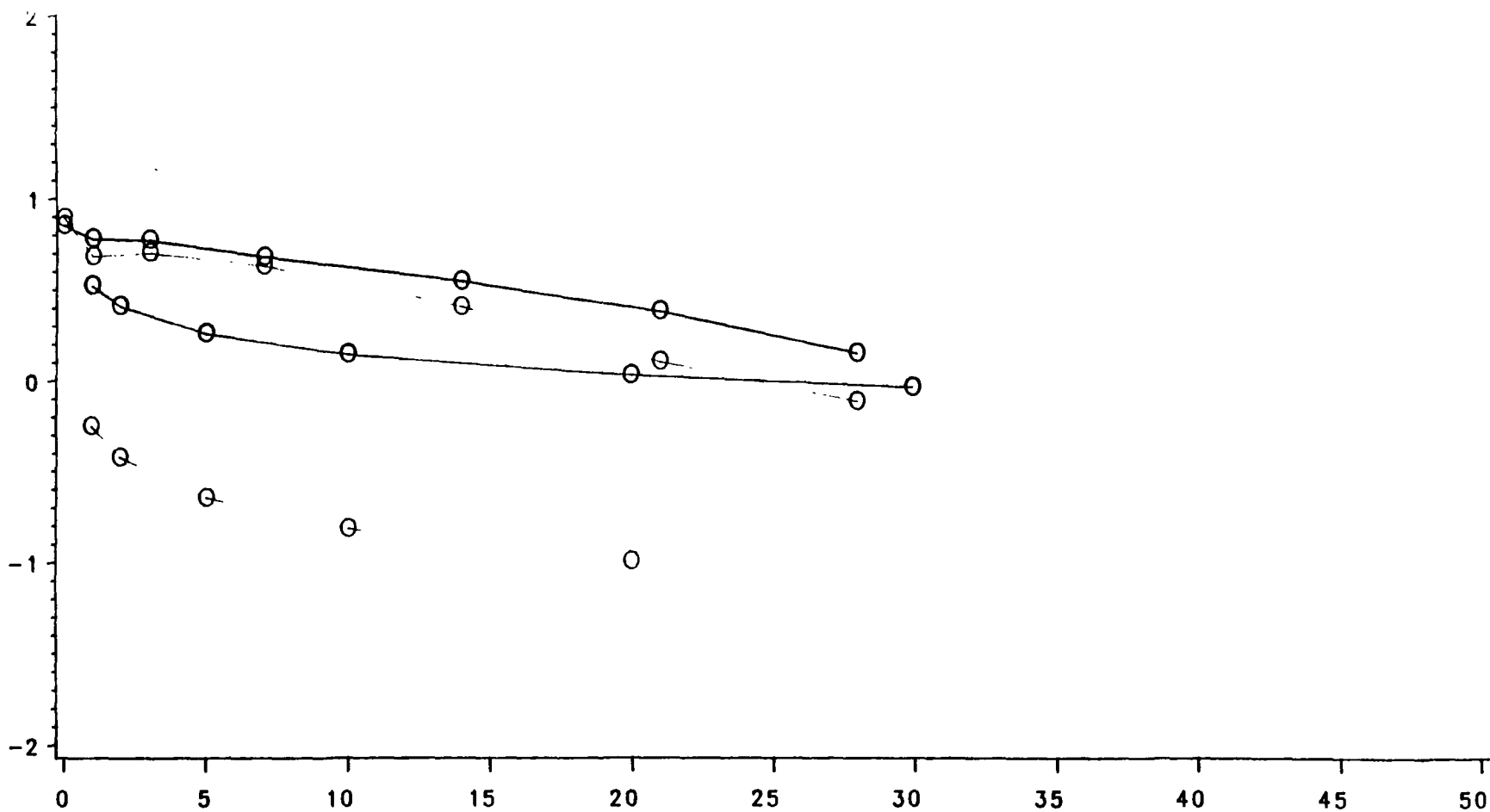
Figure 5a. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Dialifor (Torak) with the LD$_{50}$ of the oxon assumed to be 1/10th that of the parent.
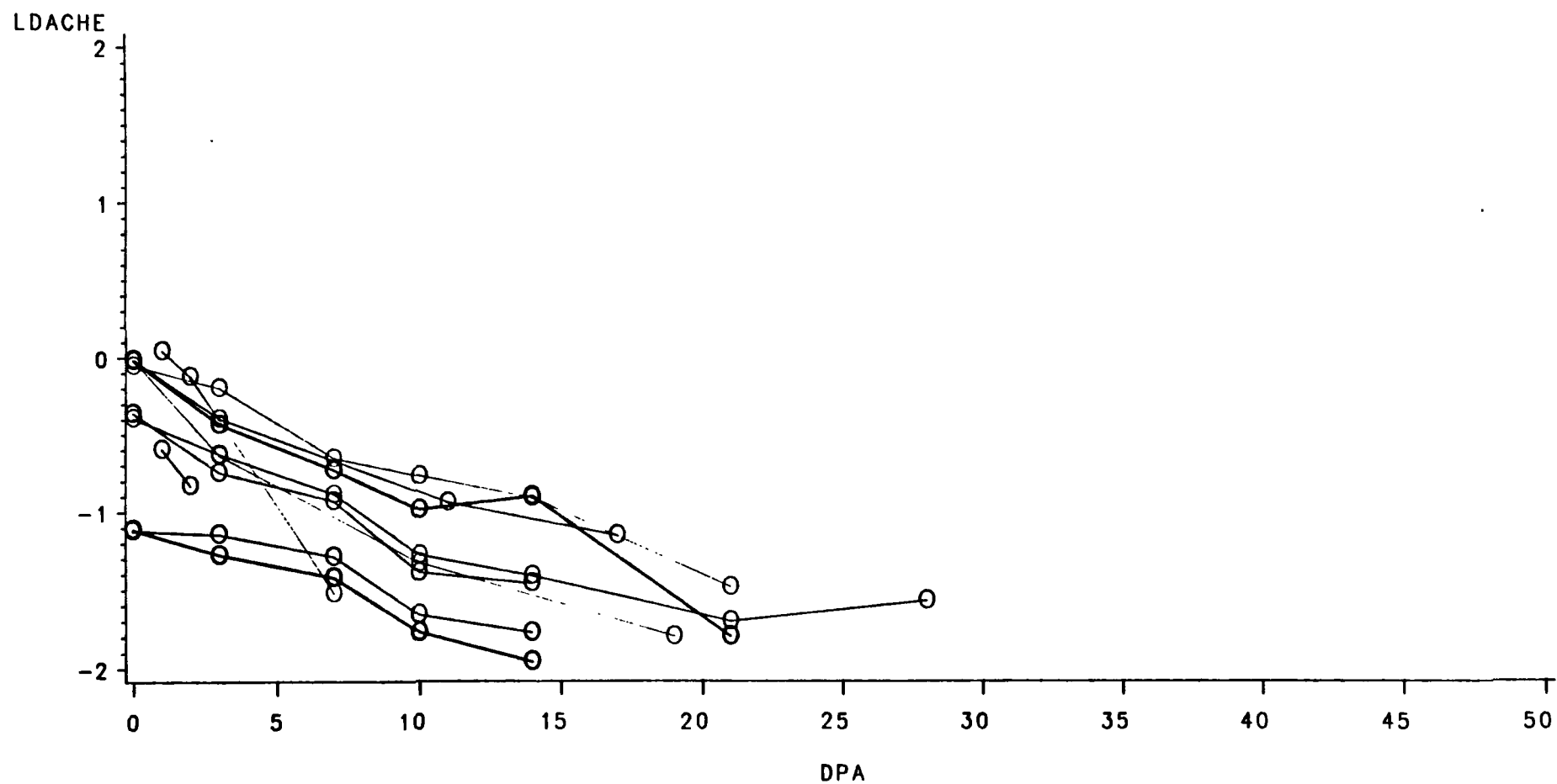
Figure 6. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Dimethoate (Cygon).
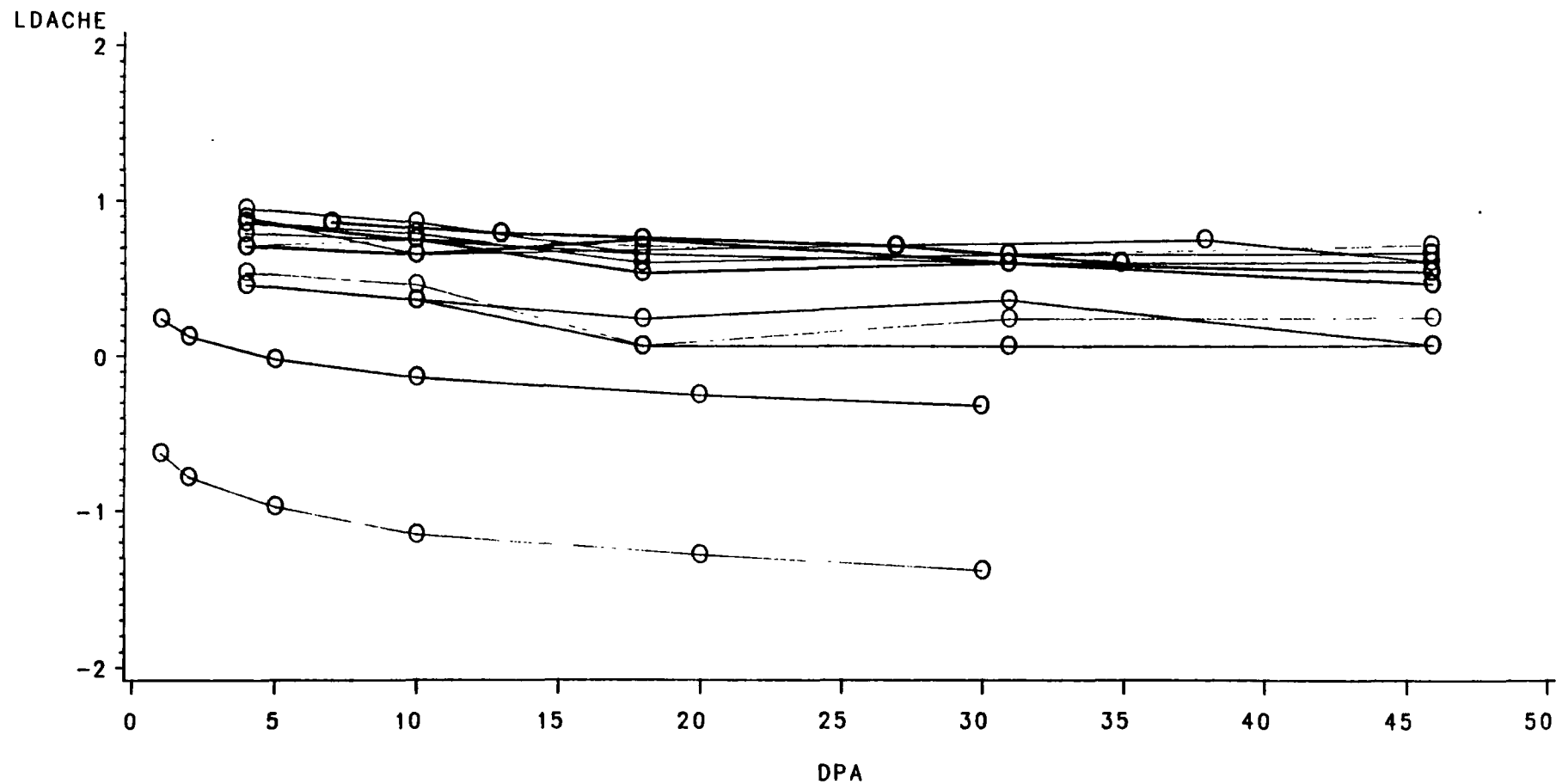
Figure 7. Plot of residue hazard (common logarithm of % dAChE) as a function
of time (days post-application, DPA) for Dioxathion (Delnav).
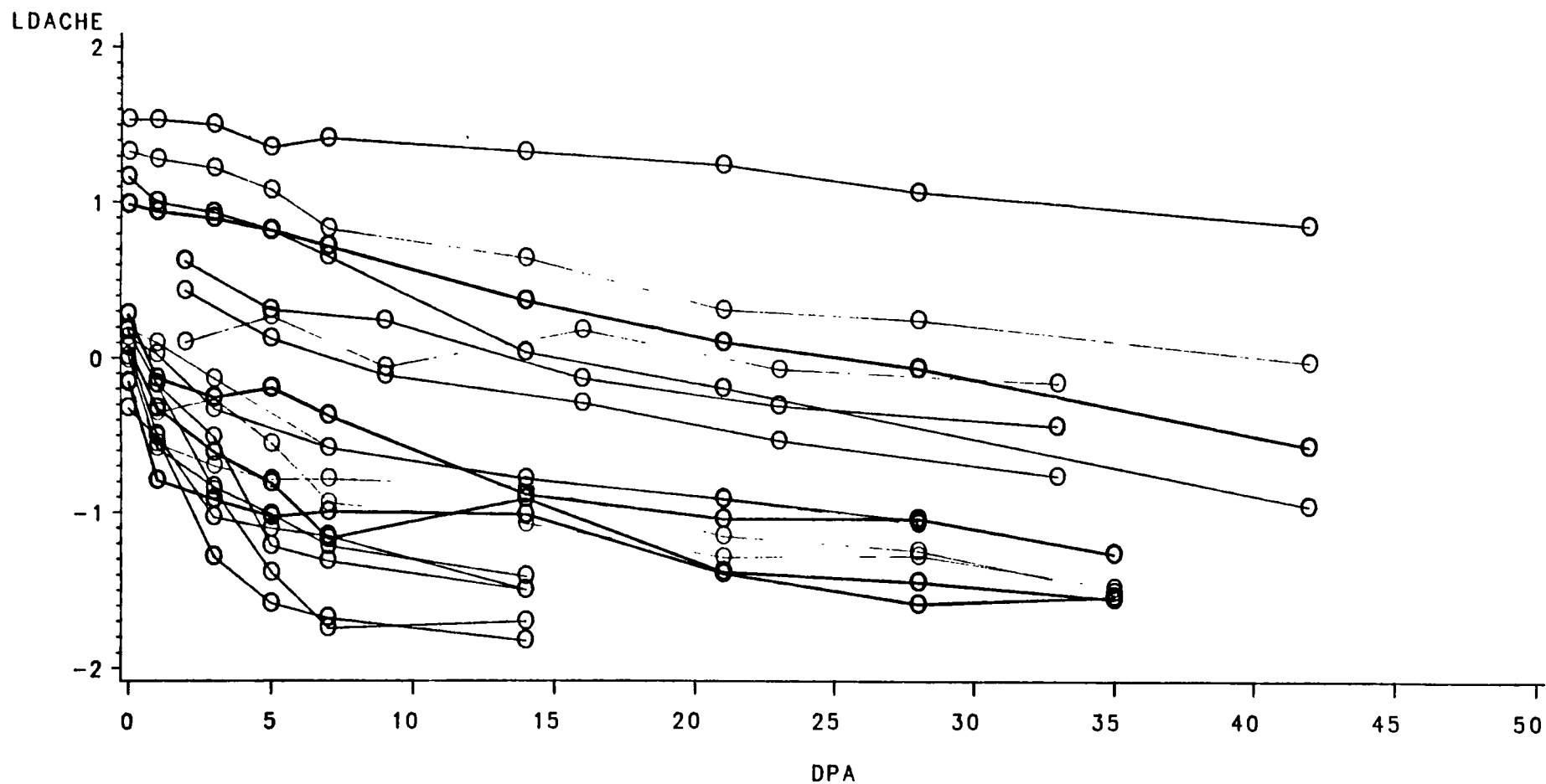
Figure 8. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for ethion.
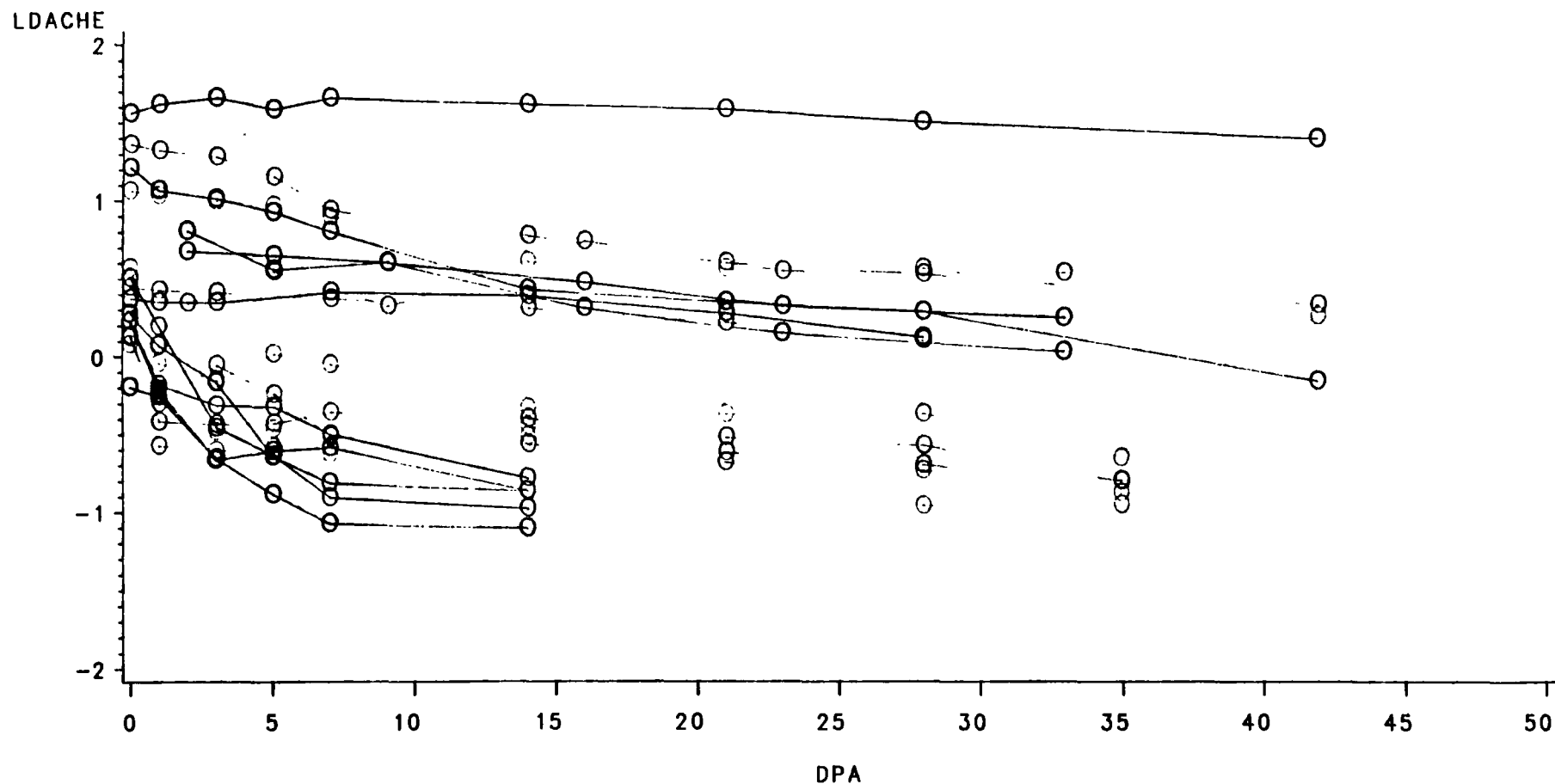
Figure 8a. Plot of residue hazard (common logarithm of 7 dAChE) as a function of time (days post-application, DPA) for Ethion with the LD50 of the monoxon assumed to be 1/10th that of the parent and the dioxon assumed to be 1/20th that of the parent.

LDACHE

DPA
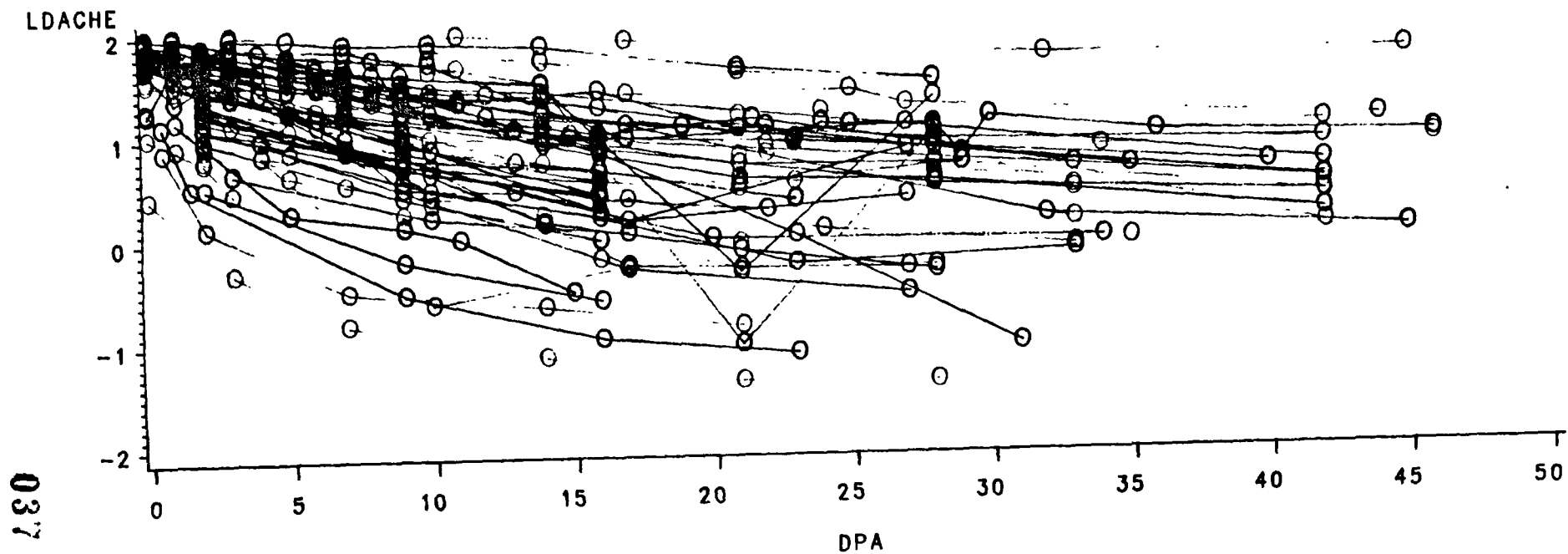
Figure 9a. Plot of residue hazard (common logarithm of 7 dAChE) as a function
of time (days post-application, DPA) for Ethyl Parathion as
reported from California.

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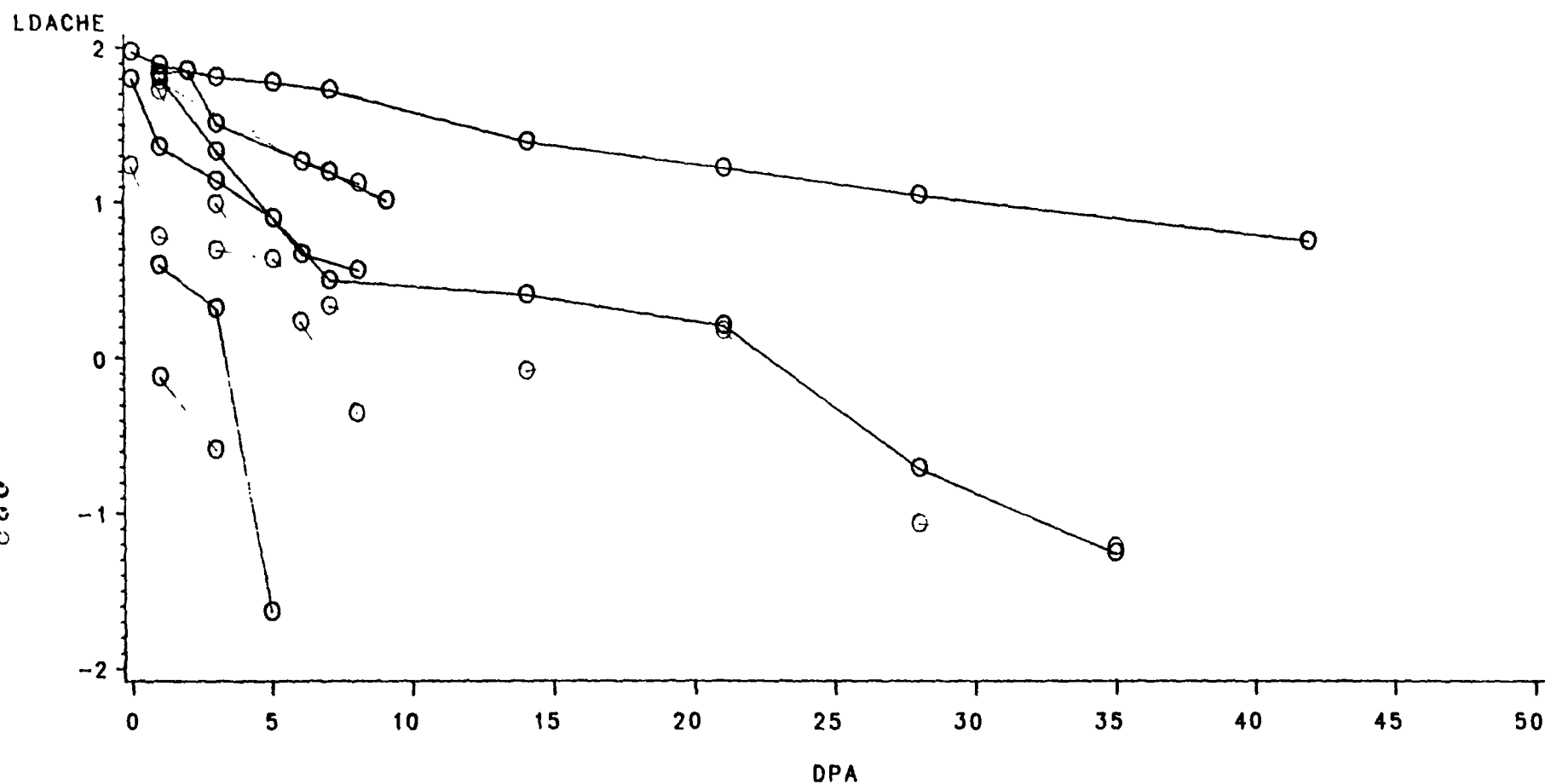
Figure 9b. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Ethyl Parathion as reported from Florida.
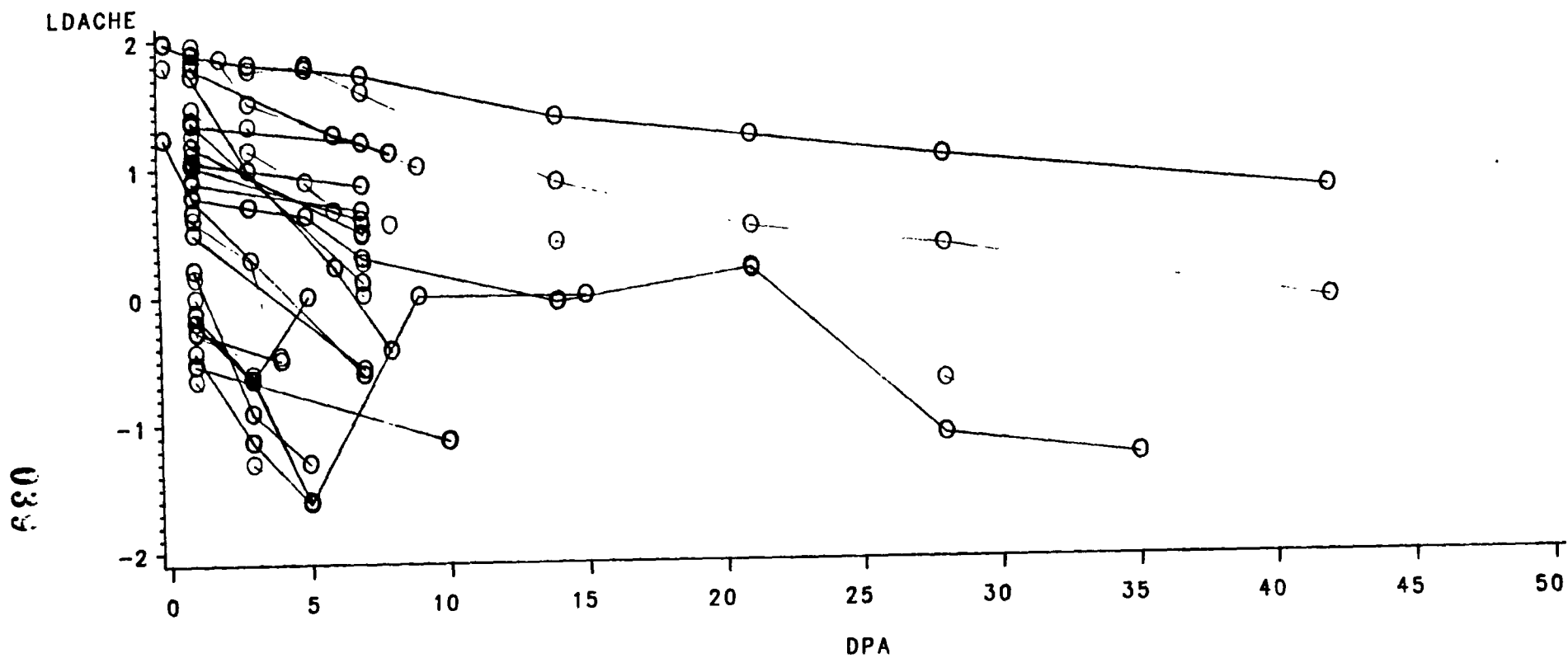
Figure 9c. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Ethyl Parathion as reported from Washington, South Carolina and Texas.
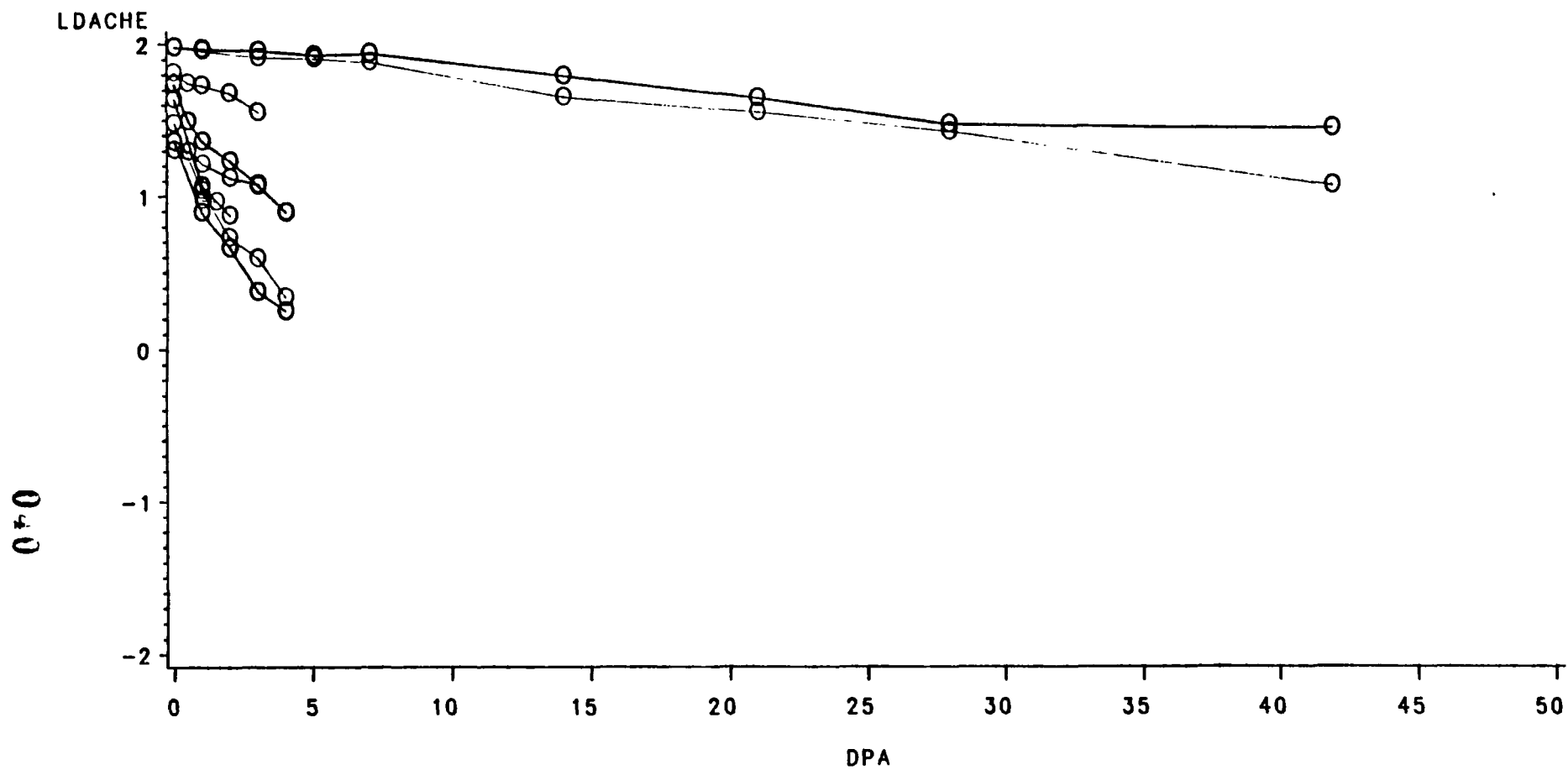
Figure 9d. Plot of residue hazard (common logarithm of % dAChF) as a function
of time (days post-application, DPA) for Ethyl Parathion as
reported from Arizona.
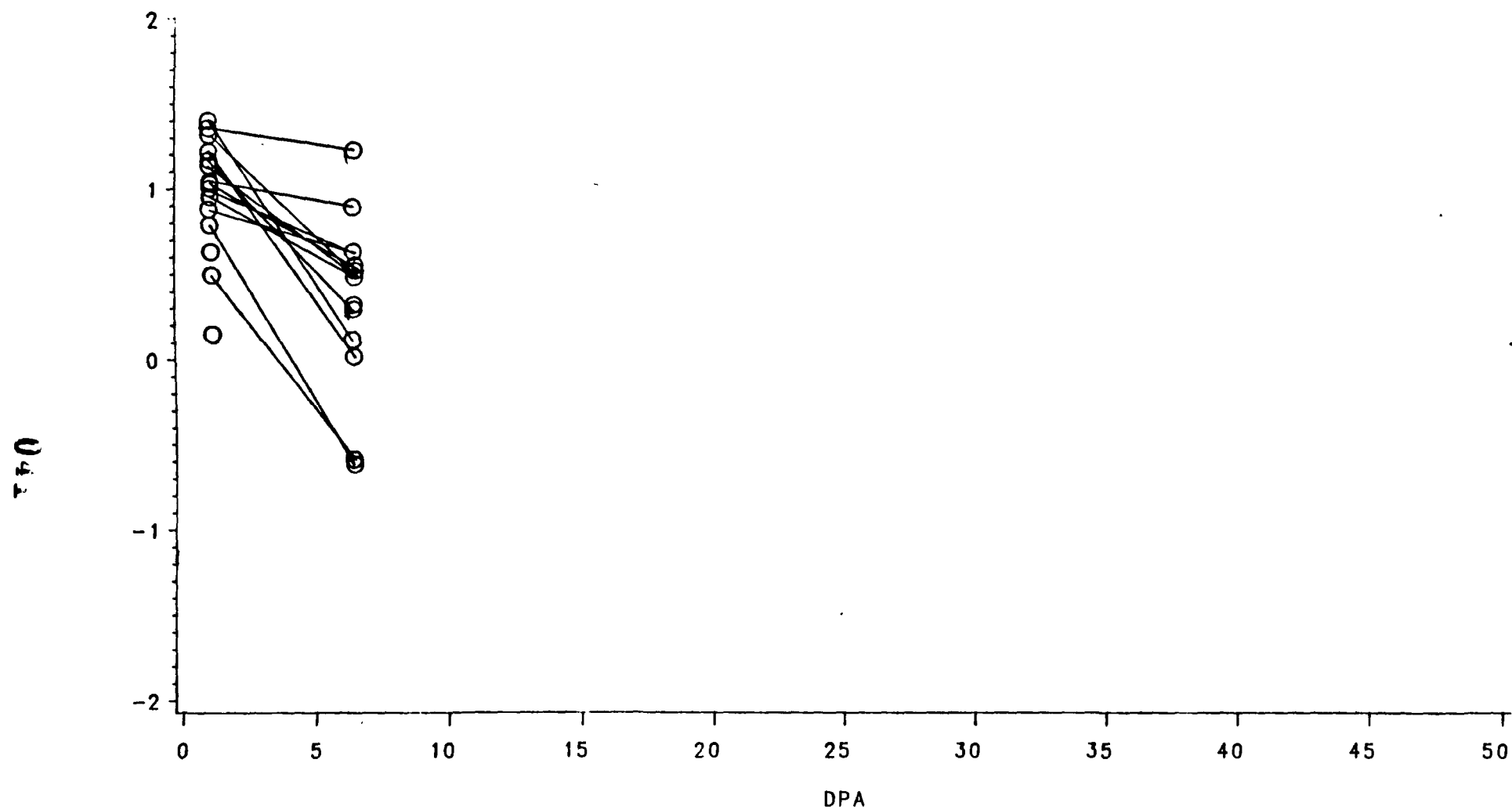
Figure 9e. Plot of residue hazard (common logarithm of % dAChE) as a function
of time (days post-application, DPA) for Ethyl Parathion as
reported from Washington.
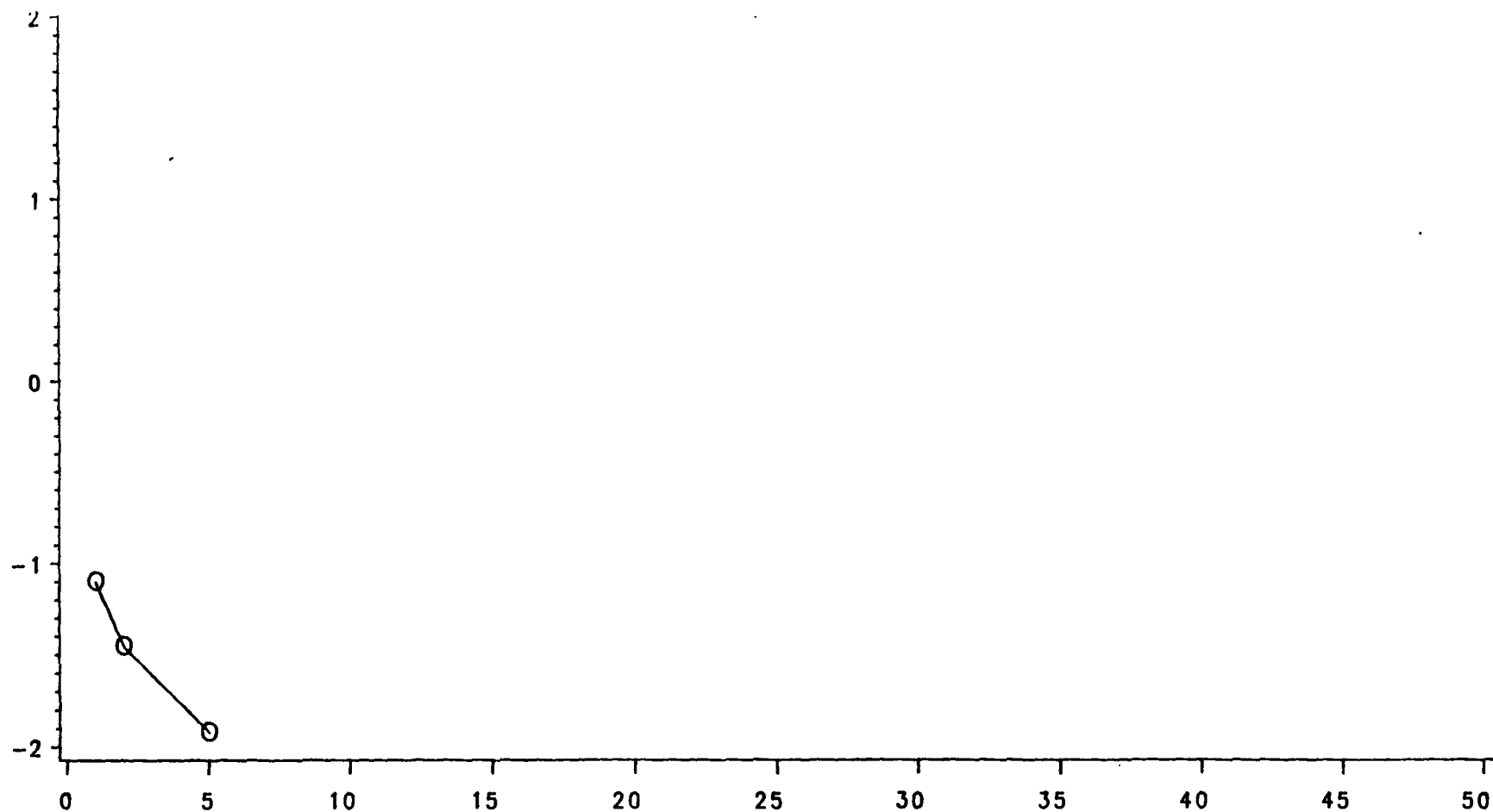
Figure 10. Plot of residue hazard (common logarithm of % dAChE) as a function
of time (days post-application, DPA) for Malathion.
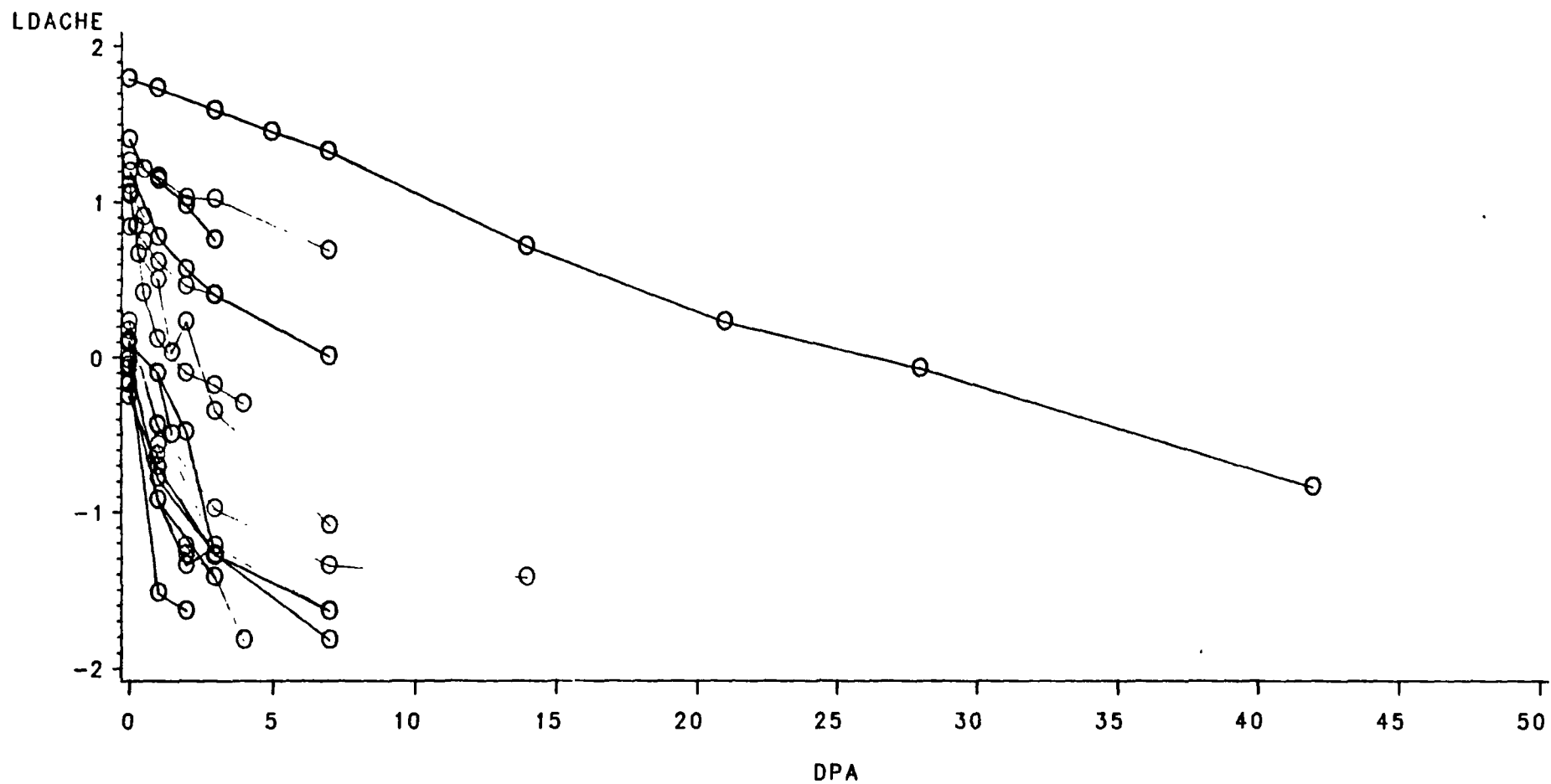
Figure 11. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Methyl Parathion.
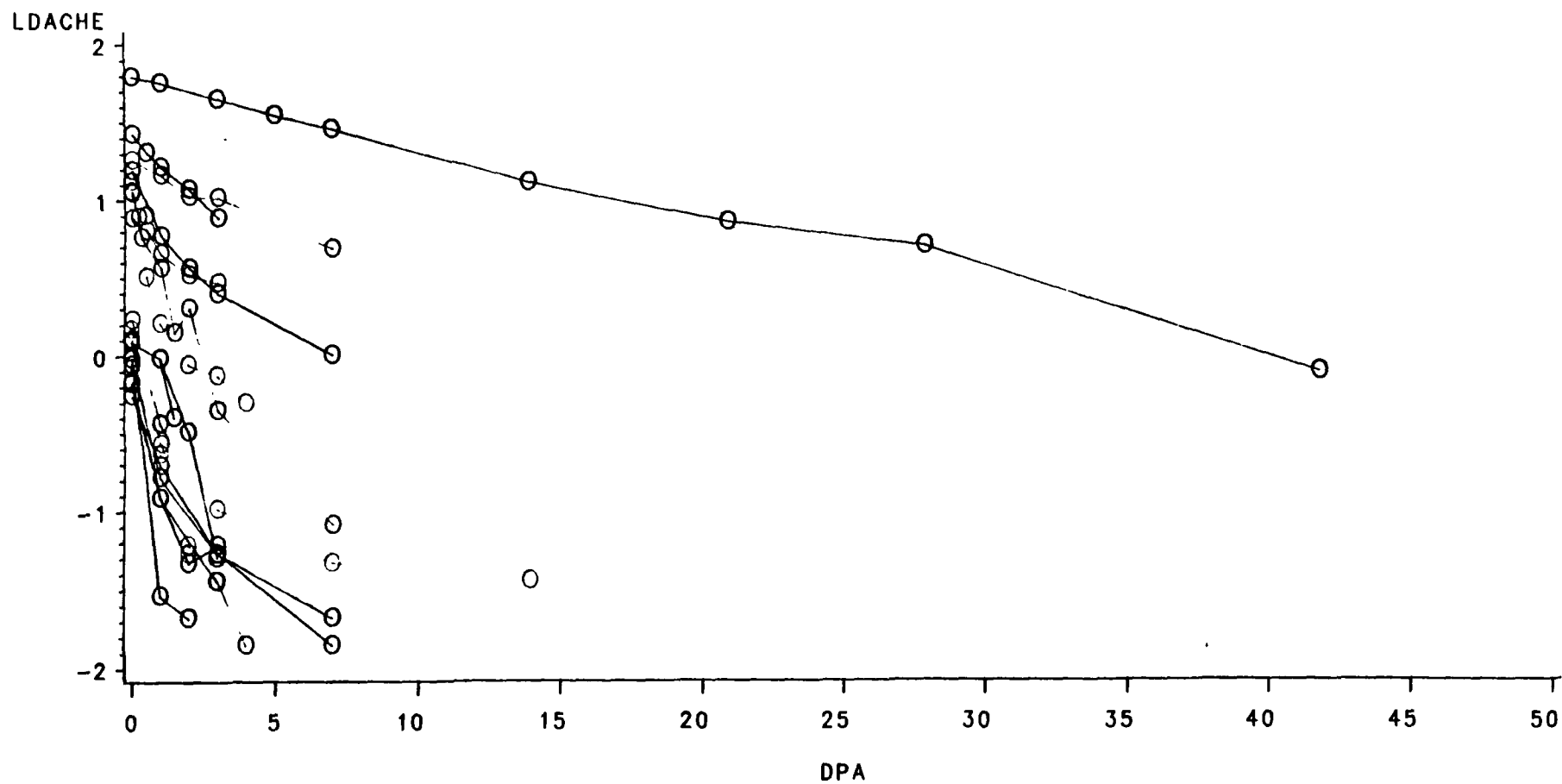
Figure 11a. Plot of residue hazard (common logarithm of % dAChE) as a function
of time (days post-application, DPA) for Methyl Parathion with an
assumed LD50 for its oxon 1/10th that of its parent.
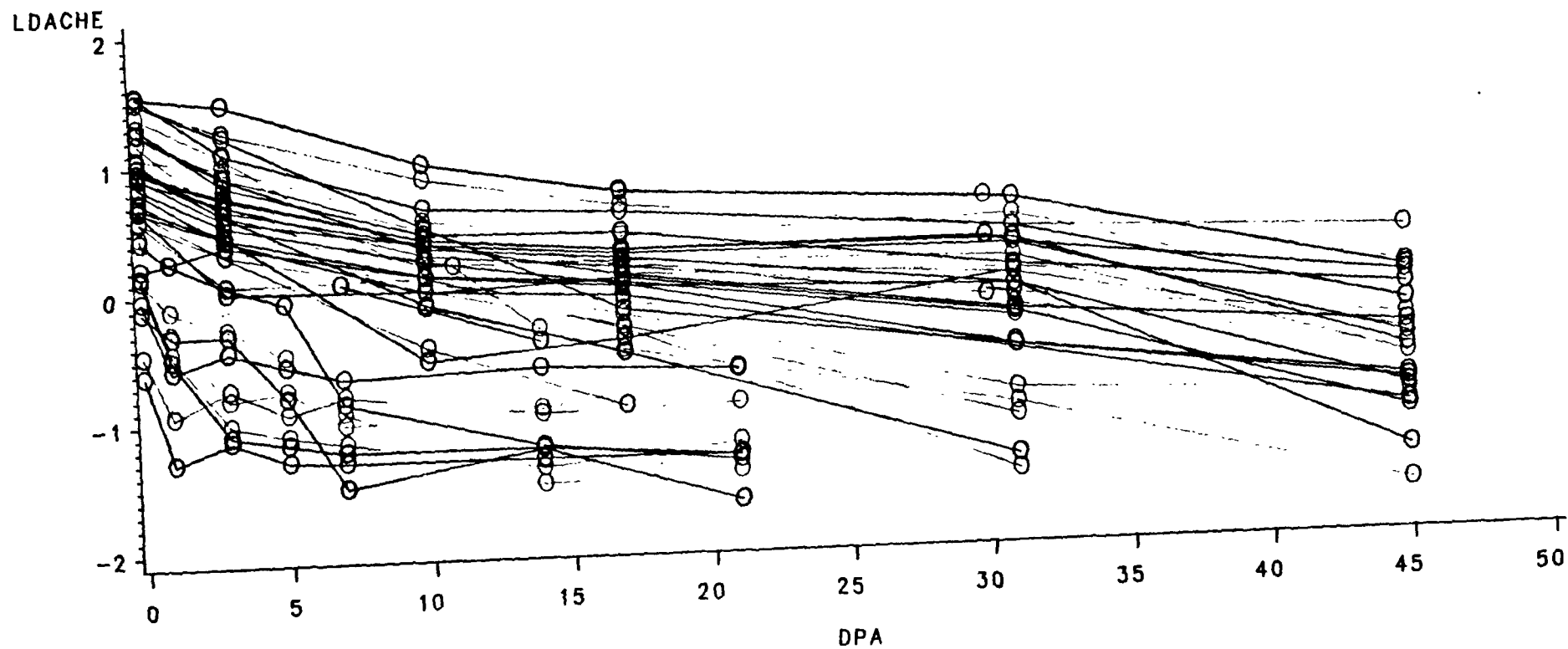
Figure 12. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Methidathion.
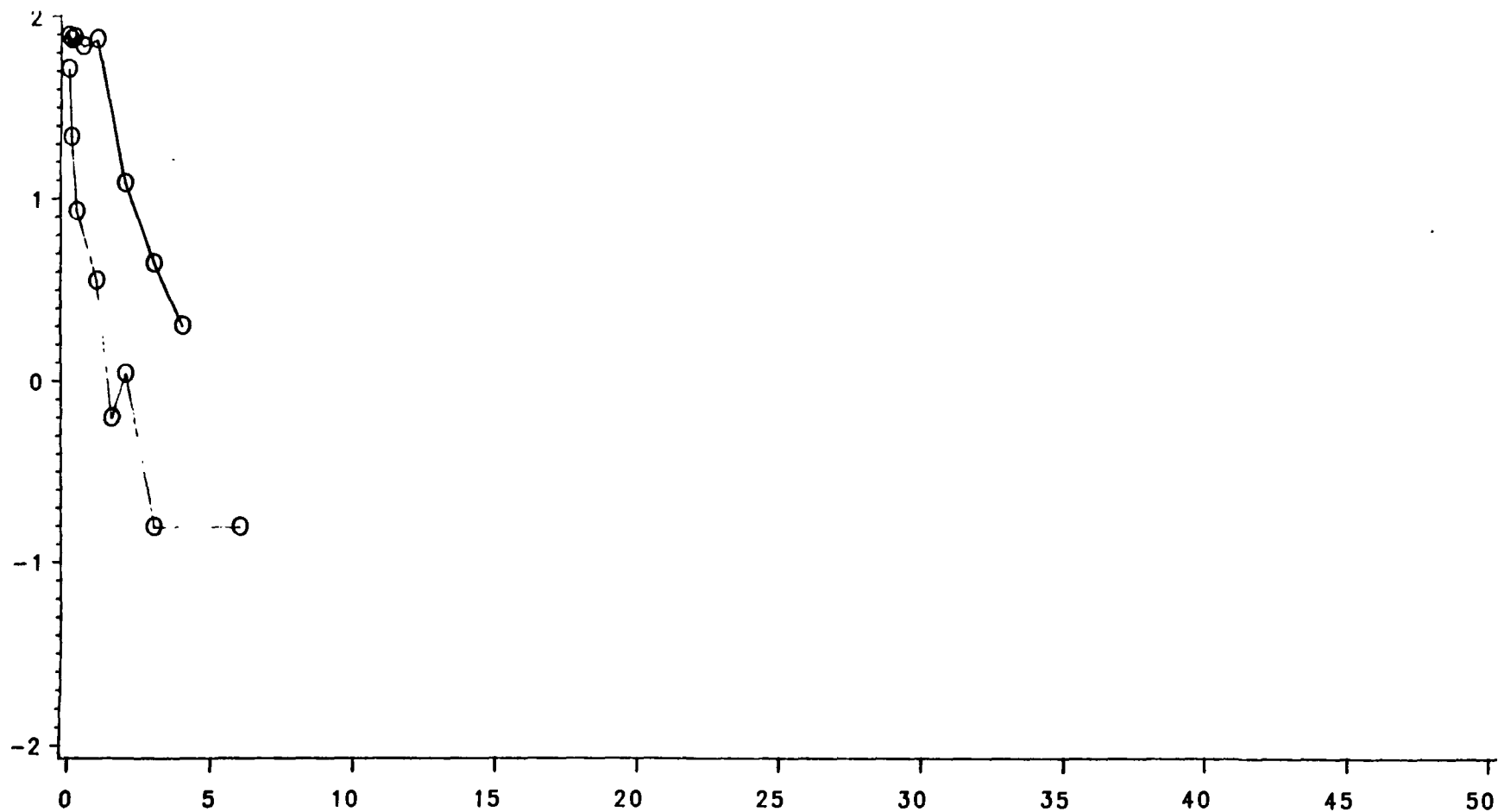
Figure 13. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Mevinphos (Phosdrin).
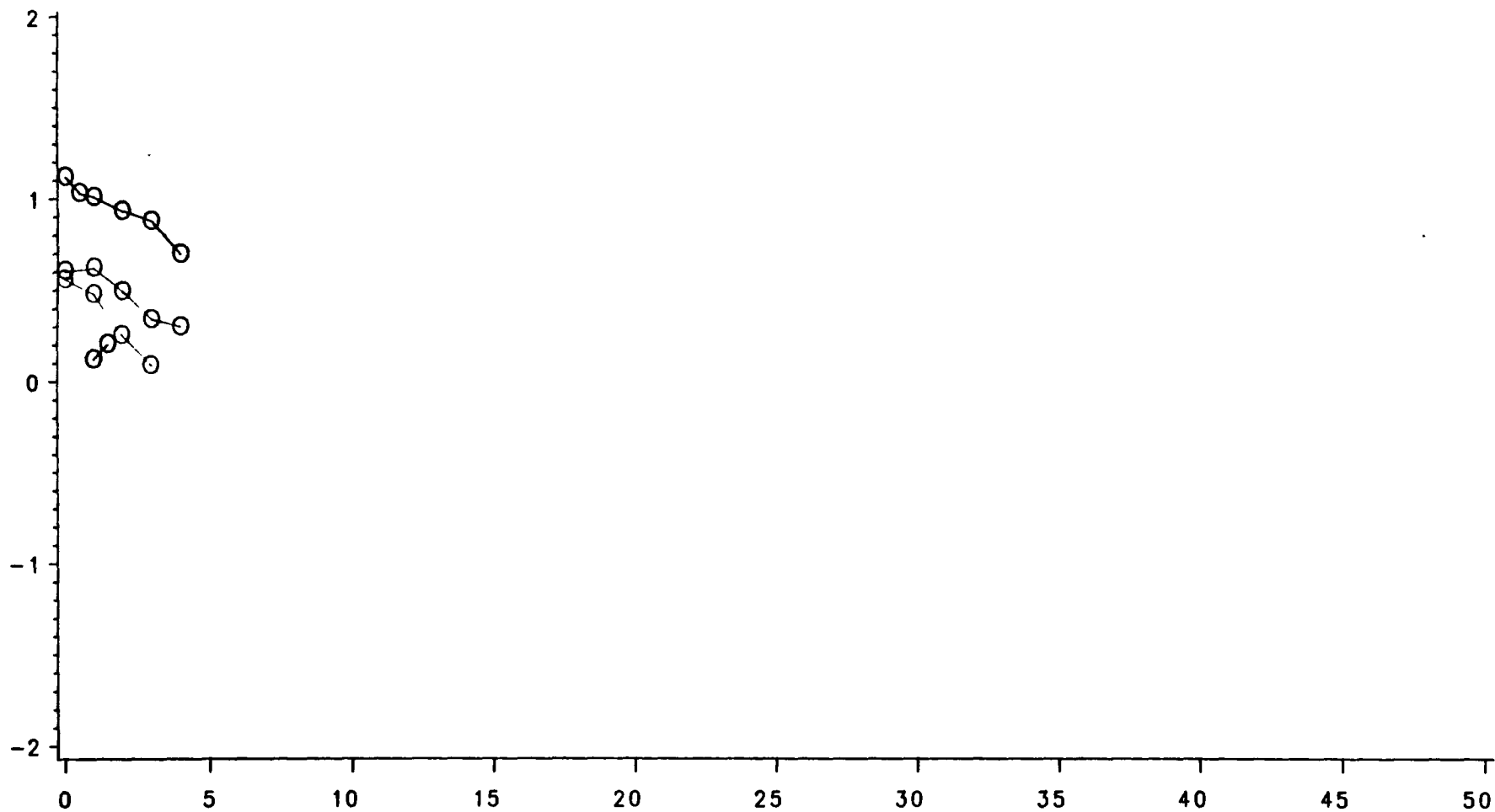
Figure 14. Plot of residue hazard (common logarithm of % dAChE) as a function
of time (days post-application, DPA) for Monocrotophos (Azodrin).
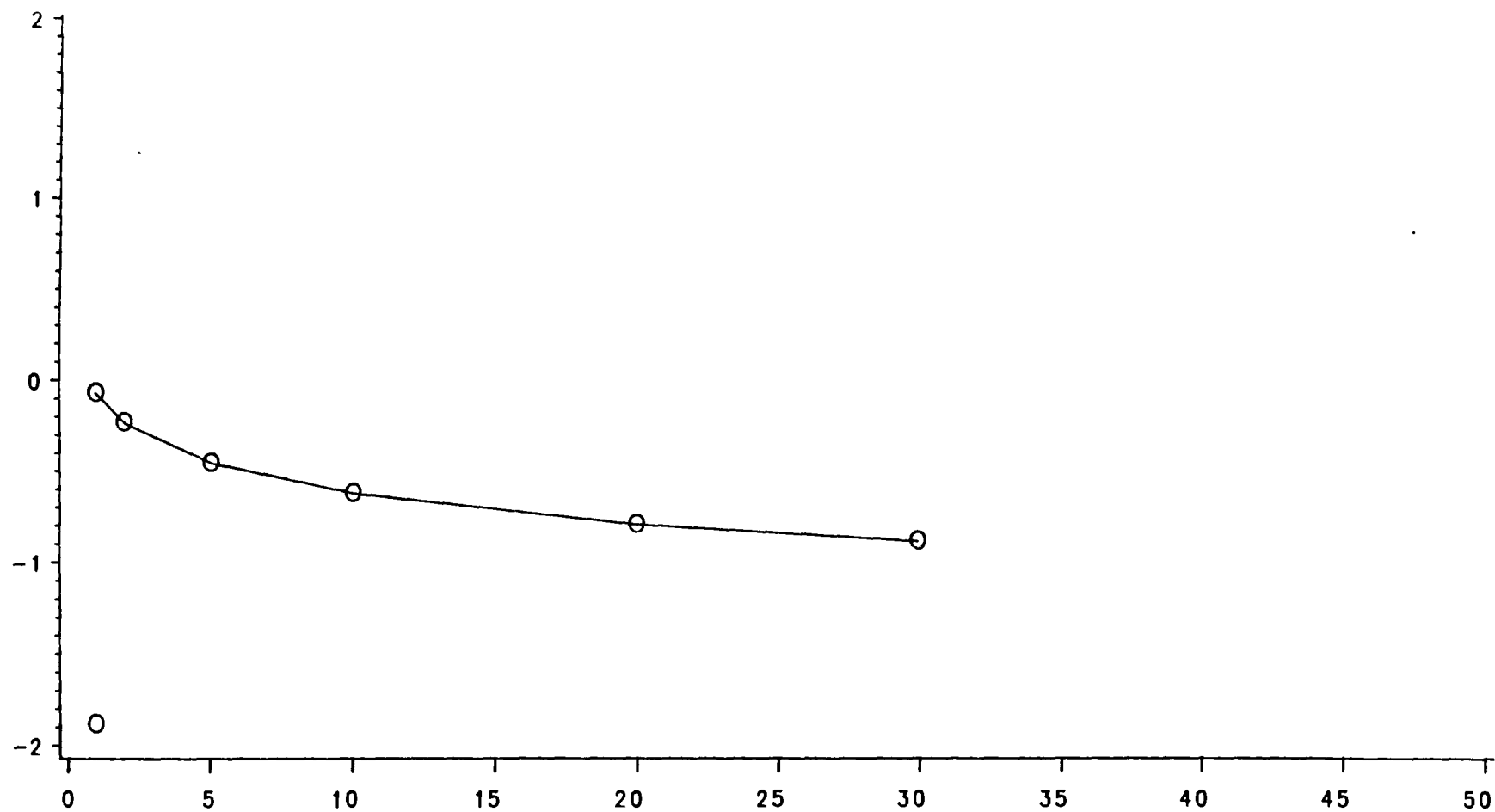
Figure 15. Plot of residue hazard (common logarithm of % dAChF) as a function
of time (days post-application, DPA) for Oxydemeton (Metasystox-R).
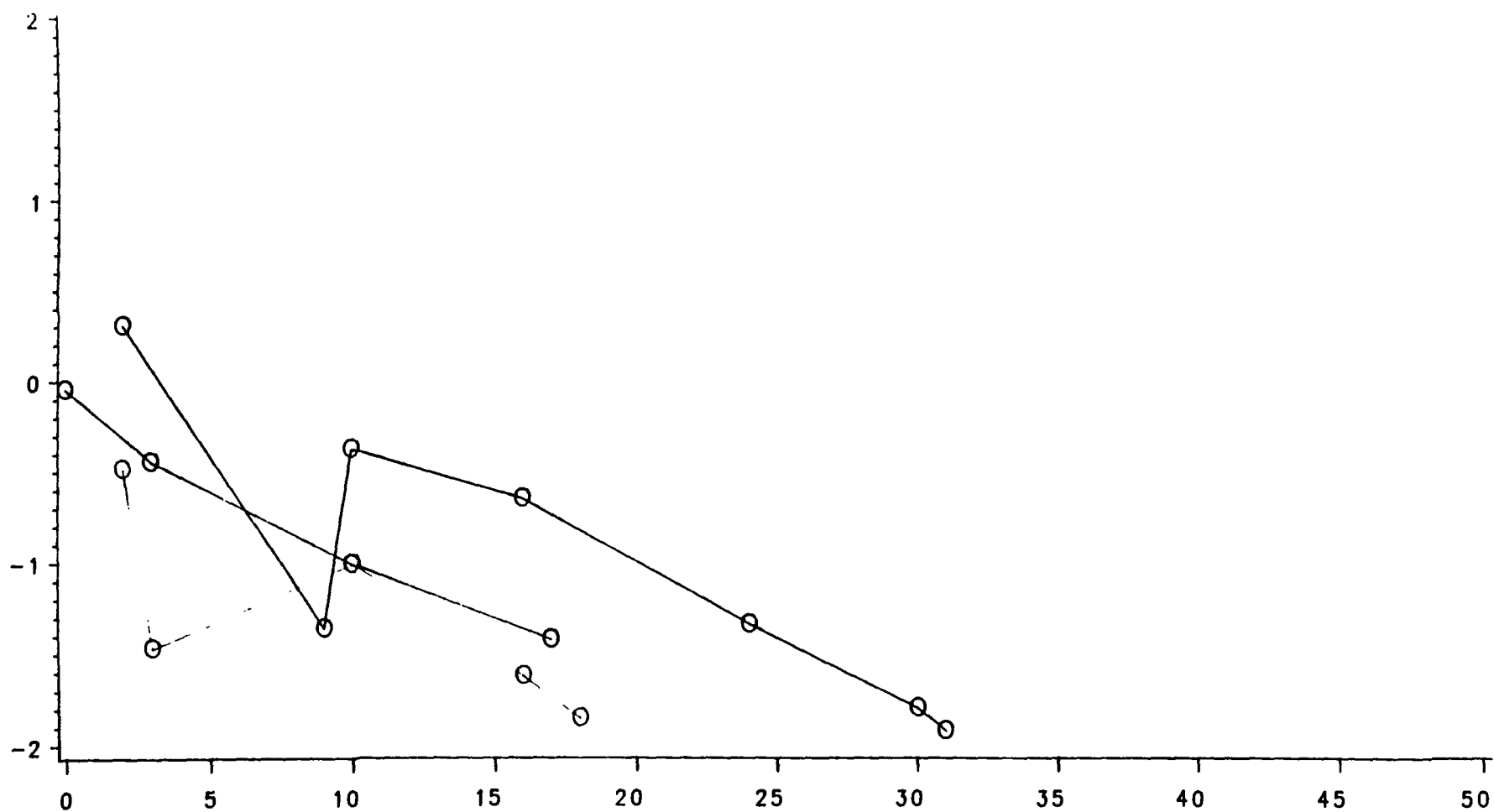
Figure 16. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Phenthoate.
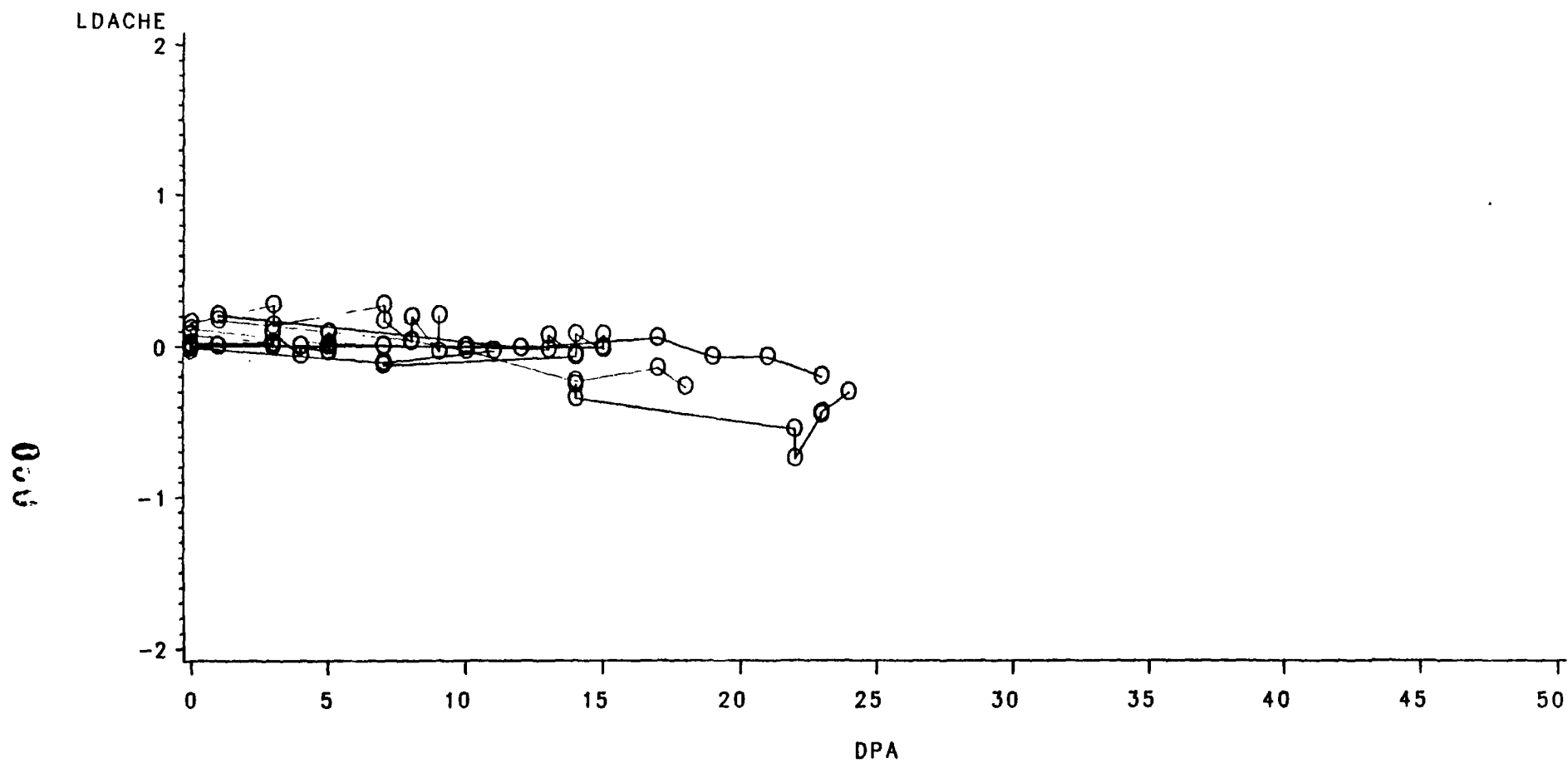
Figure 17. Plot of residue hazard (common logarithm of 7 dAChE) as a function of time (days post-application, DPA) for Phosalone (Zolone).

Figure 18. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Phosphamidon (Dimecron).
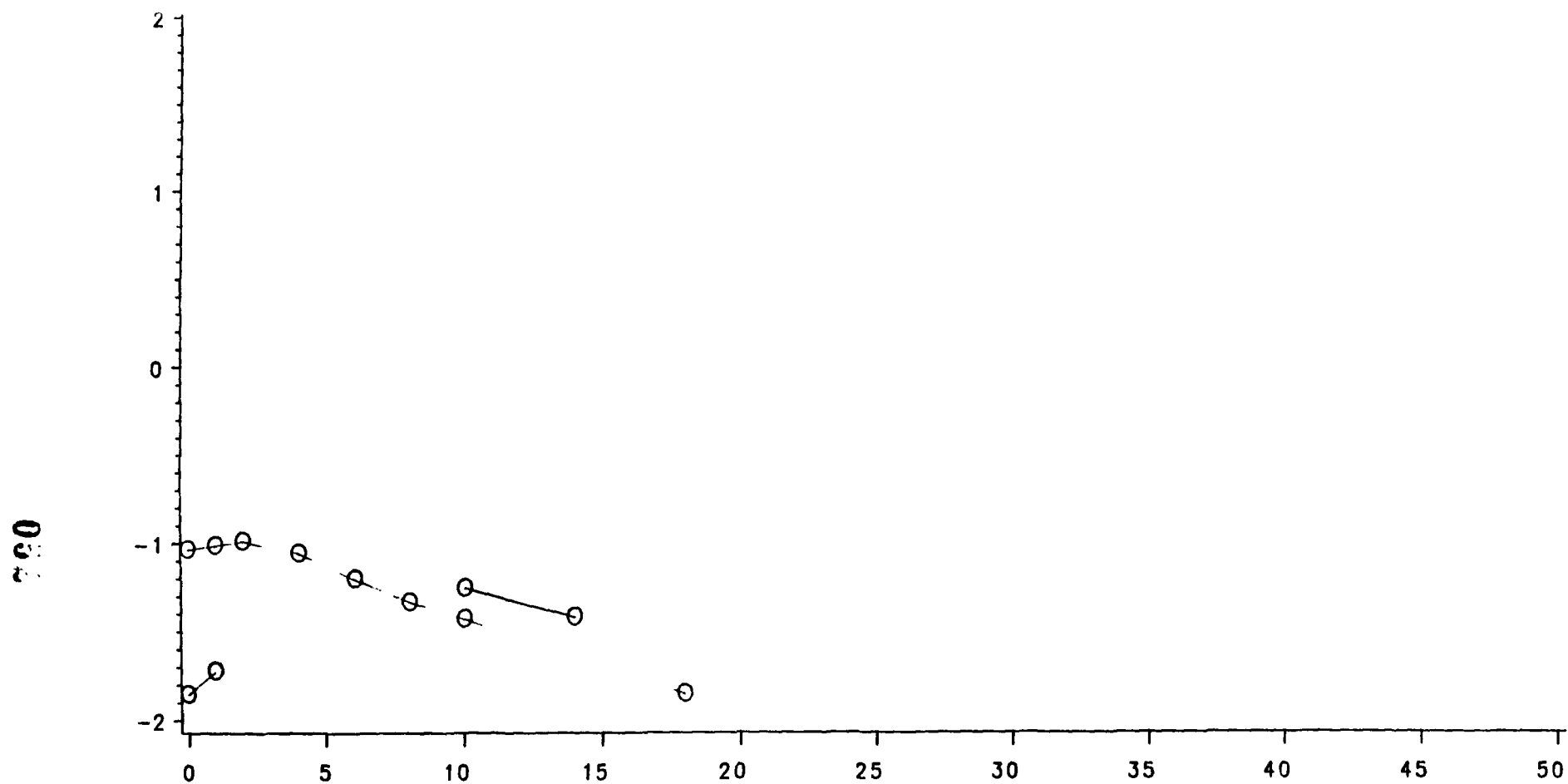
Figure 10. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Phosmet (Imidan).
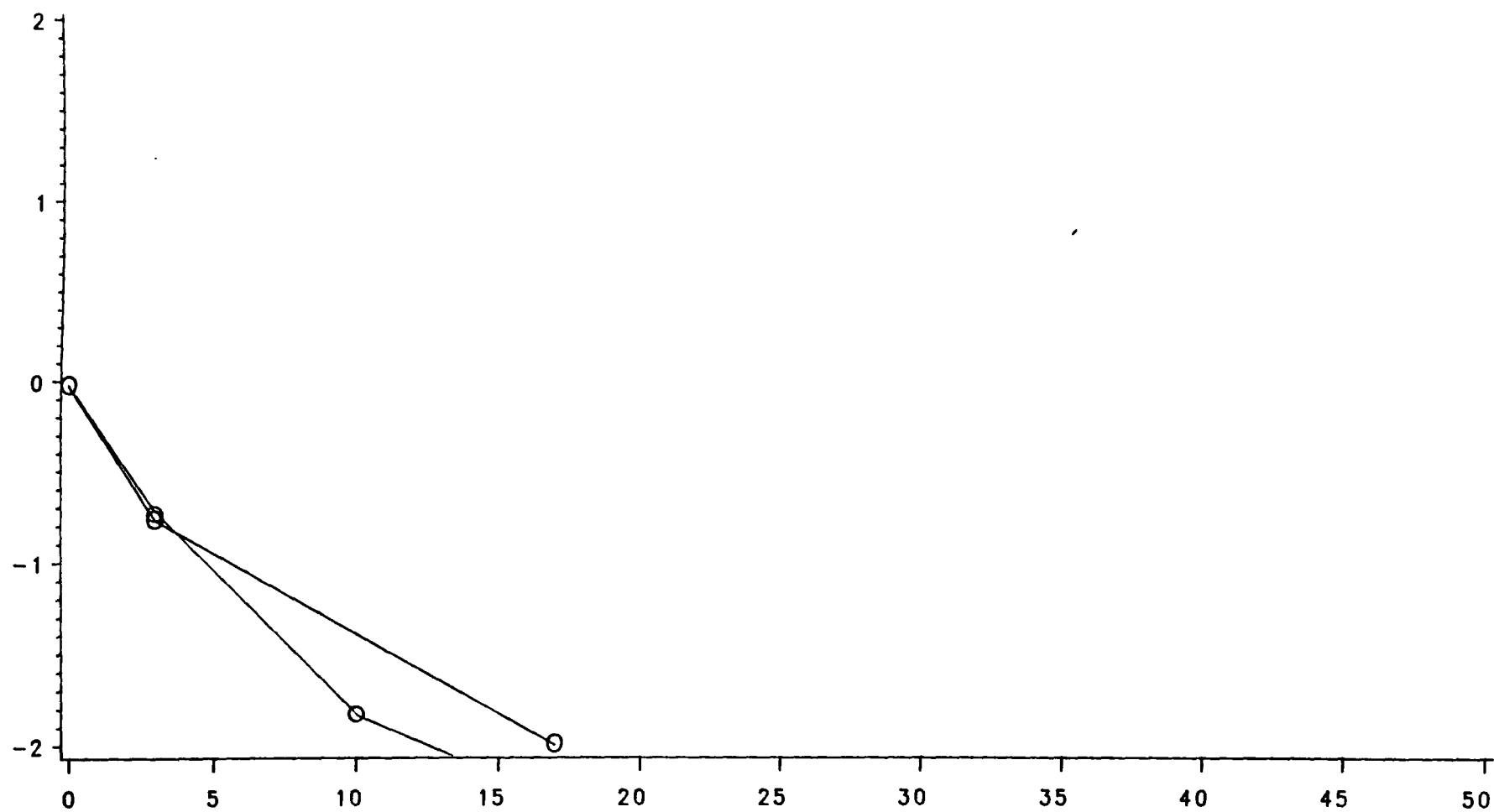
Figure 20. Plot of residue hazard (common logarithm of % dAChE) as a function of time (days post-application, DPA) for Trichlorfon.
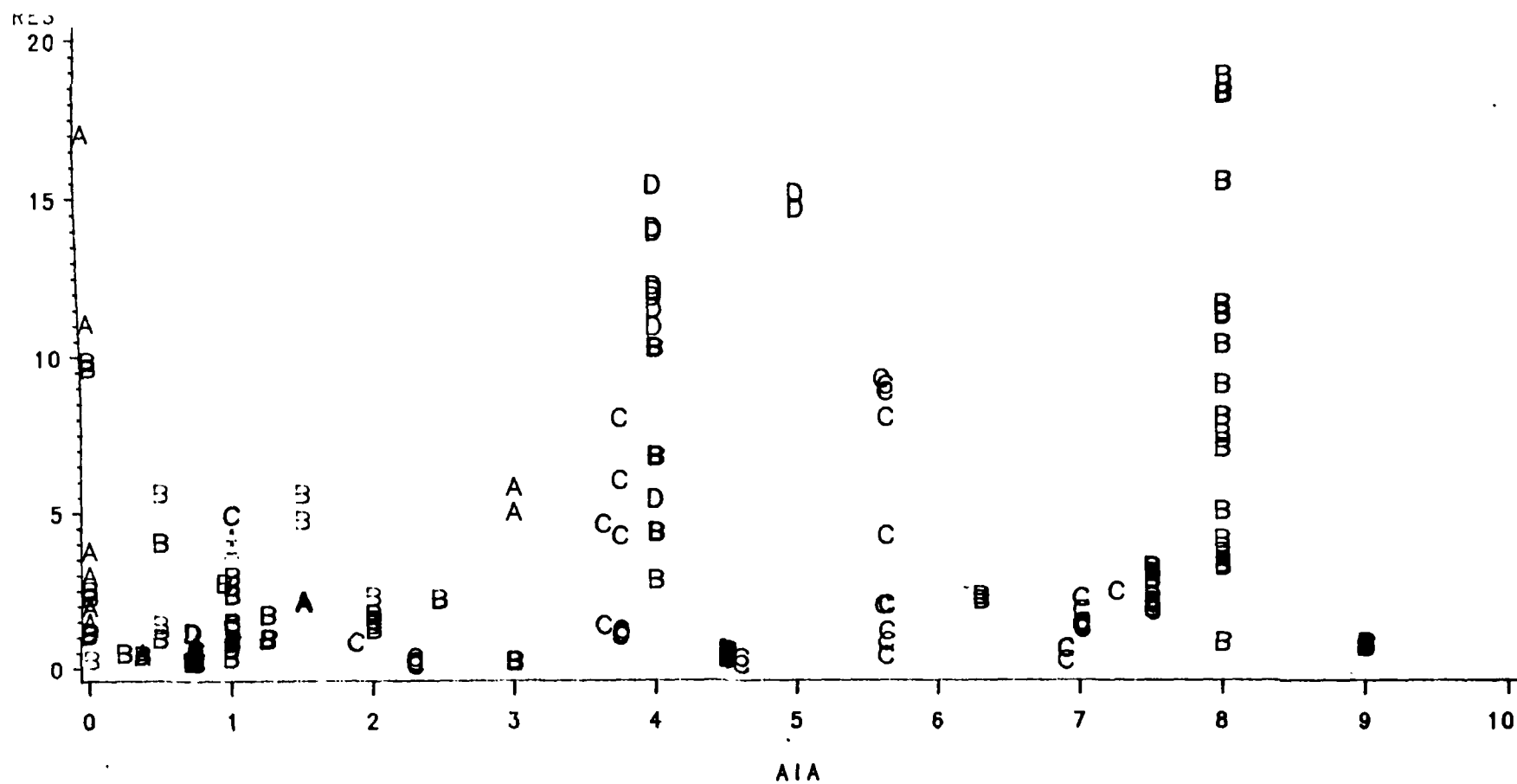
Figure 21. Plot of initial residue deposition (ug/cm^2) as a function of application rate (lb AIA) for all chemicals and all crops.
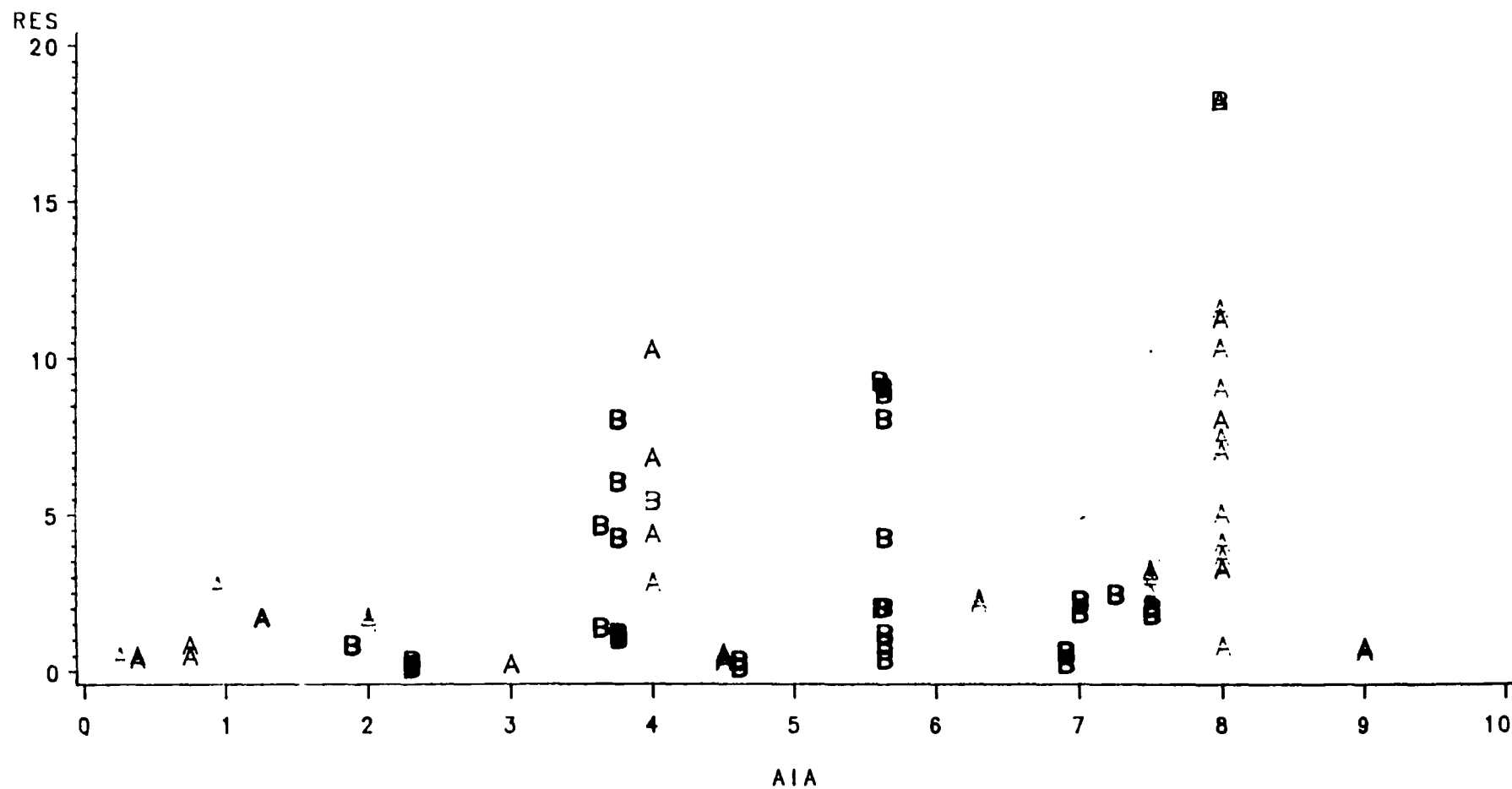
Figure 22. Plot of initial residue deposition (ug/cm^2) as a function of application rate (lb AIA) for all chemicals on citrus.
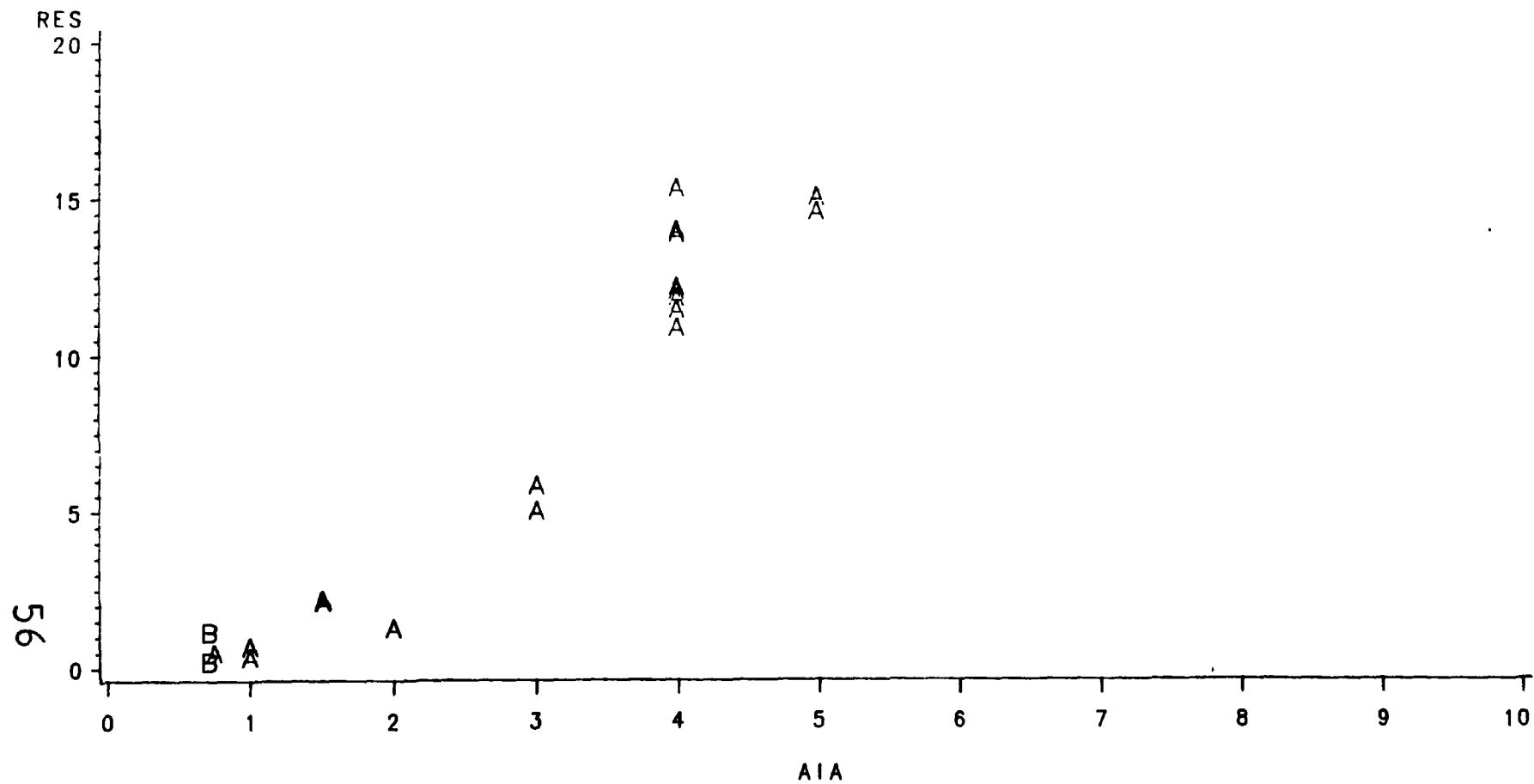
Figure 23. Plot of initial residue deposition (ug/cm^2) as a function of application rate (1b AIA) for all chemicals on peaches.
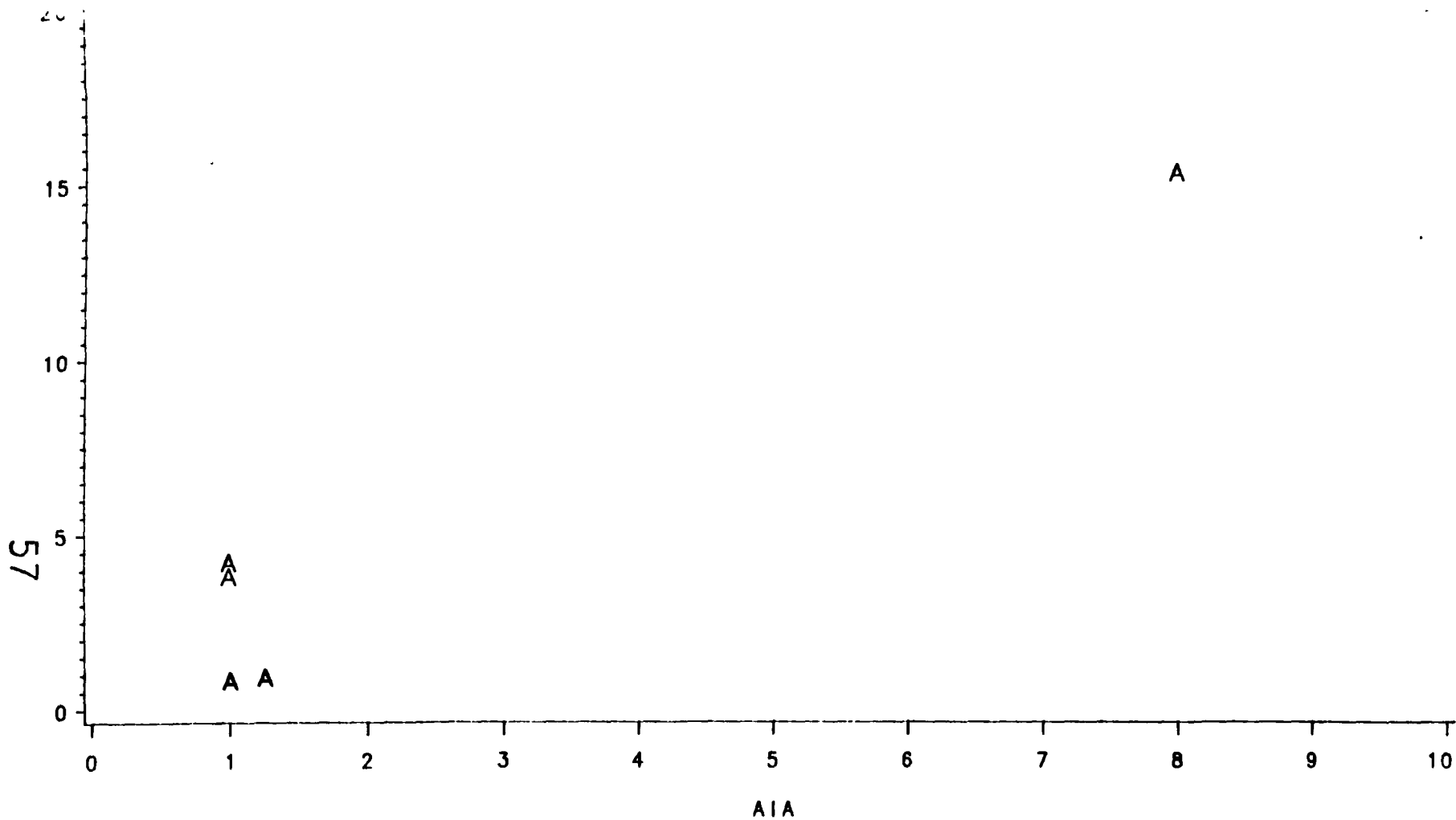
Figure 24. Plot of initial residue deposition (ug/cm^2) as a function
of application rate (lb AIA) for all chemicals on grapes.
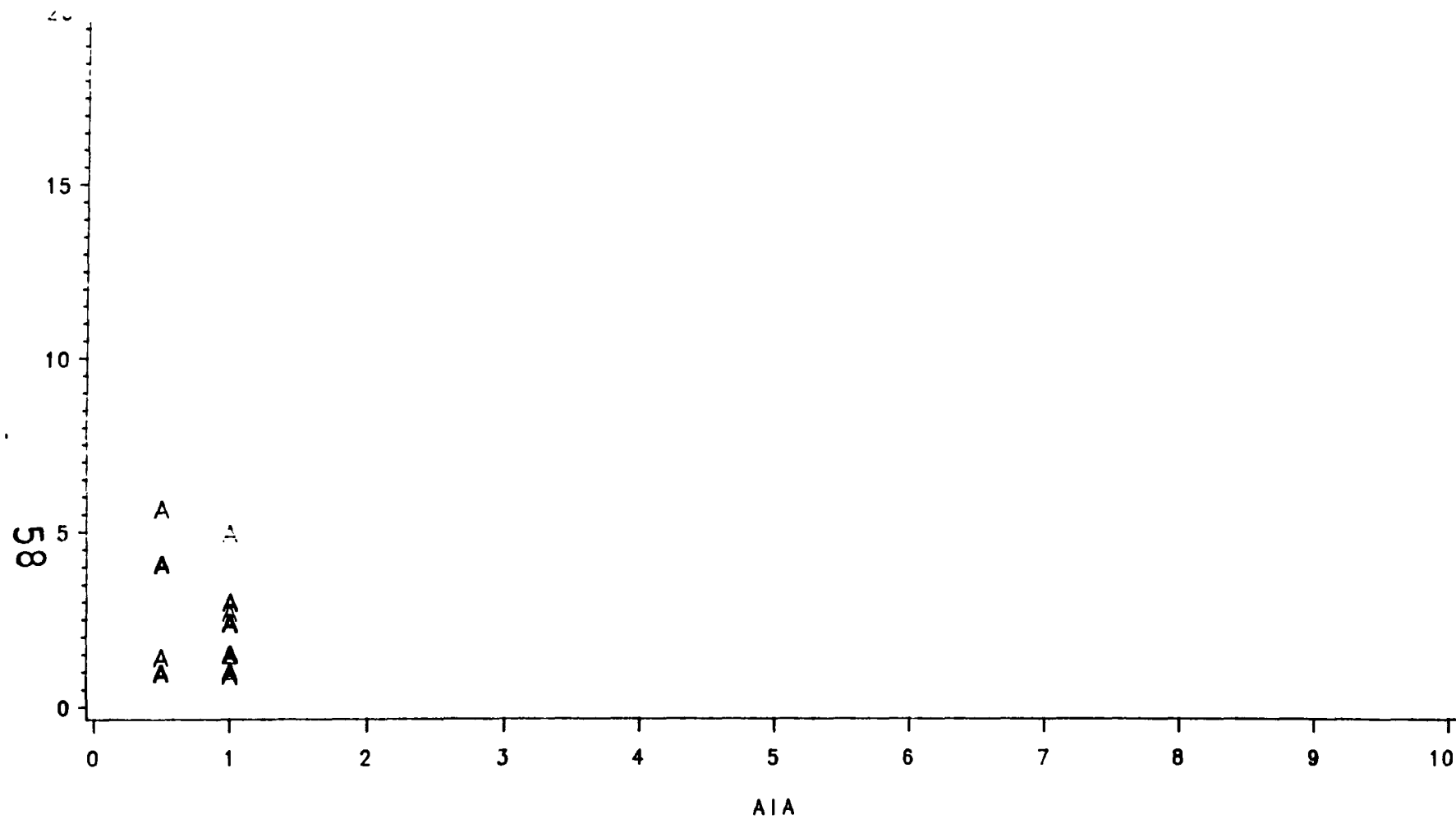
Figure 25. Plot of initial residue deposition (ug/cm^2) as a function of application rate (lb AIA) for all chemicals on cotton.
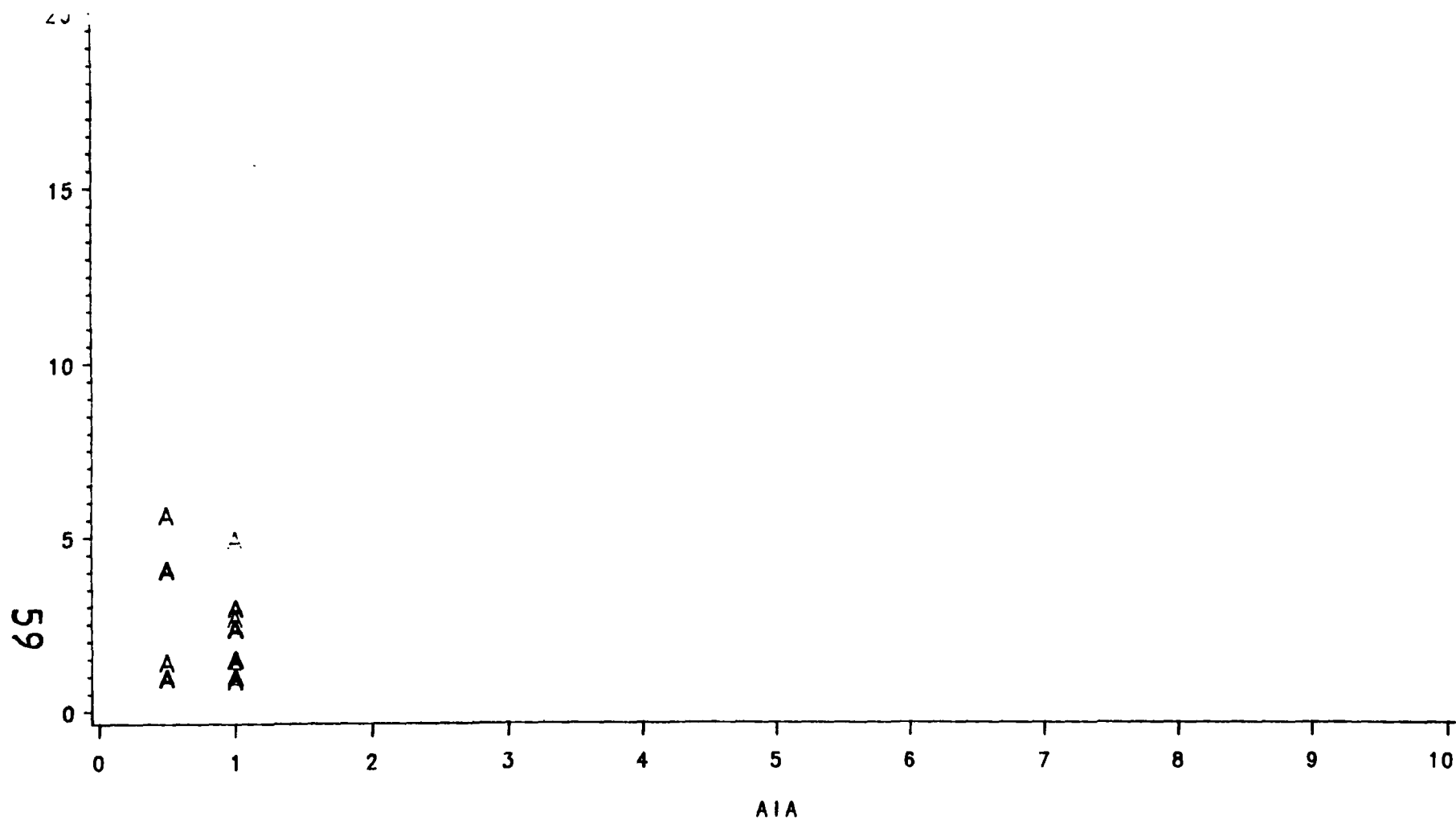
Figure 25. Plot of initial residue deposition (ug/cm^2) as a function of application rate (1b AIA) for all chemicals on cotton.

APPENDIX A: Standardized Data Sheet for
           recording pertinent data from
           published report.

Space for

citation information.

LOCATION OF STUDY_____

DATE OF STUDY_____

TYPE OF CROP(s)_____

<u>CHEMICAL(s) APPLIED</u> (Check one)

Single Chemical Applied_____

Multiple Chemicals Applied_____

Multiple Chemicals Applied Separately_____

Multiple Applications of Chemical(s)_____

<u>CHEMICAL(s) APPLIED</u>

1._____ 2._____ 3._____

<u>FORMULATION</u> (Fill in the blank)

__ WP __ EC __ LF ¦ __ WP __ EC __ LF ¦ __ WP __ EC __ LF

__ G   Other _____ ¦ __ G   Other _____ ¦ __ G   Other _____

<u>APPLICATION RATE</u> (Active Ingredient per ......)

1._____ Total/tree 2._____ Total/tree 3._____ Total/tree

     _____ Kg/Ha   _____ Kg/Ha   _____ Kg/Ha

     _____ lbs/acre   _____ lbs/acre   _____ lbs/acre

<u>FORMULATION ADDITIVES OR COMMENTS</u>

1._____ 2._____ 3. _____

  _____   _____   _____

<u>MIXTURE</u> (gallons per acre) _____

<u>SAMPLING PROCEDURE</u> (check one)

   Dislodgeable residue_____   Other residue_____   Units _____

   Leaf Punch _____   Whole Leaf_____   Other _____

   Leaf Area Calculated as: (check) One Side _____   Two Sides _____

<u>EXTRACTION SOLVENT</u> Aqueous_____

   Organic (circle one) Hex   Cloro   Tol   MeCl   Benz   Other
                        (1)   (2)   (3)   (4)   (5)   (6)

<u>WEATHER</u>	<u>Data Present</u>	(<u>Amount, if given</u>)	Residue data presented
Rainfall	_____	_____	in Tables _____
Temperature	_____	_____	Graph _____
Humidity	_____	_____	Equation _____
Ozone	_____	_____	Leaf Dust Measured:
Other	_____	_____	YES / NO

Form completed by _____ Date _____

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APPENDIX B: Bibliography for Residue Decay-Response Database.
Not every one of the following citations either
contained residue data or was included within the
data base summarized in Appendix H.

1. Awasthi,M.D., et al:
   Dissapation of metasystox and monocrotophos in or on
   soybean crop residues.
   Indian J Agric Sci. 48(4): 245-247, 1978.

2. Berck,B., Iwata,Y., Gunther,F.A.:
   Worker environment research: rapid field method for
   estimation of organophosphorus insecticide residues on citrus
   foliage and in grove soil.
   J. Agric. Food. Chem. 29(2): 209-216, 1981.

3. Bowman, A.U., Oller,W.L., Kendall,D.C., Gosnell,A.B., Oliver,K.H.:
   Determination of foliar residues for safe reentry of agricultural
   workers in the field.
   Arch.Environ.Contam.Toxicol. 11(4): 447-455, 1982.

4. Charmillot, P.J. and Blaser, C.:
   Study of the persistance of acephate, phosmet and deltamethrin used
   for the control of the summer fruit tortrix Adoxpphyes orana F.v.R.
   CA/099/065875C
   Rev Suisse Vitic, Aboric. Hortic. 15(3): 195-201, 1983.

5. Chen,Z. and Yue,R.:
   Degradative dynamics of pesticides in tea leaves and the selective
   parameters of safe pesticide design.
   CA/099/138268U
   Zhonggo Nongye Kexue (Beijing). 1: 62-70, 1983.

6. Davis,J.:
   Potential Exposure to Dislogable Residues of Two Formulations
   of Methyl Parathion to Apple Trees.
   Bull Environ Contam & Tox. 27: 95-100 (1981).

7. Davis,J.E., Staiff,D.C., Butler,L.C., and Stevens,E.R.:
   Potential exposure to dislodgable residues after application of two
   formulations of methyl parathion to apple trees.
   NTIS/PB82-247537
   Govt Reports Announcements & Index (GRA&I), 23: 1982.

8. Dikshit,A.K. and Bhattacharjee,N.S.:
   Residues of carbofuran and malathion in or on soybean crop.
   Indian J Agric Sci. New Delhi, Indian Council of Agricultural
   Research. 50(5): 441-443, 1980.

9. Everhart,L.P. and Holt,R.F.:
   Potential benlate exposure during mixer/loader operations, crop
   harvest, and home use.
   J.Agric.Food.Chem. 30(2): 222-227, 1982.

10. Fitzpatrick,G.E. and Bogan,M.D.:
    Residue dynamics of acephate and methamidophos in urban dooryard
    citrus foliage. Pompano Beach Florida, August-September 1978.
    Pestic.Monit.J. 14(1): 3-6, 1980.

11. Gegenava,N.G., Klisenco,M.A., and Pis'mennaya,M.V.:
    Dynamics of carbophos and phosalone decomposition in grape leaves
    and grapes.
    CA/098/067078Y
    Khim. Sel'sk. Khoz. 12:45-47, 1982.

12. Gehrich, John L., John A. Burkart, Dennis Y. Takade, Eugene R. Turner,
    Stanley D. Allen. Final Report: Assessment of Leaf Surface Residues
    for Selected Organophosphorus Insecticides. University of Utah
    Research Institute, Salt Lake City, Utah (1976).

13. Gehrich,J.L., Burkart,J.A., Takade,D.Y., Turner,E.R., and Allen,S.D:
    Assessment of leaf surface residues for selected oganophosphorus
    insecticides. NTIS/PB82-230046
    Govt Reports Announcements & Index (GRA&I), 21: 1982.

14. Habeebullah,B. and Balasubramanian,M.:
    Dissapation and persistance of certain insecticides on/in cowpea pods
    (var. C. 152)
    CA/097/067761V
    Madras Agric. J. 68(8): 517-526, 1981.

15. Hafner,M. and Michel,H.G.:
    Investigations on the drift of sulfur and its residues in plants
    (red clover and apple leaves from the variety "golden delicious").
    Nachrichtenbl Dtsch Pflanzenschutzd. 27(2): 24-27. [Eng. Sum.] 1975.

16. Iwata, Yutaka, Margarete Dusch, Glenn Carman, and Francis Gunther:
    Worker Environment Research* Residues from Carbaryl,
    Chlorobensilate, Dimethoate, and Trichlorfon Applied to Citrus Trees.
    J. Agricultural and Food Chemistry, 27:1141-1145 (1979).

17. Iwata, Yutaka, Glenn E. Carman, and Francis A. Gunther:
    Worker Environment Research: Methidathion Applied to Orange Trees.
    J.Agricultural Food Chemistry 27:119-129 (1979).

18. Iwata, Yutaka:
    Minimizing Occupational Exposure to Pesticides: Reentry Field
    Data- a Recapitulation.
    Residue Reviews 75: 127-147 (1980).

19. Katiha,S.M. and Nath,A.:
    Persistance of oxydemeton methyl residues in cauliflower
    CA/099/135479C
    J Entom Res. 5(1): 47-9, 1981.

APPENDIX B: page 2 of 9

20. Keil, Julian E., C. Boyd Loadholt, Bob L. Brown, Samuel H. Sandifer, and Wayne R. Sitterly: Decay of Parathion and Endosulfan Residues on Field-Treated Tobacco, South Carolina-1971.
    Pesticides Monitoring Journal, 6:73-75 (1972).

21. Keil, J.E., C.B. Loadholt, S.H. Sandfer, W.R. Sitterly, and B.L. Brown: Decay of Parathion Residues on Field-Treated Tobacco South Carolina - 1972.
    Pesticides Monitoring Journal, 6:377 (1973).

22. Kido, H., J.B. Bailey, N.F. McCalley, W.E. Yates, and R.E. Cowden. The Effect of Overhead Sprinkler Irrigation on Methyl Parathion Residue on Grape Leaves.
    Bull. Environmental Contamination and Toxicology 14:209-213 (1975).

23. Kilgore, Wendell W., Ming-yu Li, Ronald L. Mull, Wray Winterlin, Nemat Borhani, Jess Draus, Peter Kurtz, Norman Akesson, and Wesley Yates:
    Human Physiological Effects of Organophosphorus Pesticides in a Normal Agricultural Field Labor Population, A Preliminary Report, II. Scientific Aspects. Food Protection and Toxicology Center, University of California, Davis.   56 pages (1977).

24. Knaak, J.B., K.T. Maddy, M.A. Gallo, D.T. Lillie, E.M. Craine, and W.F. Serat: Worker Reentry Study Involving Phosalone Application to Citrus Groves.
    J.Toxicology and Applied Pharmacology 46:363-374 (1978).

25. Knaak, J.B., S.A. Peoples, T.J. Jackson, A.S. Fredrickson, R. Enos, K.T. Maddy, J.B. Bailey, M.E. Dusch, F.A. Gunther, and W. L. Winterlin:
    Reentry Problems Involving the Use of Dialifor on Grapes in the San Joaquin Valley of California.
    Arch. Environmental Contamination and Toxicology 7:465-481 (1978).

26. Kraus,J.F. et al:
    Monitoring of grape harvesters for evidence of cholinesterase inhibition.
    J.Toxicol.Environ.Health. 7(1): 19-31, 1981.

27. Leffingwell, J. T., R.C. Spear, and David Jenkins.
    The Persistence of Ethion and Zolone Residues on Grape Foliage in the Central Valley of California.
    Arch. Environmental Contamination and Toxicology 3:49-53 (1975).

28. Lynch,V.P., Hudson,H.R., and Pianca,M.
    Identification and determination of mecarbam and its major degradation products in water and crops.
    PESTAB/81/1797
    Pestic Sci. 12(1): 65-73 1981.

29. Maddy et al:
    CDFA Report #HS-181 (ACF 59-181)
    Worker Health and Safety Unit. A Study of Parathion and Paraoxon
    Residue in Citrus Groves Following Applicaton of Parathion at
    Various Dosage and Dilution Rates (Report #HS-181). California
    Department of Food and Agriculture, Sacramento, CA (ca 1975).

30. Maddy, Keith T., and Clifford Smith:
    A Study of the Decay Rates of Ethyl-Metyl Parathion and Endosulfan
    Applied as a Foliar Spray to a Tomato Field in the Sacramento
    Valley of California. Report #HS-293.
    Worker Health and Safety Unit, California Department of Food and
    Agriculture, Sacramento, California.

31. Maddy, Keith T., G. Sprock, A. Scott Fredrickson, and T. Jackson.
    Parathion Residue on Orange Tree Foliage in Riverside County,
    California, May-June, 1975. Report #318.
    Worker Health and Safety Unit, California Department of Food and
    Agriculture, Sacramento, California (ca 1976).

32. Maddy, Keith T., Susan Edmiston, Charles Kahn, Lilia Rivera, and
    Terry Jackson. A Study of Parathion on the Foliage of Peach Trees in
    Stanislaus County, California, June-July, 1977. Report # HS-395.
    Worker Heath and Safety Unit, California Department of Food and
    Agriculture, Sacramento, California (ca 1977).

33. Misra,S.S., Verma,S., Handa,S.K., and Lal,R.:
    BHC and parathion residues on crop of yellow-sarson (brassica).
    Indian J of Agric Sci. 41(3): 276-279, 1971.

34. Nigg, H.N., J.C. Allen, R.F. Brooks, G.J. Edwards, N.P. Thompson,
    Roy W. King, and A.H. Blagg. Dislodgeable Residues of Ethion in
    Florida Citrus and Relationships to Weather Variables.
    Arch. Environ. Contam. and Toxicology   :257-267 (1977).

35. Nigg, H.N., J.C. Allen, R.W. King, N.P. Thompson, G.J. Edwards,
    and R.F. Brooks: Dislodgeable Residues of Parathion and
    Carbophenothion in Florida Citrus: A Weather Model.
    Bull. Environmental Contamination and Toxicology 19:578-588 (1978).

36. Nigg, Herbert N:
    Comparison of Pesticide and Particulate Recoveries with the Vacuum
    and Dislodgeable Surface Pesticide Residue Techniques.
    Arch. Environmental Contamination Toxicology 8:369-381 (1979).

37. Nigg,H.N., Reinert,J.A., Stamper,J.H., and Fitzpatrick,G.E.:
    Dissapearance of acephate, methamidophos, and malathion from citrus
    foliage.   PESTAB/81/1555
    Bull Environ Contam Toxicol 26(1): 267-272, 1981.

38. Nigg, H.N. and J. H. Stamper:
    Comparative Disappearance of Dioxathion, Malathion,
    Oxydemetonmethyl and Dialifor from Florida Citrus leaf and Fruit
    Surfaces.
    Arch. Environmental Contamination Toxicology 10(4):497-504 (1981).

39. Nigg, Herbert N., Leo G. Albrigo, Harold E. Nordby, and James H. Stamper: A Method for Estimating Leaf Compartmentalization of Pesticides in Citrus.
J. Agricultural and Food Chemistry 29:750-756 (1981).

40. Ott,D.E. and Gunther,F.A.:
Colorimetric method for field-screening above-tolerance parathion residues on and in citrus fruits.
J.Assoc.Off.Anal.Chem. 65(5): 1106-1111, 1982.

41. Ott,D.E. and Gunther,F.A.:
Field screening method for above-tolerance residue of dithiocarbamate fungicides.
J.Assoc.Off.Anal.Chem. 65(4): 909-912, 1982.

42. Petrova,T.M. and Novozhilov,K.V.:
Behavior of insecticides in the soil-plant system.
CA/095/198991B
Migr. Zagryaz. Veshchestv Pochvakh Sopredel'nykh Sredakh, Tr. Vses. Soveshch., 2: 136-43, 1980.

43. Pokharker,D.S. and Dethe,M.D.:
Gas-liquid chromatographic studies on residues of endosulfan on chilli fruits.
J.Environ.Sci.Health [B]. 16(4): 439-451, 1981.

44. Pokharker,D.S. and Dethe,M.D.:
Studies on the residues of phosolone on chilli by GLC after multiband plate cleanup.
J.Environ.Sci.Health [B]. 16(5): 629-636, 1981.

45. Popendorf, W. An Industrial Hygiene Investigation into the Occupational Hazards of Parathion Residues to Citrus Harvesters. [decay surveillance data collected in conjunction with Tulare II exposure studies], dissertation: Univ. of California, Berkeley, 1976.

46. Popendorf, W. and Leffingwell,J.T.:
Natural Variations in the Decay and Oxidation of Parathion.
J. Agric. Food Chem. 26:437-441 (1978)

47. Popendorf, W., J.T.Leffingwell, and R.C.Spear: unpublished ethion data collected in conjunction with studies reported in Natural Variations in the Decay and Oxidation of Parathion.
J. Agric.Food Chem. 26:437-441, 1978.

48. Popendorf, W. et al: unpublished data collected in conjuntion with exposure studies reported in
Harvestes Exposure to Zolone (Phosalone) Residues in Peach Orchards.
J.Occup. Med. 21:189-194, 1979.

49. Prasad,R. and Saxena,A.P.:
Dissapation of malathion residues on the foliage and ears of wheat (Tritcum aestivum 1.) crop.
Indian J of Entomol. 37(3): 234-238. Sept 1975 (pub. Aug. 1977).

342

50. Prasad, Rajendra-P. and Ramasubbaiah,K.:
    Persistence of phosphamidon in bhendi crop Insecticide.
    Pesticides. Bombay: Colour Publications. 16(6): 25-26, 1982.

51. Pree,D.J., Butler,K.P., Kimball,E.R., and Stewart,D.K.R.:   343
    Persistence of foliar residues of dimethoate and azinphosmethyl
    and their toxicity to the apple maggot rhagoletis pomonella.
    J Econ Entomol. 69(4): 473-478, 1976.

52. Rajput,G.B., Khaire,J.T., and Dethe,M.D.:
    Influence of dimethoate and endosulfan sprays on level of residues
    in/on brinjal fruits.
    CA/100/019264U
    J. Maharashtra Agric Univ. 8(3): 289-290, 1983.

53. Ramasubbaiah,K. and Lal,R.:
    Studies of residues of phophamidon in okra crop insecticides.
    Indian J Entomol. 36(4): 344-351, 1974 (Pub. Aug 1976).

54. Ramasubbaiah,K. and Lal,R.:
    Studies on residues of phosphamidon in cowpea crop
    drosophilamelanogaster, test insect.
    Indian J of Entomol. 37(2): 179-184, 1975.

55. Ramasubbaiah,K. and Lal,R.:
    Residues of phosphamidon insecticide in cabbage crop.
    Indian J Entomol. [New Delhi] 40(2): 182-186, 1978.

56. Ramasubbaiah,K. and Lal,R.:
    Residues of phosphamidon insecticide in mustard crop.
    Indian J Entomol. [New Delhi] 40(3): 285-289, 1978.

57. Scheunert,I. et al:
    Fate of 14C-allylalcohol herbicide in soils and crop residues.
    J.Environ.Sci.Health [B]. 16(6): 719-742, 1981.

58. Sharma,P.B. and Chopra,S.L.:
    Persistance of malathion residues on the cauliflower crop.
    Punjab Agr Univ J Res. 7(2): 216-220, 1970.

59. Shetgar,S.S., Pawar,V.M., Puri,S.N., Raodeo,A.K. and Patil,V.K.:
    Residues and residual toxicity of monocroptophos in/on okra leaves.
    CA/100/019262S
    J. Maharashtra Agric Univ. 8(3): 260-262, 1983.

60. Shinde,V.K.R. and Yadava,C.P.S.:
    Effect of crop stage on phosphamidon residues dissapation from some
    vegetables Eggplants, chilis, peas.
    Pesticides. Bombay. Colour Publications. 15(1): 20-21, 1981.

61. Shpirt,M.B. et al:
    Establishment of differential "wating times" in treating fruit and
    vegetable crops with organophosphate pecticides.
    Vopr-Pitan. (1): 70-72, 1982.

62. Shpirt, M.B., Salpagarof,N.S., and Genis,V.I.:
    Predicting the waiting period for harvesting pesticide-treated
    agricultural crops.
    CA/099/018077J
    Zashch. Rast..(Moscow) 4: 19-20, 1983.

63. Singh,M. and Yadav,P.R.:
    Persistance of dimethoate and methyl-demeton on and on pea pod
    shells and their movement into pea grains.
    HEEP/83/09586
    Indian J Entomol. 43(3): 306-311, 1981.

64. Singh,M. and Gupta,D.S.:   ·
    Dissapation of monocroptophos in/on chickpea crop.
    CA/097/176960E
    Indian J Entomol. 43(4): 373-377, 1981

65. Smith,C.N. et al:
    The persistance and dissapearance by washoff and dryfall of
    metoxychlor from soybean foliage.--a prelimanary study.
    J.Environ.Sci.Health [B]. 16(6): 777-794, 1981.

66. Spear, R. C., T. H. Milby, J. T. Leffingwell and W. J. Popendorf.
    Some Findings on the Exposure and Response of Pickers in Parathion-
    Treated Orange Groves. Delivered at the Annual Meeting of The
    American Chemical Society, Los Angeles. April 3, 1974.

67. Spear, Robert C., William J. Popendorf, John T. Leffingwell, and
    David Jenkins. Parathion Residues on Citrus Foliage. Decay and
    Composition as Related to Worker Hazard. Journal of Agricultural
    and Food Chemistry 23:808-810 (1975).

68. Spear,R.C., Lee,Y.S., Leffingwell,J.T., and Jenkins,D.:
    Conversion of organophosphate insecticide parathion to paraoxon in
    toxic foliar residues: effect of dust level and ozone
    concentration.
    J. Agric Food Chem. 26(2): 434-436, 1978.

69. Spencer,W.F., Cliath,M.M., and Davis,K.R.:
    Persistance of parathion and its oxidation to paraoxon on the soil
    surface as related to worker reentry into treated crops.
    Bull Environ Contam Toxicol. 14(3): 265-272, 1975.

70. Staiff, D.C., S. W. Comer, and R. J. Foster.
    Residues of Parathion and Conversion Product on Apple and Peach
    Foliage Resulting from Repeated Spray Applications.
    Bull. Environmental Contamination and Toxicology 14:135-9 (1975).

71. Strankowski,K.J. and Stanley,C.W.:
    Determination of residues of Mesurol and its sulfoxide and sulfone
    in plant, animal and soil samples.
    HEEP/82/04059
    J Agric Food Chem. 29(5): 1034-1037. 1981.

344

345

72. Thompson, Neal P., Herbert N. Nigg, and Robert F. Brooks.
    Dislodgeable Residue of Supracide on Citrus Leaves.
    J. Agricultural and Food Chemistry 27:589-592 (1979).

73. Verma,S. and Dikshit,A.K.:
    Persistance of different insecticides against pea leaf-miner,
    Phytomyza atricornis Meige
    Indian J. Agric Sci. 52(1): 4-6, 1982.

74. Ware, G.W., Betty Estesen, and W. P. Cahill:
    Organophosphate Residues on Cotton in Arizona.
    Bull. Environmental Contamination and Toxicology 8:361-2 (1972).

75. Ware, G.W., Betty Estesen, and W. P. Cahill:
    Establishment of Reentry Intervals for Organophosphate-Treated
    Cotton   Fields Based on Human Data: I. Ethyl and Methyl
    Parathion.
    Arch. Environmental Contamination and Toxicology 1: 48-59 (1973).

76. Ware, G. W., Betty Estesen, and W. P. Cahill:
    Dislodgeable Leaf Residues of Insecticides on Cotton.
    Bull. Environmental Contamination and Toxicology 2:434-7 (1974).

77. Ware et al:
    Dislodgeable Leaf Residues of Insecticides on Cotton.
    Bull Env Contam & Tox. 11(5):   1974.

78. Ware, G.W., Betty Estesen, and W. P. Cahill.
    Establishment of Reentry Intervals for Organophosphate-Treated
    Cotton   Fields Based on Human Data: II. Azodrin, Ethyl and Methyl
    Parathion.
    Arch. Environmental Contamination and Toxicology 2:117-129 (1974).

79. Ware, G.W., D.P. Morgan, Betty Estesen, and W. P. Cahill.
    Establishment of Reentry Intervals for Organophosphate-Treated
    Cotton   Fields Based on Human Data: III. 12 to 72 Hours Post-
    Treatment   Exposure to Monocrotophos, Ethyl- and Metyl Parathion.
    Arch. Environmental Contamination and Toxicology 3: 289-306 (1975).

80. Westlake, W.E., F.A. Gunther, and G.E. Carman:
    Worker Environment Research: Dioxathion (Delnav) Residues On and In
    Orange Fruits and Leaves, in Dislodgeable Particulate Matter, and
    in   the Soil Beneath Sprayed Trees.
    Arch. Environmental Contamination and Toxicology 1(1): 60-83 (1973).

81. Westlake,W.E., Ittig,M., Ott,D.E., and Gunther,F.A.:
    Persistence of residues of the insecticide phosphamidon on and in
    oranges, lemons, and grapefruit, and on and in orange leaves and in
    dried citrus pulp cattle feed.
    J Agric Food Chem. 21(5): 846-850, 1973.

82. Winterlin, Wray, J. Blair Bailey, L. Langbehn, and C. Mourer:
    Degradation of Parathion Applied to Peach Leaves.
    Pesticides Monitoring Journal 8:263-269 (1975).

83. Winterlin, W., W. Kilgore, C. Mourer, R. Mull, G. Walker, J. Knaak and K. Maddy: Dilodgeable Residues of Dialifor and Phosalone and Their Oxygen Analogs Following a Reported Worker-Injury Incident in the San Joaquin Valley, California.
Bull. Environmental Contamination and Toxicology 20:255-260 (1978).

84. Winterlin, Wray, Gregory Hall, Charles Mourer, and Glen Walker: Dissipation of Parathion and Paraoxon on Citrus Foliage Dust and Dry Soil Surfaces in a Treated Orchard.
Arch. Environmental Contamination & Toxicology. 11(1):11-121 (1982).

85. Winkler,V.W. et al:
Determination of norflurazon residues in mixed crop matrices.
J.Assoc.Off.Anal.Chem. 64(6): 1309-1311, 1981.

86. Woodham,D.W., Reeves,R.G., Williams,C.B., Richardson,H.,and Bond,C.:
Residues of dimethoate and its oxygen analog on and in citrus leaves following a helicopter treatment of the trees with dimethoate ultra-low volume concentrate and high volume spray.
J Agric Food Chem. 22(4): 731-733, 1974.

87. Woodrow et al:
Airborne and Surface Residues of Ethyl Parathion and its Conversion Products in a Treated Plum Orchard Environment.
Arch Env Contam & Tox. 6:175-191 (1977).

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Appendix C: Computer database format for reported residues as corresponds to INPUT FILE SPECIFICATION (as used by program "REEN1").

		format	column

LINE "1" (precedes each set of residues)

chem	= name of chemical (abbreviated) (see "chemco" file for abbreviation code)	A8	1-8
nart	= article number (within reference system)	I2	10-11
ndset	= dataset number (within article)	I2	13-14
nox	= number of oxons or other metabolites reported (one line nameing each oxon required after optional comments); nox cannot be larger than nor can names differ in sequence from those specified in the library file "chemco".	I1	16
loc	= location by state [and within state]	A3	18-20

    AK = Arkanas
    AZ = Arizona
    CA = California
       CAi = Imperial Valley. CA
       CAs = Southern CA
       CAv = Central Valley, CA
    FL = Florida
    GA = Georgia
    IND= India
    SC = South Carolina
    TX = Texas
    WA = Washington

crop	= crop code (see "cropco" library file); selective searching by crop is an option in some programs, e.g. reen2.	A6	22-27
igph	= blank (0) if data are from a table; 1 if data points are taken from a graph.	I1	29
form	= formulation (eg. 8EC, 25WP, etc.)	A4	31-34

    CP = encapsulated, n = % active by weight
    EC = emulsifiable concentrate, n = pounds active per gallon
    WP = wettable powder, n = % active by weight

aia	= mixture active ingredient per acre (lbs./acre) [1 Liter/hectare = 0.892 gal/acre]	F5.2	36-40
gpa	= gallons water per acre	F4.0	42-45
ex	= extraction solvent used:	I1	47

    blank/default = aqueous with surfactant
    1 = hexane   4 = Methylene chloride
    2 = chloroform 5 = benzene
    3 = toluene   6 = other (see comments)

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unit	= units reported	I1	49
	blank/default = ug/cm2		
	1 = ng/cm2 3 = ppm		
	2 = mg/m2 4 = other		
nside	= number of sides of leaf used to calculate	I1	51
	residue		
	1 = 1 side 2 = 2 sides		
dapp	= day of application	I2	53-54
mapp	= month of application	A3	56-58
yapp	= year of application	I2	60-61
ncomm	= number of comment lines [optional up to 6]	I1	63
npun	= number of punches total [if unusual]	I3	65-67
isd	= blank if standard deviation not given;	I1	69
	1 if given.		

LINE "2" (comments as specified by "ncomm")

comm	= [optional] 1 - 6 comment line(s)	A79	1-79
	usually used to cite source reference		
	or observations on application, data, etc.		

LINE "3"

lox	= metabolite name(s), one per line;	A30	1-30
	the number of names is not optional but		
	must match "nox" as listed in LINE 1.		

LINE "4"

nsam	= number of residue intervals measured;	I2	1-2
	1 line [manditory] corresponding to the		
	number of residue lines which follow.		

LINE "5" (Residue data)

dpa	= days post application	F4.0	1-4
res	= residue value, in units as given in	F6.0	6-11
	original data set, unless transformed		
	to standard units (ng/cm2) by REEN1 or		
	similar calculation.		
sd	= standard deviation, if reported;	F6.0	13-18
	negative values are % relative deviation		
	(coefficient of variation).		

****

An example is provided on the following page:

****

example from file "pholon":

```
column  1           2           3           4           5           6           7
        0           0           0           0           0           0           0
c see  |n |n |n|1  |c see |i|f  |A    |g    |e|u|n|d |m  |y |n|n  |i|
h che- |a |d |o|o  |r cro-|g|o  |I    |p    |x|n|s|a |a  |a |c|p  |s|
e  mco |r |s |x|c  |o  pco|p|r  |A    |a    |s|i|i|p |p  |p |o|u  |d|
m      |t |e | |   |.p    |h|m  |     |     |o|t|d|p |p  |p | |m|  | |
       |  |t | |   |      | |   |     |     |1| |e| |  |   |  | |1|  | |
```

ethion   :34.01:1:FL :orgval: : 4EC: 3.00:1200: :1:2:29:may:75:4:160:1.
Nigg, et al: Dislodgeable Residues of Ethion in Florida Citrus and
  Relationships to Weather Variables.
Arch Env Contam & Tox. 6: 257-267, 1977.
wet season
ethion monoxon
 6
    0: 99.4:   5.5:   4.1:   2.3:   :   :
    1: 61.2:   26.3:   6.0:   3.6:   :   :
    3:   7.4:   5.4:   3.9:   1.4:   :   :
    5:   3.0:   .9:   2.7:   .8:   :   :
    7:   2.8:   2.0:   1.7:   1.1:   :   :
   14:   2.0:   .9:   1.3:   .5:   :   :
ethion   :34.02:1:FL :orgval: : 4EC: 4.50:1200: :1:2:10:nov:75:1:160:1.
dry season
ethion monoxon
 9
    0: 141.6:   25.8:   12.0:   1.9:   :   :
    1: 32.8:   8.7:   2.5:   .2:   :   :
    3: 23.3:   1.8:   3.2:   .2:   :   :
    5: 16.6:   2.3:   4.0:   1.1:   :   :
    7: 17.1:   .9:   5.1:   .1:   :   :
   14: 16.7:   4.3:   4.8:   .5:   :   :
   21:   5.1:   1.1:   3.9:   .5:   :   :
   28:   3.4:   1.7:   2.2:   1.5:   :   :
   35:   4.1:   .7:   2.2:   .3:   :   :
ethion   :34.03:1:FL :orgval: : 4EC: 4.50:1200: :1:2:29:may:75:1:160:1.
wet season
ethion monoxon
 6
    0: 284.6: 142.9:   42.2:   3.2:   :   :
    1: 124.6: 52.4:   21.7:   4.8:   :   :
etc...

Appendix D: Computer library of Unified Field Model Chemcial Coefficients.

"CHEMCO" is a tabulation of chemical codes, their
dermal LD50 values, the number of metabolites
possible for each chemical, common or trade names,
and whether the reentry interval is regulated by EPA
(E) or California (C) or both. Data for dial,
ethion, and mep are replicated in a second set of
parameters with the suffix "2" in which LD50 values
for the metabolites were assumed to be different from
the parent.

columns allocated to each parameter are as follows:

1-8	10-13	15	17-41(=25)	42-66(=25)	69	71
azinme	220	1	azinphosmethyl	[Guthion]	E	C
	7		azinphosmethyl oxon		"	"
carbaryl	4000		carbaryl	[Sevin] 63-252 FC59500		
carbop	40	3	carbophenothion	[Trithion]	E	C
	40		carbophenothion oxon		"	"
	40		carbopheno. sulfoxide		"	"
	40		carbophenothion sulfone		"	"
chlort	58	3	chlorthiophos	21923-239 TF15900		
			chlorthiophos sulfoxide			
			chlorthiophos sulfone			
			chlor. oxon sulfoxide			
dcroto	42		dicrotophos	[Bidrin]	E	C
demet	11		demeton or demeton-s	[Systox]	E	C
dial	124	1	dialifor	[Torak]		C
			dialifor oxon			"
dial2	124	1	dialifor	[Torak]		C
	12		dialifor oxon			"
diaz	640		diazinon	[Spectracide]		C
dimeth	610	1	dimethoate	[Cygon],[De-Fend]		C
			dimethoxon			"
dioxat	120		dioxathion	[Delnav]		C
endrin	15		endrin	-chlorinated HC-	E	C
epn	127		epn	[EPN-300]	E	C
ethion	153	2	ethion	[Ethion],[Nialate]	E	C
			ethion monooxon		"	"
			ethion dioxon		"	"
ethio2	153	2	ethion	[Ethion],[Nialate]	E	C
	15		ethion monooxon		"	"
	7		ethion dioxon		"	"
etp	14	1	ethyl parathion	[Phostox],[Thiophos]	E	C
	1		ethyl paraoxon		"	"
malat	4444		malathion	[Carbophos]		C
mep	67	1	methyl parathion	[Metron]	E	C
			methyl paraoxon		"	"
mep2	67	1	methyl parathion	[Metron]	E	C
	7		methyl paraoxon		"	"

methom		methomyl	[Lannate],[Nudrin]	C
metion	73 1	methidathion	[Supracide]	C
	20	methidathion oxon		"
mevin	4.5 1	mevinphos	[Phosdrin]	C
		beta isomer		"
monoos	119	monocrotophos	[Azodrin]	E
naled	800	naled	[Dibrom]	C
oxyme	165	oxydemeton-methyl	[Metasystox-R]	E
phenth	700 1	phenthoate	Fenthoate 2597-037 AI78750	
		phenthoate oxon		
pholon	1530 1	phosalone	[Zolone]	C
	380	phosalone oxon		"
phorat	4	phorate	[Thimet]	C
phosam	124	phosphamidon	[Dimecron]	C
phosmet	1550	phosmet	[Imidan]	C
tepp	2.4	tetraethyl pyrophosate	[TEPP],[Vapotone]	C
tric	2000	trichlorfon	[Dylox] 52-686 TA07000	
		carbosulfan	[Advantage]	
		chlorpyrifos		
		disulfoton	[Di-syston]	C
endosulf	2	endosulfan	[Thiodan]	C
		alpha isomer		"
		beta isomer		"
		propargite	[Omite]	
		oxymyl	[Vydate]	
		sulphur		C
		chemical requested not on file		

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☆☆☆

Appendix E: Computer library of Unified Field Model Crop Coefficients. 352

"CROPCO" is a tabulation of crop codes, their dosing coefficient (K_d), the full name of the crop, and the leaf density (estimated (as noted by ?) when otherwise unknown) to be used to convert residue reported as ppm to ng/cm2. For purposes of calculation, when the K_d was unknown, a conservative (high) default value corresponding to 5.0 (5000 cm2/hr) was assumed. Some replicated crop codes were included to match on crops coded within the data base which were sometimes right-justified.

columns allocated to each parameter are as follows:

1-6	12-15	23-42(=20)	45-48	49
apple	3.5	apple	20.	?
apple	3.5	apple	20.	?
artchk		artichoke		
cabbag		cabbage		
chili		chili		
chili		chili		
citrus	5.1	citrus	27.5	
cotton		cotton	25.	?
cowpea		cowpea		
grape	3.5	grape-unclassified	21.	
grape	3.5	grape-unclassified	21.	
graper	3.5	grape-raisin	21.	
grapet	3.5	grape-table	21.	
grapew	3.5	grape-wine	21.	
grapfr	5.1	grapefruit	27.5	
lemon	5.1	lemon	27.5	
lemon	5.1	lemon	27.5	
lettuc	5.1	lettuce-unclassified		
mustar		mustard		
okra		okra		
okra		okra		
orange	5.1	orange-unclassified	27.5	
orgnav	5.1	orange-navel	27.5	
orgval	5.1	orange-valencia	27.5	
peach	1.9	peach	20.	?
peach	1.9	peach	20.	?
plum	1.9	plum	20.	?
plum	1.9	plum	20.	?
sobean		soybean		
tobaco		tobacco	20.	?
tomato		tomato-unclassified	17.	?
wheat		wheat		
kd =		crop not on file	= ug/cm2	

In order to interpolate, extrapolate, and tabulate two-component (parent and one metabolite) residue data from any single study to a preselected criterion for re-entry days of specific interest to this report, a generalized four compartment submodel was investigated. This submodel is depicted diagrammatically in Figure F1. Conceptually, this submodel assumes that the initial parent residue is partitioned on the leaf into fast and slow decay compartments. Each of these compartments can decay by two routes; it can either become a metabolite (e.g. oxon) or become nonmeasureable (e.g. by vaporization, hydrolysis, leaf absorption, etc). One additional route attributable to material in the fast decay compartment is a transition by various mechanisms from the relatively unstable (fast) compartment into the environmentally protected (slow) decay compartment. The metabolite is also partitioned into two parallel fast and slow compartments both initially and as a result of decay from the parent, and both metabolite compartments are susceptable to transitional pathways identical to their corresponding parent compartments.

In nature, the partitioning is dictated by natural forces. In a model, the partitioning is accomplished by fitting coefficients of the equations characterizing each compartment and pathway to the experimental data . Pesticide decay is most commonly characterized by first-order differential equations, i.e. that the rate of decay is proportional to the amount material present (e.g. Popendorf and Leffingwell, 1978). The subscript numbers assigned in Figure F1 were chosen pragmatically to permit the modelling of single component pesticides (those without measureable metabolites) by only the first 5 coefficients, versus 12 for two component (four compartmet) residues. Thus, the amount of material present in each compartment is designated as follows:

	fast compartment	slow compartment
parent	a_1	a_4
metabolite	a_{11}	a_{12}

The corresponding kinetic coefficients were designated as follows:

	fast compartment	slow compartment
parent to nonmeasureable	a_2	a_5
parent fast to slow	a_3	--
parent to metabolite	a_6	a_{10}
metabolite fast to slow	a_7	--
metabolite to nonmeasureable	a_8	a_9

A generalized pesticide decay FORTRAN computer program was developed during this study to fit the coefficients to the reported data. A number of difficulties were encountered with this approach, among which were that it was time consuming (requiring considerable operator interaction), the data was often sparse or did not include initial residues, and the improvements in smoothing the variability among reported residues within any one study was outweighed by the much larger variability between studies for any given pesticide. Nonetheless, the following program can estimate the coefficients of the model described above.
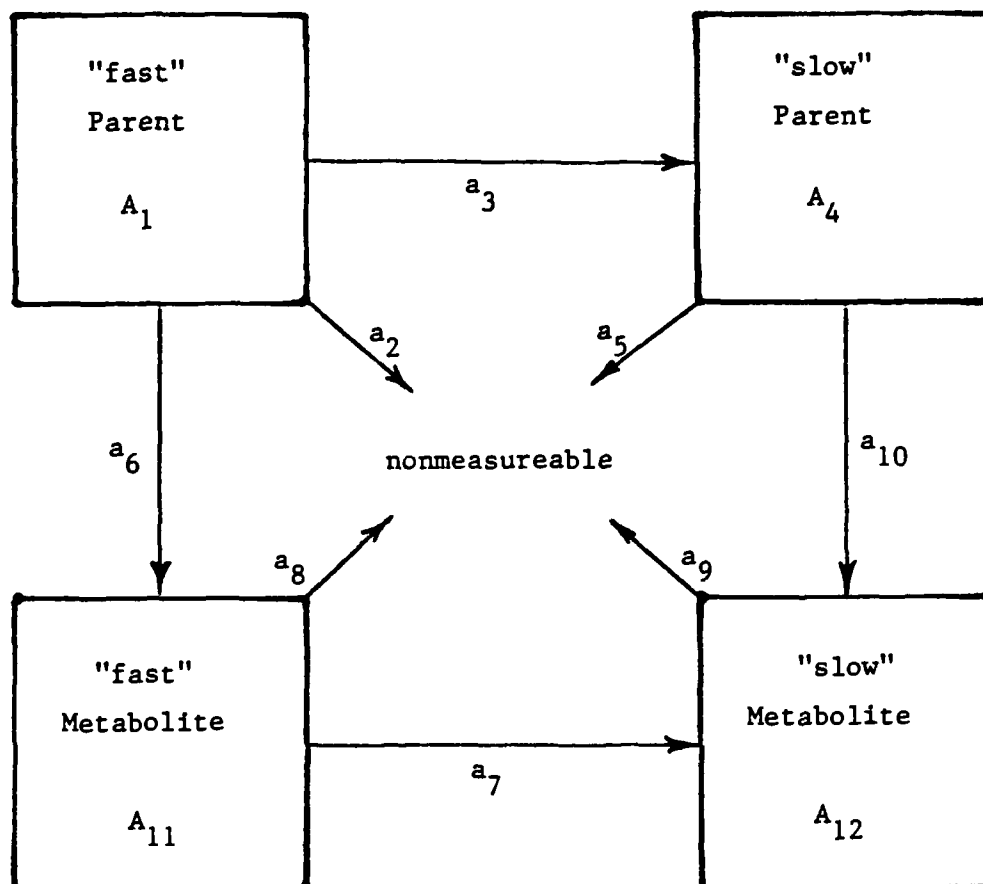
Figure F1. Schematic diagram of generalized pesticide decay model with zero or one metabolite. Coefficients defined as used in accompaning algorithm.

program REPA10

```
C.... EPA version of Rose MAIN LINE PROGRAM
C.... originally adapted from ROSENBROCK HILLCLIMB program in
C               'OPTIMIZATION TECHNIQUES WITH FORTRAN'
C                   J.L. KUESTER & J. MIZE PG 386.
C.... THIS SPECIAL HILLCLIMB PACKAGE WAS WRITTEN FOR RESIDUE DECAY ANALYSIS
C     with a model of 10 coefficients.
C.... MODIFICATIONS FOR IBM 1130 BY W. POPENDORF (1974)
C.... further modifications in lower case for FORTRAN 77 by W. Popendorf (1984)
C     USE IN GOOD HEALTH.


C.... THE FOLLOWING VARIABLES can be read from a special RPRAM file
C               [defaults are provided for in all cases following line 36]:
C     LOOPY = MAXIMUM NUMBER OF STAGES TO BE CALCULATED  (10 to 20 IS GOOD)
C     NCOEF = NUMBER OF COEFFICIENTS (UNKNOWNS) WITH FIRST GUESSES
C               [usually set to 0 to use defaults]
C     NOASK = an index setting logical LASK to bypass user options after
C               selecting filenames, thus operating in an unattended batch mode
C     NSTEP = STEP SIZE CONTROLER: 0 FOR ORIGINAL STEP SIZE AFTER ROTATION
C                                  1 FOR RETENTION OF SIZE PRIOR TO ROTATION
C     PR    = NUMBER OF STAGES BETWEEN PRINTED OUTPUTS  [3 is default];
C               A stage is when all E's have reversed direction twice.
C               Because 2 is an even number, this routine has a tendancy to
C               overestimate all coefficients (which for pesticide decay tends
C               to underestimate especially oxons); so it is better to
C               underestimate the value of each first guess.
C     delF  = THE ACCEPTABLE LIMITING DIFFERENCE IN THE OBJECTIVE FUNCTION
C               BETWEEN PRESENT AND PRIOR STAGE  [1.0E-6]
C     EV    = Sets VECTOR OF INITIAL STEP SIZES [ 0.01 ];
C               original ROSE permitted setting individual E's.
C.... the following are PROGRAMMED VARIABLEs
C     DA    = A GENERAL STORAGE VECTOR (MAX LENGTH LIMITED BY DIMENSION)
C     DELE  = THE MINIMUM STEP SIZE BEFORE PLOTTING RESULTS FOR USER
C     LA    = MAXIMUM NUMBER OF NCOEF PERMITTED BY ARRAY LIMITS AS WRITTEN
C     MM    = +1 FOR MAXIMIZATION.... -1 FOR MINIMIZATION
C     NCC   = NUMBER OF VARIABLES PLUS IMPLICIT CONSTRAINTS (SPECIFIED BY CX)
C     N     = NCC (see line 40 - 2)
C     NinDA = NUMBER OF DATA POINTS TO BE READ AND STORED IN DA
C     NIV   = NUMBER OF INPUT VARIABLES (KNOWNS) WITHIN STORED DATA SET
C     NPAR  = MAXIMUM NUMBER OF DA PERMITTED BY ARRAY LIMITS AS WRITTEN
C     X     = MULTIPLICATION or Scaler FACTORS UPON FIRST GUESSES;
C               these are the variables actual optimized.
C
C.... INPUT FILE SPECIFICATION (same file as for "REEN')
C     chem  = name of chemical (abbreviated)              A8
C               (see LDvals file for abbreviation code)
C     nart  = article number                             I2
C     ndset = dataset number                             I2
C     nox   = number of oxons or other metabolites reported  I1
C     loc   = location by state (except for CA: location by  A3
C               region within state, eg.
```

```
C                   AZ = Arizona
C                   CA = California                                  357
C                      CAi = Imperial Valley, CA
C                      CAs = Southern CA
C                      CAv = Central Valley, CA
C                   FL = Florida
C                   SC = South Carolina
C                   TX = Texas
C                   WA = Washington
C      crop  = crop code (see cropco file)                 A6
C      igph  = blank (0) if data are from a table,         I1
C                1 if data points are taken from a graph
C      form  = formulation (eg. 8EC, 25WP, etc.)           A4
C                   CP = encapsulated
C                   EC = emulsifiable concentrate
C                   WP = wettable powder
C      aia   = active ingredient per acre (lbs./acre)      F5.2
C      gpa   = gallons water per acre                      F4.0
C      ex    = extraction solvent used:                    I1
C                   blank/default = aqueous
C                   1     = hexane       4 = Me chloride
C                   2     = chloroform   5 = benzene
C                   3     = toluene      6 = other (see comments)
C      unit  = units reported                          •   I1
C                   blank/default = ug/cm2
C                   1     = ng/cm2       3 = ppm
C                   2     = mg/m2        4 = other
C      nside = number of sides of leaf used to calculate   I1
C                residue
C                   1     = 1 side       2 = 2 sides
C      dapp  = day of application                          I2
C      mapp  = month of application                        A3
C      yapp  = year of application                         I2
C      ncomc = number of comment cards, up to 6            I1
C      npun  = number of punches total                     I3
C      isd   = blank if standard deviation not given,      I1
C                1 if given
C      comm  = comment line                                A80
C      lox   = metabolite name                             A30
C      nsam  = number of residue intervals measured        I2
C      dpa   = days post application                       F4.0
C      res   = residue value, in units as given in         F6.0
C                original data set
C      sd    = standard deviation, if given                F6.0
C
 
      INTEGER      PR,NE(10)
      REAL         LC,DA(120)
      real         AL(10),B(10,10),BX(10),D(10),E(10),EINT(10),H(10),
     +             PH(10),V(10,10),VV(10,10),X(10),Z(10)
      integer      ex, unit, dapp, yapp
      real         dpa(15), res(15,3), sd(15,3), adif(3),pdif(3)
      character*1  file
      character*3  loc, mapp
      character*4  form
```

```
      character*6  crop
      character*8  chem
      character*12 input, output, newin
      character*30 lox(2)
      character*80 spec, comm(6), data(15)
      logical      lfile,lask,init,term

C.... ni = unit specifier for input filename
C.... no = "       "       "  output   "  various fit results
C.... nu = "       "       "  user (screen and console)
C.... nx = "       "       "  new input file with coefficients
C.... npram =         "       "  rpram  "    "  (rose parameters)
      NU    = 0
      NI    = 2
      NO    = 3
      NX    = 4
      NPRAM = 5
      maxc  = 8
      open (npram,file='rpram10')

    2 write (nu,1003)
 1003 format (' Type pesticide INPUT filename, up to 12 characters:')
C.... (for code, see LDvals library file)...
      read  (nu,1004) input
 1004 format (a12)
      if    ((input .eq. 'quit').or.(input .eq. 'exit').or.
     +       (input .eq. 'stop').or.(input .eq. 'end')) go to 30000
 1006 format (a1)
      open  (ni, file=input)
      rewind ni
      xv    = 0.0

      write (nu,1007)
 1007 format (/,' A duplicate inputfile SHALL be created herein with new
     + model coefficients',/,' Type NEW filename, up to 12 characters:')
      read  (nu,1004) newin
      open  (nx, file=newin, status='new')

      write (nu,1008)
 1008 format(/,' Do you want model results also written to disk? Y/N ')
      read  (nu,1006) file
      call yes(file,lfile)
      if    (.not. lfile) go to 20

      write (nu,1009)
 1009 format (' Type general OUTPUT filename, up to 12 characters:')
      read  (nu,1004) output
      open  (no, file=output, status='new')
      rewind  no

   20 continue
C.... reading data specification line
      read  (ni,2001,end=24) chem,nart,ndset,nox,loc,crop,igph,form,
     +                       aia,gpa,ex,unit,nside,dapp,mapp,yapp,ncomc,
     +                       npun,isd
```

```
      write  (nu,2001      ) chem,nart,ndset,nox,loc,crop,igph,form,
     +                     aia,gpa,ex,unit,nside,dapp,mapp,yapp,ncomc,
     +                     npun,isd
 2001 format (a8,1x,2(I2,1x),i1,1x,a3,1x,a6,1x,i1,1x,a4,1x,f5.2,1x,f4.0
     +        ,1x,3(i1,1x),i2,1x,a3,1x,i2,1x,i1,1x,i3,1x,i1)
      backspace ni
      read   (ni,2002) spec
      nres  = nox+1
      NCOEF = 4+(2*nox)
      if     (nsam .eq. 2 .and. nox .eq. 0) NCOEF=2

C.... reading up to 6 comment lines
      read   (ni,2002) (comm(i),i=1,ncomc)
      write  (nu,2002) (comm(i),i=1,ncomc)
 2002 format (a80)
C.... reading the name of the oxons or other metabolites
C.... and model coefficients 9 and 10
      read   (ni,2003) lox,da(9),da(10)
      write  (nu,2003) lox,da(9),da(10)
 2003 format (2a30,2e10.4)
C.... reading the number of samples in the following set of data,
C.... also the number of previous runs and goodness of fit indices
      read   (ni,2004) nsam,nruns,(pdif(k),k=1,nres),(adif(k),k=1,nres)
      write  (nu,2004) nsam,nruns,(pdif(k),k=1,nres),(adif(k),k=1,nres)
 2004 format (I2,i3,6e10.4)
C.... reading residue data ...
      do 21 j = 1,nsam
      read   (ni,2005) dpa(j),(res(j,k),sd(j,k),k=1,nres)
      write  (nu,2005) dpa(j),(res(j,k),sd(j,k),k=1,nres)
      backspace ni
      read   (ni,2002)   data(j)
   21 continue
 2005 format (f4.0,1x,6(f6.0,1x))
C.... reading model coefficients 1 - 8
C.... do-loop sets da = previous A (or Z)
C.... unless this is the first run of program with new data (pesticide) file
C.... then loop sets da = 0 in preparation for subroutine "TX".
      DO 22 i = 1,maxc
      if     (xv .ne. 1.0) z(i)=0.0
      da(i) = z(i)
   22 continue
      if     (nruns .eq. 0) go to 23
      READ   (NI,2006) (DA(i),i=1,maxc)
      write  (nu,2006) (DA(i),i=1,maxc)
 2006 FORMAT (8E10.4)

   23 if     ((nsam*nres) .ge. ncoef) go to 35
      write  (no,1013) nart,ndset
      write  (nu,1013) nart,ndset
 1013 format (' The data for article',i3,' dataset',i2,
     +        ' are insufficient to model!')
      go to 20
   24 write  (nu,*) 'Reading end of old input datafile.'
      go to 2
```

```
C.... subroutine to convert data to ug/cm2 projected area          360
C.... units may be nonstandard and must be individualy converted.
   35 call units(res,sd,nsam,nres,unit,nside,crop)
      if      (unit .lt. 4) go to 36
      write  (no,1014) nart, ndset
      write  (nu,1014) nart, ndset
 1014 format (' Nonstandard units in article',i3,' dataset',i3,/,
      +          ' - further calculations are discontinued!')
      go to 20
   36 continue

      CALL tx(DA,dpa,res,nsam,nres,ncoef)                           ****

      lask  = .true.
      rewind npram
      read   (npram,4001) loopy,nco,noask,nstep,pr,delF,ev
 4001 format (5i2,2f10.9)

      if     (loopy .eq. 0) loopy = 20
      if     (nco   .ne. 0) ncoef = nco
      if     (noask .eq. 0) lask  = .false.
      if     (nstep .ne. 0) nstep = 1
      if     (pr    .eq. 0) pr    = 3
      if     (delF.eq. 0.0) delF  = 1.e-6
      if     (ev   .eq. 0.0) ev    = 0.01
      LA    = 10
      dele  = 1.e-8
      MM    = -1
      NCC   = ncoef                                                 *
      next  = 1                                                     *
      niv   = 2+nox                                                 *
      NinDA = NCOEF+(nsam*niv)                                      *

   37 CONTINUE                                                      *
      XV     = 1.0                                                  *
      DO 200 K = 1,maxc                                             *
      E(K)   = EV                                                   *
      X(K)   = XV                                                   *
      Z(K)   = 0.0                                                  *
  200 CONTINUE                                                      *
  300 CONTINUE                                                      *
      WRITE  (nu,3013) nart, ndset,ncoef,nsam,chem,crop             *
 3013 FORMAT (///,' Article Number',I3,', data set #',I3,/,' Results of'*
      +,i3, ' coefficient decay model for ',i2,1x,a8,' sample points on '*
      +,a6, '.')                                                    *
      if     (.not. lfile) go to 39                                *
      write  (no,3013) nart, ndset,ncoef,nsam,chem,crop            *

C.... pseudoORIGINAL ROSE BEGINS HERE
   39 INIT   = .true.
      TERM   = .false.
      LAP    = 0
      LOOP   = 0
      KOUNT  = 0
      F1     = 0.0
```

```
          DO 40  K= 1,NCC
    40 AL(K)  = (CH(X,DA,NCC,NinDA,K)-CG(X,DA,NCC,NinDA,K))*.001
          DO 60  J= 1,NCOEF
          DO 60  I= 1,NCOEF
          V(I,J) = 0.0
          IF       (I-J) 60,61,60
    61 V(I,J) = 1.0
    60 CONTINUE
          DO 62 K= 1,NCOEF
          EINT(K)= E(K)
    62 CONTINUE


C....  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .  .

    64 continue
          write  (nu,1020)                                              *
  1020 format (' Stage/Limit Stage/Print_Limit  #_F._Evals.  Avg._F_Error*
          +      Avg._Step_Size')                                       *
    65 DO 70 K  = 1,NCOEF
C.... line 65 starts new stage
C.... Nstep=0 means return to original step size (EINT) after rotation
          IF       (NSTEP-0) 67,66,67
    66 E(K)       = EINT(K)
    67 NE(K)      = 0
    70 D(K)       = 0.0
          FBEST    = F1
C.... an implicit loop on I from 1 to ncoef starts here, ends line 441. . .
    80 I          = 1
          IF       (INIT)  go to 120
    90 DO 95  K = 1,NCOEF
    95 X(K)       = X(K) + E(I)*V(I,K)
   100 DO 110 j = 1,ncoef
          XC       = CX(X,DA,NCC,NinDA,J)
          LC       = CG(X,DA,NCC,NinDA,J)
          UC       = CH(X,DA,NCC,NinDA,J)
          if (xc .le. lc) go to 420
          if (xc .ge. uc) go to 420
   110 continue

   120 F1        = MM * F(X,DA,NCOEF,NinDA,NIV,dpa,res,nres,nsam)
          KOUNT   = KOUNT + 1
          IF (INIT) F0=MM*1.E+38
          IF (ABS(FBEST-F1) .le. delF) go to 125
   122 TERM       = .true.
          GO TO 450
   125 CONTINUE

C.... an implicit loop on J from 1 to ncoef starts here, ends line 211. . .
          J          = 1
   130 h(j)       = f0
*        the following section preceded by * was bypassed from the original prog.
*        BW         = AL(J)
*        XC         = CX(X,DA,NCC,NinDA,J)
*        LC         = CG(X,DA,NCC,NinDA,J)
*        UC         = CH(X,DA,NCC,NinDA,J)
```

APPENDIX F: page 8 of 22

```
C.... remember, F1=MM*F. F0=lastF1, and MM=-1 for minimum error fit;
C.... thus, it is desired that F1 be .gt. F0; else, change direction.
      IF (F1 .lt. F0) go to 420
*     IF (XC .lt. (LC+AL(J))) go to 160
*     IF (XC .gt. (UC-AL(J))) go to 170
*     GO TO 210
* 160 PW    = (LC+BW-XC)/BW
*     GO TO 180
* 170 PW    = (XC-UC+BW)/BW
* 180 PH(J) = 1.0-3.0*PW+4.0*PW**2-2.0+PW**3
* 190 F1    = H(J)+(F1-H(J))*PH(J)

* 210 CONTINUE
*     IF (J-NCC)        211,220,211
* 211 J     = J+1
*     GO TO 130
C.... end of implicit J loop . . . . . . . . . . . . . . . . . .
  220 INIT  = .false.
      D(I)  = D(I)+E(I)
      E(I)  = 3.0*E(I)
      F0    = F1
      IF (NE(I) .EQ. 0) NE(I) = 1

  230 DO 240  K = 1,NCOEF
      IF (NE(K) .LT. 2) GO TO 440
C.... note a "stage" is when ALL X advances have changed direction twice.
  240 CONTINUE

C.... AXES ROTATION . . to line 420 . . . . . . . . . .
C.... BMAG = progress
C.... BBMAG = lateral progress
      DO 250 K1 = 1,NCOEF
      DO 250 K2 = 1,NCOEF
  250 VV(K1,K2) = 0.0
      DO 260 K1 = 1,NCOEF
      DO 260 K2 = 1,NCOEF
      DO 265 K3 = K1,NCOEF
  265 VV(K1,K2) = D(K3)*V(K3,K2)+VV(K1,K2)
  260 B(K1,K2)  = VV(K1,K2)
      BMAG      = 0.0
      DO 280 K  = 1,NCOEF
      BMAG      = BMAG+B(1,K)**2
  280 CONTINUE
      BMAG      = SQRT(BMAG)
      BX(1)     = BMAG
      DO 310 K  = 1,NCOEF
  310 V(1,K)    = B(1,K)/BMAG

      DO 340 K1 = 2,NCOEF
      DO 340 K2 = 1,NCOEF
      SUMVM     = 0.0
      DO 330 K3 = 1,K1-1
      SUMAV     = 0.0
      DO 320 K4 = 1,NCOEF
  320 SUMAV     = SUMAV+VV(K1,K4)*V(K3,K4)
```

362

```
 330 SUMVM       = SUMAV*V(K3,K2)+SUMVM
 340 B(K1,K2)    = VV(K1,K2)-SUMVM


     DO 360 K1 = 2,NCOEF
     BBMAG       = 0.0
     DO 350 K2 = 1,NCOEF
 350 BBMAG       = BBMAG+B(K1,K2)**2
     BBMAG       = SQRT(BBMAG)
     DO 360 K2 = 1,NCOEF
 360 V(K1,K2)    = B(K1,K2)/BBMAG


     EA          = 0.0                                              *
     DO 399  k = 1,ncoef                                            *
     EA          = EA + abs(E(k))                                   *
 399 continue                                                       *
     EA          = EA / ncoef                                       *
     Ferr        = F0 / (nsam*nres)                                 *
     LOOP        = LOOP+1
     LAP         = LAP+1
     write (nu,1021) loop,loopy,lap,pr,kount,Ferr,EA               *
1021 format (3x,i2,' / ',i2,5x,i3,' /',i2,10x,i5,8x,1pe12.5,5x,1pe12.5)*
     IF (LAP-PR)                65,450,65
C.... . . . . . . . . . . . . . . . . . . . . . . . . .
C.... line 420 etc either (1) lists coefficients and indicates starting point
C.... has violated constraints if INIT is true, or
C.... (2) undoes array step advance (E) and reverses E(I) 2/3 of a step.
 420 IF (INIT) go to 450
 421 DO 430 K = 1,NCOEF
 430 X(K)        = X(K) - E(I)*V(I,K)
     E(I)        = -E(I)/2.
     IF (abs(E(I)) .lt. DELE)   go to 122
     IF (NE(I) .ge. 1)          NE(I) = 2
     GO TO 230


 440 CONTINUE
     IF (I-NCOEF)               441,80,441
 441 I           = I+1
     GO TO 90
C.... end of implicit I loop . . . . . . . . . . . . . .
 450 continue
     DO 455 I = 1,NCOEF                                             *
 455 Z(I)        = X(I)*DA(I)                                       *
C.... PRINT CURRENT VALUES OF X AND Z (COEFFICIENTS)
     WRITE (nu,3005)
3005 FORMAT (/,' Scalers to 1st Guesses,  Model Coefficients,      and S*
    +tep Sizes')
     WRITE (nu,3006) (I,X(I),I,Z(I),I,E(I), I=1,NCOEF)
3006 FORMAT (:,4X,2HX(,I1,4H) = ,0pF10.6,5X,2HA(,I1,4H) = , 1PE11.4,
    +                                    3X,2HS(,I2,4H) = , 1PE12.4)


     LAP         = 0
 461 IF (INIT)        go to 470
 462 IF (TERM)        go to 480
 463 IF (LOOP-LOOPY) 64,480,480
```

```
  470 WRITE  (nu,007)
    7 FORMAT (///, 2X,
      + 'THE STARTING POINT APPEARS TO HAVE VIOLATED THE CONSTRAINTS')
        xv       = 0.0                                                                  364
        go to 37       .


  480 CONTINUE
        if (.not. lfile) go to 601
        WRITE  (NO,3003)
 3003 FORMAT (' At exit',/,2X,5HSTAGE,4X,8HFUNCTION,5X,8HPROGRESS,5X,
      +          16HLATERAL PROGRESS,3X,'# of F EVALS.' )
        WRITE  (NO,3004) LOOP,FO,BMAG,BBMAG,KOUNT
 3004 FORMAT (1H ,I4,3E15.5,10x,I5)
        WRITE  (NO,3005)
        WRITE  (NO,3006) (I,X(I),I,Z(I),I,E(I), I=1,NCOEF)                                *

C.... This section TO LIST AND PLOT THE MEASURED AND PREDICTED VALUES.
C.... THE TELL SUBROUTINE WAS DEVELOPED DURING THE INITIAL PLANNING (1974),
C.... BUT RPI WAS DEVELOPED FROM 'DKRP' DURING 1976.  SEE PROGRAM DK.


  601 continue
  605 CALL RP1  (   z,ncoef,dpa,res,nsam,nres,nart,ndset,next,lfile)
        CALL TELL (da,z,ncoef,dpa,res,nsam,nres,nart,ndset,next,lfile,
      +          adif,pdif)

C.... ask if coefficients are OK, then
C.... recalulate if necessary or go on to next set of data
        if (lask) go to 611
  607 write  (nu,3021)
 3021 format (' Type ''#'' of any coefficient you wish to reset,',
      +        /,'    a ''11'' if you wish to reoptimize from here, or',
      +        /,'    a ''0'' if this is OK and to continue:' )
      read    (nu,*) next
      next = next +1
      go to  (611,612,612,612,612,612,612,612,612,612,612,619), next

C.... the following write statements recreate the specification line,
C.... comment line(s), metabolite-name line, sample-number line,
C.... residue lines, and coefficient lines, respectively.
  611 nruns = nruns+1
      write  (nx,2002)  spec
      write .(nx,2002) (comm(i),i=1,ncomc)
      write  (nx,2003) lox,z(9),z(10)
      write  (nx,2004) nsam,nruns,(pdif(k),k=1,nres),(adif(k),k=1,nres)
      write  (nx,2002) (data(i),i=1,nsam)
      write  (nx,2006) (z(j),j=1,maxc)
      next  = 0
      CALL RP1  (   z,ncoef,dpa,res,nsam,nres,nart,ndset,next,lfile)
      CALL TELL (da,z,ncoef,dpa,res,nsam,nres,nart,ndset,next,lfile,
      +          adif,pdif)
      go to 20

  612 next  = next - 1
      write  (nu,3023) next,z(next)
 3023 format (' The current value of coef(',i2,') = ',1pe10.4,/,
```

```
     +          ' Type the desired new value; minus value to end')
         read   (nu,*) z(next)
C.... a "backdoor" exit with filesave is provided here for user to manually
C.... set any coefficient to a MINUS value.  Use it in good health.
         if     (z(next))   615,613,614
  613 z(next) = da(next)*x(next)
         go to 607
  614 da(next)= z(next)
         x(next) = 0.0
         write  (nu,3024)
 3024 format (' Type ''#'' of another coefficient you wish to reset,',
     +       /,'    a ''11'' to see fit with reset coefs, or',
     +       /,'    a ''0'' to reoptimize from here,'  )
         read   (nu,*) next
         next = next +1
         go to (619,612,612,612,612,612,612,612,612,612,612,605), next


  615 z(next) = da(next)*x(next)
         nruns    = nruns+1
         write  (nx,2002)  spec
         write  (nx,2002) (comm(i),i=1,ncomc)
         write  (nx,2003) lox,z(9),z(10)
         write  (nx,2004) nsam,nruns,(pdif(k),k=1,nres),(adif(k),k=1,nres)
         write  (nx,2002) (data(i),i=1,nsam),
         write  (nx,2006) (z(j),j=1,maxc)
         next = 0
         CALL RP1  (   z,ncoef,dpa,res,nsam,nres,nart,ndset,next,1file)
         CALL TELL (da,z,ncoef,dpa,res,nsam,nres,nart,ndset,next,1file,
     +          adif,pdif)
         go to 2


  619 next = 1
         DO 620 j = 1,ncoef
  620 if (x(j) .ne. 0.0) da(j)=da(j)*x(j)
         go to    37


C.... A few notes on the logic of "next"
C       initially set next = 1 at line 36+7.
C       in RP1  line 130+2: if next=0 (and other conditions) the plot is copied
C                       onto file NO for later examination.
C       in TELL line 1+2: unless next=0, results will not be written to file NO;
C             line 96: if next=0, model error is not typed to the screen (in
C                       otherwords, next should = 0 only on last pass thru TELL)
C       in REPA line 607+1: read next from screen, i1, therefore -1<next<10;
C                   607+2: next=next+1 and used in computed goto;
C         if next=0, next reset=0,
C                   call TELL (for final output),
C                   goto 20 and on to 36+7 as initially run;
C         if 0<next<9, a new coefficient is specified by user, and
C                   next is reread at line 614+2 (similarly to 607+1 above);
C                   here if next=0, program is routed thru RP1 and TELL with
C                   next=1 without resetting any other parameters, cf. below;
C....     if next=9, line 619: next=1, goto    37 to continue optimization.
30000 STOP 'Have a good day'
         END
```

```
C.................................................................
      subroutine units (res,sd,nsam,nres,unit,sides,crop)
C.... to convert residue units to ug/cm2 and 1-side (projected area)
C        unit   = units reported
C                 blank/default = ug/cm2
C                 1      = ng/cm2      3 = ppm
C                 2      = mg/m2       4 = other
      integer     sides, unit
      real        res(15,3), sd(15,3)
      character*6 crop

      if (unit .eq. 0) go to 17
        do 16 k=1,nres
          do 15 j=1,nsam
            if (unit.gt.1) go to 12
            res(j,k) = res(j,k)/1000.
            go to 15
 12         if (unit.gt.2) go to 13
            res(j,k) = res(j,k)/10.
            go to 15
 13         if (unit.gt.3) go to 20
            call conppm (res,sd,crop,unit,nsam,nres)
 15         continue
 16       continue
 17   if (sides.ne.2) go to 20
        do 19 k=1,nres
          do 18 j=1,nsam
            res(j,k) = res(j,k)*2.
 18         continue
 19       continue
 20   continue
      return
      end
C.................................................................
      Subroutine conppm (res,sd,crop,unit,nsam,nres)
C.... to convert ppm to ng/cm2
      integer     unit
      dimension   res(15,3), sd(15,3)
      character*6 crop
C.... for now, hand calc...
      write (nu,*) ' residue data must be converted from ppm'
      unit = 9
      return
      end
C.................................................................
      subroutine tx (da,dpa,res,nsam,nres,ncoef)
C.... to provide preset guesses into DA as a first starting point
C     if the coefficients in input datafile were zero (previously
C     estimated coefficients will be used after the first dset), and
C.... to copy dpa and residue data into remaining DA array expected by ROSE;
C     in the process, it is assumed that any dpa=0 (exactly) can in reality
C     be no less than 0.1 (or two hours post application).

      real da(120),dpa(15),res(15,3),wag(10)
      data wag/1.,.3,.3,.3,.05,.1,.3,.05,.05,.1/
```

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```fortran
      if (da(1) .ne. 0.0) go to 20
      do 10  k = 1,ncoef
      da(k)    = wag(k)
   10 continue
   20 do 30  j = 1,nsam
      k        = ncoef+1+((1+nres)*(j-1))
      da(k)    = dpa(j)
      do 30  i = 1,nres
      da(k+i)  = res(j,i)
   30 continue
      if (dpa(1) .eq. 0.0) da(ncoef+1)=0.1
      return
      end
C....................................................................
      FUNCTION  F(X,DA,N,NinDA,NIV,dpa,res,nres,nsam)
      DIMENSION X(10),DA(120),A(10),dpa(15),res(15,3)
      DO 2 I = 1,N
      A(I)    = DA(I)*X(I)
    2 CONTINUE
      FX      = 0.
C>>>>>USER WORKING AREA...........<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
   27 CONTINUE
      A23     = a(2)+a(3)
      A234    = A23 +a(4)
      A56     = a(5)+a(6)
      A78     = a(7)+a(8)
      A1x3    = a(1)*a(3)
      A13d6   = A1x3/(A56-A234)
      A1x4    = a(1)*a(4)
      A14d8   = A1x4/(A78-A234)
      if (nres .gt. 3) STOP 'NRES error in FUNCTION F'
      DO 70 i= 1,nsam
      di      = dpa(i)
      if (dpa(i) .eq. 0.0) di=0.1
      go to (55,53,51),nres
   51 Stop 'No model is provided for 2 metabolites!'
   53 F2      =                (A14d8*(exp(-A234*di)-exp(-A78 *di)))      X1
     + +(((a(7)*A14d8)+(a(6)*A13d6))*(exp(-A234*di)-exp(-a(9)*di))/
     +                                           (a(9)-A234)) X2
     + +(((a(7)*A14d8/(a(9)-A78)))  *(exp(-A78 *di)-exp(-a(9)*di)))      X2
     + +((a(6)*(a(10)-A13d6))       *(exp(-A56 *di)-exp(-a(9)*di))/
     +                                           (a(9)-A56))  X2
      IF (res(i,2) .gt. 0.0 .and. F2 .gt. 0.0)
     +    FX = FX + exp(ABS(alog(res(i,2)/F2))) -1.

   55 F1      = (a(1) *exp(-A234*di))
     + +   (A13d6*exp(-A234*di)) + ((a(10)-A13d6)*exp(-A56*di))
      IF (res(i,1) .gt. 0.0 .and. F1 .gt. 0.0)
     +    FX = FX + exp(ABS(alog(res(i,1)/F1))) -1.
   70 continue
C>>>>>USER WORKING AREA...........<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
    1 CONTINUE
      F  = FX
      RETURN
      END
```

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```
C...................................................................
      FUNCTION CX(X,DA,N,NinDA,K)
      DIMENSION X(10), DA(120)
      CX = X(K)
      RETURN
      END
C...................................................................
      FUNCTION CG(X,DA,N,NinDA,K)
      DIMENSION X(10),DA(120)
      CG = 0.0
      RETURN
      END
C...................................................................
      FUNCTION CH(X,DA,N,NinDA,K)
C.... to limit the upper bounds of X
      DIMENSION X(10),DA(120)
      GO TO (10,10,50,50,100,50,100,10,50,10),K
   10 CH = 10.
      RETURN
   50 CH = 50.
      RETURN
  100 CH = 100.
      RETURN
      END
C...................................................................
      SUBROUTINE RP1 (a,ncoef,x,yor,nsam,nres,nart,ndset,next,lfile)
      character*1 MARK(8), LINE(62,16)
      real x(15),y(15,3),yor(15,3),a(10),vx(7)
      logical lfile
C....               1    2    3    4    5    6    7    8
      DATA MARK/'+','o','#',' ','*','.','-','x'/
      TLOG(X)=ALOG(X)/2.30258

      NU   = 0
      NO   = 3
C.... on the last pass thru RP next will = 0,
C.... resulting in plot printed onto 'output' instead of user screen.
      if (( next .eq. 0) .and. lfile ) nu = no
C.... line marks for Blank, Asterisk, Dot, hyphon, etc.
      LB   = 4
      LA   = 5
      LD   = 6
      LH   = 7
      LT   = 8
C.... limits of vertical Y axis and horizontal X axis are set and arrays + 1
      lx   = 50
      ly   = 15
      lpx  = lx+1
      lpy  = ly+1

      WRITE (nu,205) nart, ndset
  205 FORMAT (//,' PLOT: article',i3,',  set ',i2,
     +': Parent  1st-Metab. 2nd-Metab.     Other',/,11x,
     +'SYMBOLS Measured:    +          o           #       * = Overlay',/
     +,19x,  'Modelled:    -          .           x       x = initial +')
```

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```
C.... the following finds max and min (greater than zero) residues reported
      YMAX    = -1.0E30
      YMIN    = 1.0E30
      DO 47 L = 1,nsam
      DO 47 M = 1,nres
      y(1,m)  = 0.0
      if (yor(1,m) .le. 0.0) go to 47
      y(1,m)  = tlog(yor(1,m))
   43 IF (y(1,m) .gt. YMAX) YMAX = y(1,m)
   45 IF (y(1,m) .lt. YMIN) YMIN = y(1,m)
   47 CONTINUE
      yy      = tlog(a(1)+a(7))
      if (yy .gt. YMAX)      YMAX = yy

      xll     = 0.
      xul     = fnext2(x(nsam))
      YUL     = FLOAT(IFIX(YMAX+1.))
      YLL     = FLOAT(IFIX(YMIN))
      if (YMIN .lt. 0.0)     YLL = YLL-1.
C.... we want yul-yll to be either 1,3,or5 orders-of-magnitude (logs of Y)
C.... to be spaced conveniently on the screen.
   50 logy    = ifix(yul-yll+.0001)
   51 if (logy - 1)                    54,59,52
   52 if (logy - 3)                    54,60,53
   53 if (logy - 5)                    54,60,59
   54 IF (ABS(YUL-YMAX)-ABS(YMIN-YLL)) 55,57,57
   55 YUL     = YUL+1.
   56 GO TO 50
   57 YLL     = YLL-1.
   58 GO TO 50
   59 logy    = 5
   60 continue
      kl      = ly/logy

      YI      = (YUL-YLL)/ly
      XI      = (XUL-XLL)/lx
   63 continue
C....  .   .   .   .   .   .   .   .   .   .  .   .   .   .   .   .   .   .
C     The following bigins plotting array "line"
C     with i subscript for row
C           j subscript for column
C           k index  for X and Y labels
C           L subscript for samples
C           M subscript for residues within samples
C     characters start blank
C     borders are added (dots and pluses) in lines 64-68
C     reported data are scanned and added in lines 68-91
C     the model is run and dots are added when in plot in lines 91-110
C         MARK   1   2   3   4   5   6   7   8
C....           '+','o','#',' ','*','.','-','x'

      DO   64 I = 1,lpx
      DO   64 J = 1,lpy
      LINE(I,J) = MARK(LB)
```

```
   64 CONTINUE
      DO    65 I   = 1,lpx
      LINE(I,1)  =  MARK(LD)
      LINE(I,lpy)=  MARK(LD)
   65 continue
      DO    66 I  = 1,lpx,5
      LINE(I,1)  =  MARK(1)
      LINE(I,lpy)=  MARK(1)
   66 continue
      DO    67 J  = 1,lpy
      LINE(1,J)  =  MARK(LD)
      LINE(lpx,J)=  MARK(LD)
   67 continue
      DO    68 J  = 1,lpy,k1
      LINE(1,J)  =  MARK(1)
      LINE(lpx,J)=  MARK(1)
   68 continue
C.... mark the model initial parent with an x
      yy         = (yy-YLL)/YI
      J          = lpy-ifix(round(yy,0))
      LINE(1,J)  =  MARK(LT)

      DO  91 L   = 1,nsam
      xx         = (x(L)-XLL)/XI
      I          = 1 + ifix(round(xx,0))
      if ((I .lt. 1) .or. (I .gt. lpx)) go to 91
      DO  90 M   = 1,nres
      if (yor(L,M) .le. 0.0) go to 90
      LM         = M
      vy         = (y(L,M)-YLL)/YI
      J          = lpy-ifix(round(yy,0))
      if ((J .lt. 1) .or. (J .gt. lpy)) go to 90
      IF (LINE(I,J) .ne. MARK(LB)) LM=LA
      LINE(I,J)  = MARK(LM)
   90 continue
   91 continue


C.... find values of model
C....    DI = x interval (i.e. day post-application)
C....    PYn = plotted value of model at DI
   27 CONTINUE
      A23  = a(2)+a(3)
      A234 = A23 +a(4)
      A56  = a(5)+a(6)
      A78  = a(7)+a(8)
      A1x3 = a(1)*a(3)
      A13d6= A1x3/(A56-A234)
      A1x4 = a(1)*a(4)
      A14d8= A1x4/(A78-A234)
      DO 110 I = 1,lpx
      DI   = XI*FLOAT(I-1)
      go to (155,153,151),nres
  151 Stop 'No model is provided for 2 metabolites!'
  153 F2   =              (A14d8*(exp(-A234*di)-exp(-A78 *di)))        X1
     + +(((a(7)*A14d8)+(a(6)*A13d6))*(exp(-A234*di)-exp(-a(9)*di))/
```

```
      +                                                  (a(9)-A234))  X2
      + +(((a(7)*A14d8/(a(9)-A78)))  *(exp(-A78 *di)-exp(-a(9)*di)))   X2
      + +((a(6)*(a(10)-A13d6))       *(exp(-A56 *di)-exp(-a(9)*di))/
      +                                                  (a(9)-A56))   X2   371
  155 F1  = (a(1) *exp(-A234*di))
      + +    (A13d6*exp(-A234*di)) + ((a(10)-A13d6)*exp(-A56*di))
      if (F1 .le. 0.0) go to 100
      PY1 = TLOG(F1)
      yy  = (PY1-YLL)/YI
      J   = lpy-ifix(round(yy,0))
      if ((J .lt. 1) .or. (J .gt. lpy)) go to 100
      IF (LINE(I,J) .eq. MARK(LB)) line(I,J) = mark(LD)
  100 if (DI .le. 0.0 .or. F2 .le. 0.0) go to 110
      PY2 = TLOG(F2)
      yy  = (PY2-YLL)/YI
      J   = lpy-ifix(round(yy,0))
      if ((J .lt. 1) .or. (J .gt. lpy)) go to 110
      IF (LINE(I,J) .eq. MARK(LB)) line(I,J) = mark(LH)
  110 CONTINUE
  111 CONTINUE

      k   = kl-1
      nkl = 0                                                          !
C.... DUMMY K STARTS=kl-1 AND PUTS unit labels
C.... ON EVERY  3RD or 5TH Y, AND 10TH X
      DO 125  J = 1,lpy
      k   = k+1
      if (k-kl)            121,123,121
  121 if (J .le. ncoef+nkl) go to 122                                  !
      WRITE  (nu,206) (LINE(I,J),I=1,lpx)
      go to 125
  122 nc  = j-nkl                                                      !
      WRITE  (nu,209) (LINE(I,J),I=1,lpx),nc,a(nc)                     !
      go to 125                                                        !
C.... VY IS MANTISSA AND iPY IS CHARACTERISTIC ON BASE 10 LOG (TLOG)   !
  123 k   = k-kl
      nkl = nkl + 1                                                    !
      YY  = YLL + (float(lpy-j)*yi)
      iPY = IFIX(ROUND(YY,0))
      VY  = 10.**(YY-iPY)
      VY  = ROUND(VY,2)
      WRITE  (nu,207) VY,iPY,(line(I,J),I=1,lpx)
  125 CONTINUE
  206 FORMAT (1H ,12X,61A1)
  209 FORMAT (1H ,12X,51A1, 2x,'A',I1,'=',e10.4)                       !
  207 FORMAT (1H ,1X,F5.2,' E',I3,1x,61a1)
      DO 130 I = 1,7
      VX(I)      = XLL+(XI*10.*float(I-1))
      VX(I)      = ROUND(VX(I),1)
  130 CONTINUE
      WRITE  (nu,208) (VX(I),I=1,6)
  208 FORMAT (1H , 4X,7(5x,F5.1))
  150 RETURN
      END
```

```
      function fnext2 (x)
C.... to find the next smallest multiple of x among 2,4,6,8,or10x
      xd      = (10.**ifix(alog10(x)))
      do 1 n = 1,5
      fnext2 = 2.*float(n)*xd
      if (fnext2 .ge. x) go to 2
    1 continue
    2 return
      end
C.....................................................................
      function round(r,i)
C.... where r=number to be rounded and
C....       i=intergers remaining after decimal
      round = 0.0
      n      = 1
      r0     = 10.**i
      if (i .eq. 0)          r0 = 1.
      if (r)                 11,9,1
   11 n      = -1
    1 r1     = r*r0*float(n)
    2 i1     = ifix(r1)
    3 r2     = r1-float(i1)
    4 if (r2-0.5)            8,5,7
    5 r3     = float(i1)/2.
    6 if (r3-ifix(r3)-.25)   7,7,8
    7 i1     = i1+1
    8 round = float(i1*n)/r0
    9 return
      end
C.....................................................................
      SUBROUTINE TELL (da,a,ncoef,dpa,res,nsam,nres,nart,ndset,next,
     +                 lfile,adif,pdif)

C.... ROUTINE WILL LIST PREDICTED POINTS AND COMPARE THEM TO INPUTS
C.... IT IS IDEALLY SUITED TO TIME SERIES DATA IN WHICH TIME IS FIRST
C.... USER MUST SUPPLY DEFINITIONS OF F1, F2, F3, IN USER'S WORKING AREA

      DIMENSION X(10), DA(120), A(10), dpa(15), res(15,3)
      integer nnzr(3)
      real pred(3),dif(3),pdif(3),chi2(3),adif(3)
      logical lfile,lhold,match

      nu      = 0
      NO      = 3
      do 1 i  = 1,nres
      PDIF(i) = 0.
      CHI2(i) = 0.
      ADIF(i) = 0.
      nnzr(i) = 0
    1 CONTINUE

C.... a Holding status is introduced into file to hold printing of model results
C.... until the last pass through TELL.
      lhold = lfile
```

```
        if (next .ne. 0) lfile = .false.
        if (.not. lfile) go to 23
        WRITE (NO,100)
    100 FORMAT (/,' MODEL RESULTS',7('.'),'parent',12('.'),1x,12('.'),
       +          'metabolite(s)',10('.'),'>',
       + /,' TIME   ',2(   9HPREDICTED,2X,8HMEASURED,3X,9HPCT.DIFF.),
       + /,' days',   2(5x,'ug/cm2',4x,'ug/cm2',8x,'%',1x))
C.... format 100 will currently only accept 2 residues; 3 OK on wide paper.

     23 CONTINUE
        list   = 61
C.... PROGRAM REQUIRES INPUT DATA TO BE CHRONOLOGICALLY ORDERED
C.... lastd SET AT 1.5 TIMES THE LAST INPUT TIME
C.... but list of days shall not exceed 61
        lastd  = IFIX(dpa(nsam)*1.5)
        NT     = 1
     15 IF ((lastd/NT)-list)  17,17,16
     16 NT     = 2*NT
        GO TO 15
     17 CONTINUE

        i      = 0
        A23    = a(2)+a(3)
        A234   = A23 +a(4)
        A56    = a(5)+a(6)
        A78    = a(7)+a(8)
        A1x3   = a(1)*a(3)
        A13d6  = A1x3/(A56-A234)
        A1x4   = a(1)*a(4)
        A14d8  = A1x4/(A78-A234)
C.... This is a BIG 'double' (i and j) do loop down to line 90
        DO 90 j=NT,lastd,NT
     18 match  = .false.
        DI     = FLOAT(j-NT)
        if (i+1 .gt. nsam) go to 20
        if (dpa(i+1) .gt. float(j)-(.5*float(nt))) go to 20
        i      = i+1
        DI     = dpa(i)
        if (dpa(i) .eq. 0.0) di=0.1
        match  = .true.
     20 CONTINUE
C>>>>>THIS IS THE USER'S WORKING AREA...<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
C>>>>>WITHIN ITS BOUNDS, DEFINE pred(1)=OP, pred(2)=metabolite, etc.<<<<
     27 CONTINUE
        go to (55,53,51),nres
     51 Stop 'No model is provided for 2 metabolites!'
     53 F2        =                  (A14d8*(exp(-A234*di)-exp(-A78 *di)))      X1
       + +(((a(7)*A14d8)+(a(6)*A13d6))*(exp(-A234*di)-exp(-a(9)*di)))/
       +                                               (a(9)-A234))  X2
       + +(((a(7)*A14d8/(a(9)-A78)))   *(exp(-A78 *di)-exp(-a(9)*di)))      X2
       + +((a(6)*(a(10)-A13d6))        *(exp(-A56 *di)-exp(-a(9)*di))/
       +                                               (a(9)-A56))   X2
        pred(2) = F2

     55 F1        = (a(1) *exp(-A234*di))
```

```
      + +    (A13d6*exp(-A234*di)) + ((a(10)-A13d6)*exp(-A56*di))
         pred(1) = F1
```

C.... THIS model WAS DEVELOPED TO ESTIMATE 7 COEFFICIENTS

```
C        PARENT     P. =      P1 +      P1
C            d(P)/d(t) = -(a2+a3+a4)*P1 + (a3*P1) - (a5+a6)*P2
C        METABOLITE X =      X1 +      X2
C            d(X)/d(t) =  a4*P1 + a6*P2 + (a3*X1) - a2*X1 - a5*X2
C
C        AT  t = 0.
C        P1(0) = A1
C        P2(0) = A7
C        X1(0) = X2(0) = 0.
C        TO model parent only, SET DA(4)=0.0
C                                   DA(6)=0.0
C>>>>>THIS IS THE END OF THE USER'S WORKING AREA...<<<<<<<<<<<<<<<<<<<<<<
   80 CONTINUE

         if (.not. match) go to 86
C.... the following composite values are determined and reported
C.... pdif = percent error in observed over expected
C.... chi2 = sum of squares of dif (Chi-squared)
C.... adif = percent absolute error in observed over expected
         do 82 k = 1,nres
         if      (res(i,k) .eq. 0.0) go to 82
         if      (pred(k)  .le. 0.0) go to 82
         dif(k)  = (pred(k)- res(i,k))/pred(k)
         chi2(k) = chi2(k) + (dif(k)**2)
         dif(k)  = dif(k) * 100.
         pdif(k) = pdif(k) + dif(k)
         adif(k) = adif(k) + abs(dif(k))
         nnzr(k) = nnzr(k) + 1
   82 CONTINUE

         if      (.not. lfile) go to 18
         WRITE  (NO,102) di,(pred(k),res(i,k),dif(k),k=1,nres)
  102 FORMAT ( F7.2,2x,3(:,1pe9.3,2x,1pE9.3,1X,0pf7.2,3x))
         go to 18
   86 if      (.not. lfile) go to 90
         WRITE  (NO,101) DI,(pred(k),k=1,nres)
  101 FORMAT (F7.2,2x,3(:, 1pE9.3,:,22X))
   90 CONTINUE

         do 92 k = 1,nres
         if      (nnzr(k) .le. 0) go to 92
         pdif(k) = pdif(k)/FLOAT(nnzr(k))
         adif(k) = adif(k)/FLOAT(nnzr(k))
   92 CONTINUE

         if      (.not. lfile) go to 96
         WRITE  (NO,103) (chi2(k),k=1,nres)
         WRITE  (NO,104) (pdif(k),k=1,nres)
         WRITE  (NO,105) (adif(k),k=1,nres)
  103 FORMAT (/,14X,          'CHI SQUARE = ',2x,3(1pE10.3,:,20X))
  104 FORMAT (  8X,   'MEAN   %   ERROR = ',    3(2pE12.4,:,18x))
```

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```fortran
105 FORMAT (   8X,    'MEAN % ABS ERROR = ',   3(2pE12.4,:,18X))

 96 if      (next .eq. 0) go to 98
    write  (nu,106) (k,pdif(k),k=1,nres)
106 format (' MEAN  %  ERROR: Res(',i1,')=',f6.1,
   +                    2(:,' Res(',i1,')=',f6.1))
    write  (nu,107) (k,adif(k),k=1,nres)
107 format (' MEAN ¦%¦ ERROR: Res(',i1,')=',f6.1,
   +                    2(:,' Res(',i1,')=',f6.1))

 98 lfile = lhold
    RETURN
    END
C................................................................
    subroutine yes (letter,choice)
    character*1 letter
    logical choice
    choice = .false.
    if (letter .eq. 'y') choice = .true.
    if (letter .eq. 'Y') choice = .true.
    return
    end
```

375

Appendix G: Computer Program to Standardize Residues and Tabulate Responses   376
          Using the Unified Field Model.
          A short description of each symbol is given at the end of this ·
          appendix (see also Appendix C).

```
      program REEN

c.... version 3 (to create a one-line/sample file containing
c          chem,nart,ndset,loc,crop,aia and form [as spec1],
c          dpa,(res(i),i=1,4),den,dAChE,kdcom,ldass

c**********************************************************************c
c                                                                    c
c     Purpose: To estimate AChE inhibition [optionally for a         c
c              given crop and pesticide] for a given level(s) of     c
c              residue.  Estimations are determined using the        c
c              'unified field model':                                c
c                                                                    c
c              A compilation of dislodgeable foliar residue          c
c              studies serves as the data base, along with           c
c              various other coefficient and toxicity files.         c
c                                                                    c
c     Dose:   D = kd*t*R/m                                           c
c               where D    = dose, mg/kg                             c
c                     kd   = crop specific dosing constant           c
c                     t    = duration of exposure (hrs)              c
c                     R    = residue, ug/cm2                         c
c                     m    = body mass, = 70 kg (50 %ile man)        c
c                                                                    c
c     Response: dAChE = 1 - exp(-ke*D/LD50)                          c
c               where dAChE = a fraction (%/100) of RBC cholinesterase c
c                               inhibited                            c
c                     LD50 = acute toxicity, mg/kg                   c
c                     ke   = enzyme constant, = 6.0                  c
c                                                                    c
c                                                                    C
c**********************************************************************c
      integer     ex, unit, dapp, yapp,
     +            file0, file1, file2, file3, file4, file5, file6
      real        dpa(30),res(30,4),sd(30,4),LD50(4),dAChE(30),kd,leafd
      character*1 file,den,kdcom
      character*3 loc, locrq,  mapp
      character*4 form
      character*6 crop,croprq
      character*8 chem,chemrq
      character*12 input,output,spec1
      character*20 cropname
      character*25 chemname(4),comname
      character*30 lox(3)
      character*79 comm(6)
      logical     crmat,chmat
```

```
c.... file 1 = user screen and console...format 1000 series reserved I/O.
c            (PC assumes this device to be "0")
c.... file 2 = pesticide residue data base (filename =  'INPUT')
c            (filename specified by user)
c.... file 3 = the output file          ( "      = 'OUTPUT')
c            (filename specified by user)
c.... file 4 = crop coefficient library    ( "      = 'cropco.lib')
c.... file 5 = chemical coefficient library ( "      = 'chemco.lib')

      file0=0
      file2=2
      file3=3
      file4=4
      file5=5
      file6=6


c     limits set for max number of requested effects (array), coefficients,
c     number of samples and residues within each sample.
      maxr   = 4
      maxs   = 30
      crmat  = .false.
    1 continue

      DO 3 i = 1,maxs
         DO  2  j = 1,maxr
            res(i,j) = 0.0
            sd(i,j)  = 0.0
            ld50(j)  = 0.0
    2       continue
    3    continue

      chmat  = .false.
      write  (file0,1003)
 1003 format (' Type residue INPUT filename, up to 12 characters:')
      read   (file0,1004) input
 1004 format (a12)
      if     ((input .eq. 'quit').or.(input .eq. 'exit').or.
     +        (input .eq. 'stop').or.(input .eq. 'end')) goto 30000

      open   (file2, file = input)
      open   (file4, file='cropco.lib')
      open   (file5, file='chemco.lib')
      rewind file2
      rewind file4
      rewind file5


    5 continue
      write  (file0,1005)
 1005 format (' A specific chemical (coded) can be requested;',/,
     +        ' type chemical (a8) or ''all'' for all crops:')
      read   (file0,1006) chemrq
 1006 format (a6)
      write  (file0,1007)
 1007 format (' A specific location (coded) can be requested;',/,
```

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```
      +          ' type location (a3) or ''all'' for all locations:')
           read  (file0,1008) locrq
 1008 format (a3)
           write (file0,1009)
 1009 format (' A specific crop (coded) can be requested;',/,
      +          ' type crop (a6) or ''all'' for all crops:')
           read  (file0,1010) croprq
 1010 format (a6)

           write (file0,1011)
 1011 format (' Type data OUTPUT filename, up to 12 characters:')
           read  (file0,1004) output
           write (file0,1012)
 1012 format (' Type 0 to show input data on screen',/,
      +          '   or 1 to exclude this option:')
           read  (file0,1013) file1
 1013 format (i1)
           if    (file1 .eq. 0) goto 7
           open  (file1)
           rewind file1
    7 open  (file3, file = output, status='new')
           rewind file3

c.... READ DATA SPECIFICATION FILE ...................................
   51 read  (file2,2001,end=85) chem,nart,ndset,nox,loc,crop,igraph,
      +form,aia,gpa,ex,unit,nsides,dapp,mapp,yapp,ncomm,npunpr,isd
 2001 format(a8,1x,2(I2,1x),i1,1x,a3,1x,a6,1x,i1,1x,a4,1x,f5.2,1x,f4.0,
      +        1x,3(i1,1x),i2,1x,a3,1x,i2,1x,i1,1x,i3,1x,i1)
           write (file1,2001        ) chem,nart,ndset,nox,loc,crop,igraph,
      +form,aia,gpa,ex,unit,nsides,dapp,mapp,yapp,ncomm,npunpr,isd
           backspace file2
           read  (file2,2011) spec1
 2011 format(34x,a12)
           call chemck (chem,noxa,1d50,chemname,comname,chmat,file5)
c.... the above subroutine searches to match chemical with data in chemco file
           nres = nox + 1
           ldass = 0

c.... reading up to 6 comment lines
   52 if    (ncomm .le. 0) goto 53
           read  (file2,2002,end=9002) (comm(i),i=1,ncomm)
           write (file1,2002)          (comm(i),i=1,ncomm)
 2002 format(a79)

c.... reading the name of the oxons or other metabolites
   53 if    (nox .le. 0) goto 54
           read  (file2,2003,end=9003) (lox(i), i=1,nox)
           write (file1,2003)          (lox(i), i=1,nox)
 2003 format(a30)

c.... reading the number of samples in the following set of data
   54 read  (file2,2004,end=9004) nsam
           write (file1,2004)          nsam
 2004 format(i2)
```

```
c.... reading residue data ...
        if      (nsam .le. 0) goto 56
        DO 55 j=1,nsam
            read  (file2,2005,end=9005) dpa(j),(res(j,k),sd(j,k),k=1,nres)
            write (file1,2005)          dpa(j),(res(j,k),sd(j,k),k=1,nres)
    55      continue
  2005 format(f4.0,1x,8(f6.0,1x))


C.... QC-tolerance checks follow (line 56 to line 71):
    56 continue
        if      (chemrq .ne. chem .and. chemrq .ne. 'all      ') goto 51
        if      (croprq .ne. crop .and. croprq .ne. 'all    ' ) goto 51
        if      (locrq  .ne. loc  .and. locrq  .ne. 'all'     ) goto 51
        if      ( nox   .gt. noxa) goto 9015
        if      ( nres  .gt. maxr) goto 9016
        if      ( nsam  .gt. maxs) goto 9017
        if      (.not. chmat)      goto 9018
        if      (1d50(1) .le. 0.0) goto 9019
        if      (nox .le. 0) goto 64
        do 58 k=2,nres
            if (1d50(k) .ne. 0.0) goto 58
            write  (file0,1021) chemname(k),nart,ndset
  1021      format (' The LD50 for ',a25,' in article ',i2,' data set ',i2,
        +          /,' is unknown but assumed = parent.')
            ldass = ldass + 1
            1d50(k)=1d50(1)
    58      continue


    64 kdcom = ' '
        call cropck (crop,kd,cropname,leafd,den,crmat,file4)
c.... the above subroutine searches to match crop with data in cropco file
        if      (.not. crmat) goto 9028
    65 if      (kd .ne. 0.0) goto 66
        write (file0,1026) crop,nart,ndset
  1026 format(' Dosing coefficient (kd) for ',a6,' in article ',i2,
        +' dataset ',i2,/, '  not listed in cropco library! Default value =
        + 5000 cm2/hr.')
        kd = 5.0
        kdcom = '?'
    66 continue


    70 call units (res,sd,nsam,nres,unit,nsides,crop,leafd)
c.... above subroutine to convert to ug/cm2 projected area
c     units may be nonstandard and must be individualy converted.
        if      (unit  .ge.   4) goto 9014
        if      (leafd .le. 0.0) goto 9029


    71 call dosres (dpa,res,LD50,dAChE,nres,nsam,kd)
c.... above subroutine to convert from residue to dose and AChE...
```

```
C.... the following write statements create the modified (one-line)
C     "output" file
      DO 75 j=1,nsam
C                                    spec1 equivalent to :aia:gpa:
         write (file3,3005) chem,nart,ndset,loc,crop,spec1,
     +                      dpa(j),(res(j,k),k=1,maxr),den,dAChE(j),
     +                      kdcom,ldass
c....                V        V        V <-- potentially removable delimiters
 3005 format(a8,':',2i2,':',a3,a6,a12,f4.1,':',
     +       4(f6.3,':'),a1,f7.3,a1,i1)
         do 74 k=1,maxr
C           arrays reset to avoid carry-over of "oxon" values between data sets
         res(j,k) = 0.0
         sd(j,k)  = 0.0
 74         continue
 75      continue
      goto 51

 85   write (file0,*) 'Reading end of requested chem.-input datafile.'
      goto 1


C.... The following lines are various error and data-set reject modes:
 9002 write (*,*) ' Unexpected End-of-file while reading comment lines!'
      goto 1
 9003 write (*.*) ' Unexpected End-of-file while reading "oxon" lines!'
      goto 1
 9004 write (*,*) ' End-of-file while reading number-of-samples lines!'
      goto 1
 9005 write (*,*) ' End-of-file while reading sample-data lines!'
      goto 1
 9014 write (file0,1014) nart, ndset
 1014 format(' Nonstandard units in article ',i2,' dataset ',i2,/,
     +       ' - no further calculations are made on this data.')
      goto 51
 9015 write (file0,1015) nart,ndset
 1015 format(' More metabolites in article ',i2,' dataset ',i2,
     +       ' than listed in chemco.')
      goto 1
 9016 write (file0,1016) nart,ndset,maxr
 1016 format('Metabolites in article ',i2,' dataset ',i2,' exceed array
     +limit of ',i1)
      goto 1
 9017 write (file0,1017) nart,ndset,maxs
 1017 format('Samples in article ',i2,' dataset ',i2,' exceed array limi
     +t of ',i2)
      nsam = maxs
      goto 64
 9018 write (file0,1018) chem,input,input
 1018 format(1x,a8,' as listed in ',a12,
     +' was not found within chemco library.',/,
     +' Please check ',a12,' for proper code or update chemco.lib.')
      goto 51
 9019 write (file0,1019) chem
 1019 format(1x,a8,' found within chemco library but without LD50!')
```

```fortran
 9028 write (file0,1028) crop
 1028 format(1x,a6,' not found within cropco library. Please check listi
     +ng for proper code.')
      goto 51
 9029 write (file0,1029) crop,nart,ndset
 1029 format(' Unable to convert ppm for ',a6,' in article ',i2,
     +         ' dataset ',i2,' to ug/cm2')
      goto 51

30000 STOP 'Have a good day'
      END
C................................................................
      subroutine units (res,sd,nsam,nres,unit,nsides,crop,leafd)
c ... to convert residue units to ug/cm2 and 1-side (projected area) values
C       unit  = units reported
C               0/blank = ug/cm2 [default]
C               1         = ng/cm2     3 = ppm
C               2         = mg/m2      4 = other
      integer     unit
      real        res(30,4), sd(30,4),leafd
      character*6 crop

      if (unit .eq. 0) goto 17
      do 16 k=1,nres
        do 15 j=1,nsam
          if (unit .gt. 1) goto 12
c....     to convert from ng/cm2
          res(j,k) = res(j,k)/1000.
          goto 15
   12     if (unit .gt. 2) goto 13
c....     to convert from mg/m2
          res(j,k) = res(j,k)/10.
          goto 15
   13     if (unit .gt. 3) goto 20
c....     to convert from ppm
          if (leafd .eq. 0.0) goto 20
          res(j,k) = res(j,k)*leafd/1000.
   15     continue
   16   continue
      unit = 0
   17 if (nsides .ne. 2) goto 20
c.... to convert from residues per 2 sides of a leaf
      do 19 k=1,nres
        do 18 j=1,nsam
          res(j,k) = res(j,k)*2.
   18   continue
   19 continue
      nsides = 1
   20 continue
      return
      end
C................................................................
```

```
      Subroutine cropck (crop,kd,cropname,leafd,den,crmat,file4)
c.... to find crop match and transfer pertinent parameters
      character*1  den
      character*6  .crop,code,stdcode
      character*20 cropname
 .    integer      file4
      logical      crmat
      real         kd,leafd

      crmat = .false.
      rewind file4
    1 read  (file4,4001,end=10) code,kd,cropname,leafd,den,stdcode
 4001 format(a6,5x,f4.1,7x,a20,2x,f4.1,a1,2x,a6)
      if (crop .ne. code) goto 1
      crmat = .true.
      crop  = stdcode
   10 return
      end
c.......................................................................
      Subroutine chemck (chem,noxa,ld50,chemname,comname,chmat,file5)
c.... to find chemical match and transfer pertinent parameters
      character*8  chem,code
      character*25 chemname(4),comname
      integer      file5
      logical      chmat
      real         ld50(4)

      chmat = .false.
      rewind file5
    1 read  (file5,5001,end=10) code,ld50(1),noxa,chemname(1),comname
 5001 format(a8,1x,f4.0,1x,i1,1x,a25,a25,2x,a1,1x,a1)
      if (chem .ne. code) goto 1
      do 3 i = 1,noxa
         read  (file5,5002,end=10)   ld50(i+1),   chemname(i+1)
 5002 format(   9x,f4.0,      3x,a25              )
    3    continue
    9 chmat = .true.
   10 return
      end
c.......................................................................
      Subroutine dosres (dpa,res,LD50,dAChE,nres,nsam,kd)
c.... to convert residue to dose (mg/kg) and dAChE (%) ...
      real dpa(30),res(30,4),LD50(4),dAChE(30),kd,mass
c.... kd   = crop specific dose rate, from cropco.lib file
c.... LD50 = dermal toxicity(s),      from chemco.lib file
c.... mass = 70 kg for 50%ile man
      mass = 70.
c.... workday = 8 hours
      work = 8.0
c.... ke   = enzyme constant = 6.0
      ke   = 6.0

      do 35 i=1,nsam
         sum = 0.0
```

```
      do 30 j=1,nres
        if (mass .eq. 0.0 .or. ld50(j) .eq. 0.0) write (*,*)
   +         mass, j, ld50(j)
        D=kd*work*res(i,j)/mass
        sum = sum + (D/ld50(j))
30      continue
      dAChE(i)=100.*(1.-exp(-ke*sum))
35    continue
      return
      end
```

c..

Name	Type	Variables use in main program REEN1
AIA	REAL	Active Ingredient per Acre
CHEM	CHAR	coded CHEMical name
CHEMNA	CHAR	full CHEMical NAme
CHEMRQ	CHAR	CHEMical ReQuested by user
CHMAT	LOGI	CHemical MATch
COMM	CHAR	COMMents (up to 6 lines)
COMNAM	CHAR	COMmon chemical NAMe
CRMAT	LOGI	CRop MATch
CROP	CHAR	coded CROP name
CROPNA	CHAR	full CROP NAme
CROPRQ	CHAR	CROP ReQuested by user
DACHE	REAL	delta AChE (%)
DAPP	INTE	Date of APPlication
DEN	CHAR	symbol for surety of leaf DENsity
DPA	REAL	Days Post-Application
EX	INTE	coded foliar residue EXtraction solvent
FILE0	INTE	input/output device
FILE1	INTE	input file on disk
FILE2	INTE	output file on disk
FILE3	INTE	input file on disk
FILE4	INTE	input file on disk
FILE5	INTE	input file on disk
FILE6	INTE	input file on disk
FORM	CHAR	FORMulation of parent chemical
GPA	REAL	Gallons mixture Per Acre applied
I	INTE	subscript
IGRAPH	INTE	code for Input data originally from a GRAPH or equation
INPUT	CHAR	INPUT file name
ISD	INTE	code designating statistical parameters on residues
J	INTE	subscript
K	INTE	subscript
KD	REAL	Dosing coefficient
KDCOM	CHAR	symbol for surety of Dosing coefficient
LD50	REAL	dermal Lethal Dose 50%
LDASS	INTE	number of metabolite LD50s assumed equal to parent
LEAFD	REAL	LEAF Density (mg/cm2)
LOC	CHAR	coded LOCation
LOCRQ	CHAR	coded LOCation ReQuested by user
LOX	CHAR	name of metabolites [Label of OXon]
MAPP	CHAR	Month of APPlication
MAXR	INTE	MAXimum number of Residues permitted by array definition

```
MAXS    INTE    MAXimum number of Samples permitted by array definition
NART    INTE    citation Number of ARTicle
NCOMM   INTE    Number of COMMent lines
NDSET   INTE    Number of DataSET within cited article
NOX     INTE    Number of metabolites (OXons) in study
NOXA    INTE    maximum Number of "OXons" Already in chemco.lib
NPUNPR  INTE    Number of PUNches within sample (if not nominal 48-60)
NRES    INTE    Number of RESidues reported in study [= NOX+1]
NSAM    INTE    Number of SAMples in study
NSIDES  INTE    Number of SIDES used to calculate ug/cm2
OUTPUT  CHAR    name of OUTPUT file
RES     REAL    RESidue values
SD      REAL    Standard or relative Deviation of residues
SPEC1   CHAR    dummy array to avoid write errors
UNIT    INTE    UNITs of residue reported
YAPP    INTE    Year of APPlication


C...............................................................
```

Appendix H: Compilation of Reported Residue and Calculated Response Data.

Tabulation format includes the chemical name (coded),   385
the article (citation) number, the study number
within the article (sequential), the location
(coded), crop (coded), application rate (lb AIA),
mixture (gallons/acre), the day post-application, 4
residues (ug/cm^2), an optional "?" when the residues
were converted from ppm with only estimated leaf
density, the calculated 8-hour cholinesterase
response (% dAChE), a second optional "?" for crops
for which the default dosing coefficient was assumed
(default = 5000 cm^2/hr), and a single digit
indicating the number of metabolites whose dermal
toxicity was _assumed_ equal to the parent.

```
azinme  :18 1:CAsOrange:06.00:0100: 3.0:20.200:  .078:  .000:  .000:  30.237 0
azinme  :18 1:CAsOrange:06.00:0100:10.0:11.400:  .066:  .000:  .000:  19.280 0
azinme  :18 1:CAsOrange:06.00:0100:17.0:10.600:  .106:  .000:  .000:  19.865 0
azinme  :18 1:CAsOrange:06.00:0100:31.0:10.400:  .090:  .000:  .000:  18.964 0
azinme  :18 1:CAsOrange:06.00:0100:44.0: 9.400:  .076:  .000:  .000:  17.088 0
azinme  :18 1:CAsOrange:06.00:0100:59.0: 7.600:  .012:  .000:  .000:  11.909 0
azinme  :18 2:CAsOrange:06.00:1200: 3.0: 9.200:  .000:  .000:  .000:  13.605 0
azinme  :18 2:CAsOrange:06.00:1200:10.0: 3.200:  .000:  .000:  .000:   4.960 0
azinme  :18 2:CAsOrange:06.00:1200:17.0: 2.600:  .000:  .000:  .000:   4.049 0
azinme  :18 2:CAsOrange:06.00:1200:31.0: 1.860:  .000:  .000:  .000:   2.913 0
azinme  :18 2:CAsOrange:06.00:1200:44.0: 2.000:  .000:  .000:  .000:   3.129 0
azinme  :18 2:CAsOrange:06.00:1200:59.0: 1.600:  .000:  .000:  .000:   2.511 0
azinme  :18 3:CAsOrange:02.00:0500: 3.0: 4.000:  .000:  .000:  .000:   6.161 0
azinme  :18 3:CAsOrange:02.00:0500:10.0: 1.400:  .000:  .000:  .000:   2.201 0
azinme  :18 3:CAsOrange:02.00:0500:17.0: 1.240:  .000:  .000:  .000:   1.952 0
azinme  :18 3:CAsOrange:02.00:0500:31.0:  .940:  .000:  .000:  .000:   1.483 0
azinme  :18 3:CAsOrange:02.00:0500:44.0:  .760:  .000:  .000:  .000:   1.201 0
azinme  :18 3:CAsOrange:02.00:0500:59.0:  .600:  .000:  .000:  .000:    .949 0
azinme  :18 4:CAsOrange:01.00:0500: 3.0: 1.560:  .000:  .000:  .000:   2.449 0
azinme  :18 4:CAsOrange:01.00:0500:10.0:  .600:  .000:  .000:  .000:    .949 0
azinme  :18 4:CAsOrange:01.00:0500:17.0:  .560:  .000:  .000:  .000:    .886 0
azinme  :18 4:CAsOrange:01.00:0500:31.0:  .400:  .000:  .000:  .000:    .634 0
azinme  :18 4:CAsOrange:01.00:0500:44.0:  .280:  .000:  .000:  .000:    .444 0
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azinme  : 2 2:CAvPeach :03.00:0100: 4.0: 5.800:  .000:  .000:  .000:? 3.376 0
```

```
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azinme  :51 6:CANApple :   . :   :35.0:  .600:  .000:  .000:  .000:?  .652 0
```

Appendix H, page 2

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```
azinme   :51 6:CANApple :  . :      :42.0:  .400:  .000:  .000:  .000:?  .435 0
azinme   : 3 1:AK Peach :00.75:0150:  .0:  .444:  .000:  .000:  .000:?  .263 0
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azinme   : 3 1:AK Peach :00.75:0150: 3.0:  .378:  .000:  .000:  .000:?  .224 0
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azinme   : 3 1:AK Peach :00.75:0150: 7.0:  .190:  .000:  .000:  .000:?  .112 0
azinme   : 3 1:AK Peach :00.75:0150:10.0:  .142:  .000:  .000:  .000:?  .084 0
azinme   : 3 1:AK Peach :00.75:0150:14.0:  .050:  .000:  .000:  .000:?  .030 0
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carbaryl: 3 1:AK Peach :01.50:0150: 1.0: 1.880:  .000:  .000:  .000:?  .061 0
carbaryl: 3 1:AK Peach :01.50:0150: 2.0: 1.040:  .000:  .000:  .000:?  .034 0
carbaryl: 3 1:AK Peach :01.50:0150: 4.0:  .015:  .000:  .000:  .000:?  .000 0
carbaryl: 3 1:AK Peach :01.50:0150: 5.0:  .019:  .000:  .000:  .000:?  .001 0
carbaryl: 3 2:AK Peach :01.50:0150:  .0: 2.070:  .000:  .000:  .000:?  .067 0
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carbop   :12 1:AZ Orange: 6.8 : 272: 1.0:24.904:  .356:  .372:  .094: 89.452 0
carbop   :12 1:AZ Orange: 6.8 : 272: 3.0:18.230:  .502: 1.138:  .342: 82.917 0
carbop   :12 1:AZ Orange: 6.8 : 272: 5.0:14.562:  .592: 1.500:  .676: 78.022 0
carbop   :12 1:AZ Orange: 6.8 : 272: 7.0:10.172:  .634: 1.544:  .858: 68.487 0
carbop   :12 2:AZ Orange:06.8 :0272:  .0:34.424:  .166:  .000:  .000: 95.140 0
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carbop   :35 2:FL Orange:0.375: 100:21.0:  .011:  .000:  .000:  .000:  .098 0
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carbop   :35 2:FL Orange:0.375: 100:35.0:  .005:  .000:  .000:  .000:  .042 0
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carbop   :35 3:FL Orange:00.75: 100: 5.0:  .021:  .000:  .000:  .000:  .180 0
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carbop   :35 3:FL Orange:00.75: 100:14.0:  .003:  .000:  .000:  .000:  .026 0
carbop   :35 4:FL Orange:00.75: 100:  .0:  .467:  .019:  .000:  .000: 4.153 0
carbop   :35 4:FL Orange:00.75: 100: 1.0:  .228:  .000:  .000:  .000: 1.972 0
```

```
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carbop  :35 4:FL Orange:00.75: 100: 5.0:  .081:  .000:  .000:  .000:    .709 0
carbop  :35 4:FL Orange:00.75: 100: 7.0:  .064:  .000:  .000:  .000:    .556 0
carbop  :35 4:FL Orange:00.75: 100:14.0:  .029:  .000:  .000:  .000:    .255 0
carbop  :35 4:FL Orange:00.75: 100:21.0:  .026:  .000:  .000:  .000:    .224 0
carbop  :35 4:FL Orange:00.75: 100:28.0:  .011:  .000:  .000:  .000:    .100 0
carbop  :35 4:FL Orange:00.75: 100:35.0:  .011:  .000:  .000:  .000:    .093 0
chlort  :18 1:CAsCitrus:00.80:0100: 3.0: 2.400:  .780:  .340:  .032:  19.279 3
chlort  :18 1:CAsCitrus:00.80:0100: 6.0:  .800:  .840:  .260:  .044:  11.061 3
chlort  :18 1:CAsCitrus:00.80:0100:10.0:  .360:  .440:  .164:  .050:   5.931 3
chlort  :18 1:CAsCitrus:00.80:0100:17.0:  .140:  .720:  .140:  .056:   6.169 3
chlort  :18 1:CAsCitrus:00.80:0100:24.0:  .150:  .600:  .116:  .064:   5.453 3
chlort  :18 1:CAsCitrus:00.80:0100:43.0:  .044:  .340:  .086:  .042:   3.040 3
chlort  :18 1:CAsCitrus:00.80:0100:59.0:  .000:  .134:  .000:  .000:    .805 3
dial    :25 1:CAvGrapes:01.00:0025:  .0: 3.800:  .000:  .000:  .000:   7.091 0
dial    :25 1:CAvGrapes:01.00:0025: 1.0: 3.200:  .000:  .000:  .000:   6.006 0
dial    :25 1:CAvGrapes:01.00:0025: 3.0: 3.140:  .000:  .000:  .000:   5.896 0
dial    :25 1:CAvGrapes:01.00:0025: 7.0: 2.540:  .000:  .000:  .000:   4.797 0
dial    :25 1:CAvGrapes:01.00:0025:14.0: 1.860:  .000:  .000:  .000:   3.536 0
dial    :25 1:CAvGrapes:01.00:0025:21.0: 1.260:  .000:  .000:  .000:   2.409 0
dial    :25 1:CAvGrapes:01.00:0025:28.0:  .740:  .000:  .000:  .000:   1.422 0
dial    :25 2:CAvGrapes:01.00:0100:  .0: 4.200:  .000:  .000:  .000:   7.807 0
dial    :25 2:CAvGrapes:01.00:0100: 1.0: 2.540:  .000:  .000:  .000:   4.797 0
dial    :25 2:CAvGrapes:01.00:0100: 3.0: 2.660:  .000:  .000:  .000:   5.018 0
dial    :25 2:CAvGrapes:01.00:0100: 7.0: 2.260:  .000:  .000:  .000:   4.280 0
dial    :25 2:CAvGrapes:01.00:0100:14.0: 1.340:  .000:  .000:  .000:   2.560 0
dial    :25 2:CAvGrapes:01.00:0100:21.0:  .660:  .000:  .000:  .000:   1.269 0
dial    :25 2:CAvGrapes:01.00:0100:28.0:  .400:  .000:  .000:  .000:    .771 0
dial    :83 1:CAvGrapes:   .  :    :59.0:  .214:  .043:  .000:  .000:    .497 1
dial    :83 1:CAvGrapes:   .  :    :59.0:  .199:  .052:  .000:  .000:    .486 1
dial    :83 1:CAvGrapes:   .  :    :60.0:  .121:  .045:  .000:  .000:    .321 1
dial    :38 1:FL Orange: 4.00: 750: 1.0: 1.200:  .000:  .000:  .000:   3.328 0
dial    :38 1:FL Orange: 4.00: 750: 2.0:  .922:  .000:  .000:  .000:   2.567 0
dial    :38 1:FL Orange: 4.00: 750: 5.0:  .650:  .000:  .000:  .000:   1.816 0
dial    :38 1:FL Orange: 4.00: 750:10.0:  .500:  .000:  .000:  .000:   1.400 0
dial    :38 1:FL Orange: 4.00: 750:20.0:  .384:  .000:  .000:  .000:   1.077 0
dial    :38 1:FL Orange: 4.00: 750:30.0:  .330:  .000:  .000:  .000:    .926 0
dial    :38 2:FL Orange: 4.00: 750: 1.0:  .200:  .000:  .000:  .000:    .562 0
dial    :38 2:FL Orange: 4.00: 750: 2.0:  .134:  .000:  .000:  .000:    .377 0
dial    :38 2:FL Orange: 4.00: 750: 5.0:  .080:  .000:  .000:  .000:    .225 0
dial    :38 2:FL Orange: 4.00: 750:10.0:  .054:  .000:  .000:  .000:    .152 0
dial    :38 2:FL Orange: 4.00: 750:20.0:  .036:  .000:  .000:  .000:    .101 0
dimeth  :16 1:CAsOrange:01.25:0500:  .0: 1.680:  .000:  .000:  .000:    .959 1
dimeth  :16 1:CAsOrange:01.25:0500: 3.0:  .640:  .062:  .000:  .000:    .402 1
dimeth  :16 1:CAsOrange:01.25:0500:11.0:  .122:  .080:  .000:  .000:    .116 1
dimeth  :16 1:CAsOrange:01.25:0500:17.0:  .048:  .076:  .000:  .000:    .071 1
dimeth  :16 2:CAsCitrus: 1.25: 500:  .0: 1.680:  .000:  .000:  .000:    .959 1
dimeth  :16 2:CAsCitrus: 1.25: 500: 3.0:  .360:  .044:  .000:  .000:    .231 1
dimeth  :16 2:CAsCitrus: 1.25: 500:10.0:  .040:  .042:  .000:  .000:    .047 1
dimeth  :16 2:CAsCitrus: 1.25: 500:19.0:  .000:  .028:  .000:  .000:    .016 1
dimeth  :51 1:CANApple :   .  :    :  .0: 1.112:  .000:  .000:  .000:?   .437 0
dimeth  :51 1:CANApple :   .  :    : 3.0:  .460:  .000:  .000:  .000:?   .181 0
dimeth  :51 1:CANApple :   .  :    : 7.0:  .300:  .000:  .000:  .000:?   .118 0
dimeth  :51 1:CANApple :   .  :    :10.0:  .104:  .000:  .000:  .000:?   .041 0
dimeth  :51 1:CANApple :   .  :    :14.0:  .088:  .000:  .000:  .000:?   .035 0
```

```
dimeth  :51 1:CANApple :  .  :    :21.0:  .012:  .000:  .000:  .000:?   .005 0
dimeth  :51 2:CANApple :  .  :    :  .0: 2.456:  .000:  .000:  .000:?   .962 0
dimeth  :51 2:CANApple :  .  :    : 3.0:  .936:  .000:  .000:  .000:?   .368 0
dimeth  :51 2:CANApple :  .  :    : 7.0:  .476:  .000:  .000:  .000:?   .187 0
dimeth  :51 2:CANApple :  .  :    :10.0:  .264:  .000:  .000:  .000:?   .104 0
dimeth  :51 2:CANApple :  .  :    :14.0:  .324:  .000:  .000:  .000:?   .127 0
dimeth  :51 2:CANApple :  .  :    :21.0:  .040:  .000:  .000:  .000:?   .016 0
dimeth  :51 3:CANApple :  .  :    :  .0: 1.028:  .000:  .000:  .000:?   .404 0
dimeth  :51 3:CANApple :  .  :    : 3.0:  .600:  .000:  .000:  .000:?   .236 0
dimeth  :51 3:CANApple :  .  :    : 7.0:  .332:  .000:  .000:  .000:?   .131 0
dimeth  :51 3:CANApple :  .  :    :10.0:  .136:  .000:  .000:  .000:?   .053 0
dimeth  :51 3:CANApple :  .  :    :14.0:  .100:  .000:  .000:  .000:?   .039 0
dimeth  :51 3:CANApple :  .  :    :21.0:  .052:  .000:  .000:  .000:?   .020 0
dimeth  :51 3:CANApple :  .  :    :28.0:  .068:  .000:  .000:  .000:?   .027 0
dimeth  :51 4:CANApple :  .  :    :  .0: 2.256:  .000:  .000:  .000:?   .884 0
dimeth  :51 4:CANApple :  .  :    : 3.0: 1.616:  .000:  .000:  .000:?   .634 0
dimeth  :51 4:CANApple :  .  :    : 7.0:  .564:  .000:  .000:  .000:?   .222 0
dimeth  :51 4:CANApple :  .  :    :10.0:  .436:  .000:  .000:  .000:?   .171 0
/dimeth :51 4:CANApple :  .  :    :14.0:  .316:  .000:  .000:  .000:?   .124 0
dimeth  :51 4:CANApple :  .  :    :21.0:  .084:  .000:  .000:  .000:?   .033 0
dimeth  :51 4:CANApple :  .  :    :28.0:  .024:  .000:  .000:  .000:?   .009 0
dimeth  :51 5:CANApple :  .  :    :  .0:  .192:  .000:  .000:  .000:?   .076 0
dimeth  :51 5:CANApple :  .  :    : 3.0:  .184:  .000:  .000:  .000:?   .072 0
dimeth  :51 5:CANApple :  .  :    : 7.0:  .132:  .000:  .000:  .000:?   .052 0
dimeth  :51 5:CANApple :  .  :    :10.0:  .056:  .000:  .000:  .000:?   .022 0
dimeth  :51 5:CANApple :  .  :    :14.0:  .044:  .000:  .000:  .000:?   .017 0
dimeth  :51 5:CANApple :  .  :    :21.0:  .024:  .000:  .000:  .000:?   .009 0
dimeth  :51 5:CANApple :  .  :    :28.0:  .008:  .000:  .000:  .000:?   .003 0
dimeth  :51 5:CANApple :  .  :    :35.0:  .008:  .000:  .000:  .000:?   .003 0
dimeth  :51 5:CANApple :  .  :    :42.0:  .004:  .000:  .000:  .000:?   .002 0
dimeth  :51 6:CANApple :  .  :    :  .0:  .196:  .000:  .000:  .000:?   .077 0
dimeth  :51 6:CANApple :  .  :    : 3.0:  .136:  .000:  .000:  .000:?   .053 0
dimeth  :51 6:CANApple :  .  :    : 7.0:  .096:  .000:  .000:  .000:?   .038 0
dimeth  :51 6:CANApple :  .  :    :10.0:  .044:  .000:  .000:  .000:?   .017 0
dimeth  :51 6:CANApple :  .  :    :14.0:  .028:  .000:  .000:  .000:?   .011 0
dimeth  :51 6:CANApple :  .  :    :21.0:  .008:  .000:  .000:  .000:?   .003 0
dimeth  :51 6:CANApple :  .  :    :28.0:  .004:  .000:  .000:  .000:?   .002 0
dimeth  :51 6:CANApple :  .  :    :35.0:  .004:  .000:  .000:  .000:?   .002 0
dimeth  :51 6:CANApple :  .  :    :42.0:  .004:  .000:  .000:  .000:?   .002 0
dimeth  :86 1:TX Orange: 1.00:   5: 1.0:  .432:  .012:  .000:  .000:    .254 1
dimeth  :86 1:TX Orange: 1.00:   5: 2.0:  .248:  .010:  .000:  .000:    .148 1
dimeth  :86 1:TX Orange: 1.00:   5: 7.0:  .011:  .002:  .000:  .000:    .007 1
dimeth  :86·1:TX Orange: 1.00:   5:14.0:  .001:  .000:  .000:  .000:    .000 1
dimeth  :86 2:TX Orange: 1.00:   0: 1.0: 1.922:  .018:  .000:  .000:   1.106 1
dimeth  :86 2:TX Orange: 1.00:   0: 2.0: 1.274:  .039:  .000:  .000:    .750 1
dimeth  :86 2:TX Orange: 1.00:   0: 7.0:  .042:  .011:  .000:  .000:    .030 1
dimeth  :86 2:TX Orange: 1.00:   0:14.0:  .004:  .000:  .000:  .000:    .002 1
dioxat  :80 1:CAsOrange: 5.00: 100: 4.0: 2.600:  .000:  .000:  .000:   7.297 0
dioxat  :80 1:CAsOrange: 5.00: 100:10.0: 2.200:  .000:  .000:  .000:   6.210 0
dioxat  :80 1:CAsOrange: 5.00: 100:18.0: 1.400:  .000:  .000:  .000:   3.998 0
dioxat  :80 1:CAsOrange: 5.00: 100:31.0: 1.600:  .000:  .000:  .000:   4.556 0
dioxat  :80 1:CAsOrange: 5.00: 100:46.0: 1.600:  .000:  .000:  .000:   4.556 0
dioxat  :80 1:CAsOrange: 5.00: 100:59.0: 1.200:  .000:  .000:  .000:   3.437 0
dioxat  :80 2:CAsOrange: 5.00: 100: 4.0: 2.600:  .000:  .000:  .000:   7.297 0
dioxat  :80 2:CAsOrange: 5.00: 100:10.0: 2.000:  .000:  .000:  .000:   5.662 0
```

```
dioxat  :80 2:CAsOrange: 5.00: 100:18.0: 1.200:  .000:  .000:  .000:  3.437 0
dioxat  :80 2:CAsOrange: 5.00: 100:31.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :80 2:CAsOrange: 5.00: 100:46.0: 1.000:  .000:  .000:  .000:  2.872 0
dioxat  :80 2:CAsOrange: 5.00: 100:59.0: 1.600:  .000:  .000:  .000:  4.556 0
dioxat  :80 3:CAsOrange: 5.00: 100: 4.0: 3.200:  .000:  .000:  .000:  8.904 0
dioxat  :80 3:CAsOrange: 5.00: 100:10.0: 2.600:  .000:  .000:  .000:  7.297 0
dioxat  :80 3:CAsOrange: 5.00: 100:18.0: 1.600:  .000:  .000:  .000:  4.556 0
dioxat  :80 3:CAsOrange: 5.00: 100:31.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :80 3:CAsOrange: 5.00: 100:46.0: 1.200:  .000:  .000:  .000:  3.437 0
dioxat  :80 3:CAsOrange: 5.00: 100:59.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :80 4:CAsOrange: 5.00: 250: 4.0: 1.800:  .000:  .000:  .000:  5.111 0
dioxat  :80 4:CAsOrange: 5.00: 250:10.0: 2.000:  .000:  .000:  .000:  5.662 0
dioxat  :80 4:CAsOrange: 5.00: 250:18.0: 1.800:  .000:  .000:  .000:  5.111 0
dioxat  :80 4:CAsOrange: 5.00: 250:31.0: 1.600:  .000:  .000:  .000:  4.556 0
dioxat  :80 4:CAsOrange: 5.00: 250:46.0: 1.800:  .000:  .000:  .000:  5.111 0
dioxat  :80 4:CAsOrange: 5.00: 250:59.0: 1.000:  .000:  .000:  .000:  2.872 0
dioxat  :80 5:CAsOrange: 5.00: 250: 4.0: 2.200:  .000:  .000:  .000:  6.210 0
dioxat  :80 5:CAsOrange: 5.00: 250:10.0: 2.000:  .000:  .000:  .000:  5.662 0
dioxat  :80 5:CAsOrange: 5.00: 250:18.0: 1.600:  .000:  .000:  .000:  4.556 0
dioxat  :80 5:CAsOrange: 5.00: 250:31.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :80 5:CAsOrange: 5.00: 250:46.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :80 5:CAsOrange: 5.00: 250:59.0: 1.000:  .000:  .000:  .000:  2.872 0
dioxat  :80 6:CAsOrange: 5.00: 250: 4.0: 1.800:  .000:  .000:  .000:  5.111 0
dioxat  :80 6:CAsOrange: 5.00: 250:10.0: 1.600:  .000:  .000:  .000:  4.556 0
dioxat  :80 6:CAsOrange: 5.00: 250:18.0: 2.000:  .000:  .000:  .000:  5.662 0
dioxat  :80 6:CAsOrange: 5.00: 250:31.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :80 6:CAsOrange: 5.00: 250:46.0: 1.200:  .000:  .000:  .000:  3.437 0
dioxat  :80 6:CAsOrange: 5.00: 250:59.0:  .600:  .000:  .000:  .000:  1.733 0
dioxat  :80 7:CAsOrange: 5.00:1250: 4.0: 1.000:  .000:  .000:  .000:  2.872 0
dioxat  :80 7:CAsOrange: 5.00:1250:10.0:  .800:  .000:  .000:  .000:  2.304 0
dioxat  :80 7:CAsOrange: 5.00:1250:18.0:  .600:  .000:  .000:  .000:  1.733 0
dioxat  :80 7:CAsOrange: 5.00:1250:31.0:  .800:  .000:  .000:  .000:  2.304 0
dioxat  :80 7:CAsOrange: 5.00:1250:46.0:  .400:  .000:  .000:  .000:  1.159 0
dioxat  :80 7:CAsOrange: 5.00:1250:59.0:  .400:  .000:  .000:  .000:  1.159 0
dioxat  :80 8:CAsOrange: 5.00:1250: 4.0: 1.200:  .000:  .000:  .000:  3.437 0
dioxat  :80 8:CAsOrange: 5.00:1250:10.0: 1.000:  .000:  .000:  .000:  2.872 0
dioxat  :80 8:CAsOrange: 5.00:1250:18.0:  .400:  .000:  .000:  .000:  1.159 0
dioxat  :80 8:CAsOrange: 5.00:1250:31.0:  .600:  .000:  .000:  .000:  1.733 0
dioxat  :80 8:CAsOrange: 5.00:1250:46.0:  .600:  .000:  .000:  .000:  1.733 0
dioxat  :80 8:CAsOrange: 5.00:1250:59.0:  .400:  .000:  .000:  .000:  1.159 0
dioxat  :80 9:CAsOrange: 5.00:1250: 4.0: 1.000:  .000:  .000:  .000:  2.872 0
dioxat  :80 9:CAsOrange: 5.00:1250:10.0:  .800:  .000:  .000:  .000:  2.304 0
dioxat  :80 9:CAsOrange: 5.00:1250:18.0:  .400:  .000:  .000:  .000:  1.159 0
dioxat  :80 9:CAsOrange: 5.00:1250:31.0:  .400:  .000:  .000:  .000:  1.159 0
dioxat  :80 9:CAsOrange: 5.00:1250:46.0:  .400:  .000:  .000:  .000:  1.159 0
dioxat  :80 9:CAsOrange: 5.00:1250:59.0:  .200:  .000:  .000:  .000:   .581 0
dioxat  :8010:CAsOrange: 5.00: 100: 7.0: 2.600:  .000:  .000:  .000:  7.297 0
dioxat  :8010:CAsOrange: 5.00: 100:13.0: 2.200:  .000:  .000:  .000:  6.210 0
dioxat  :8010:CAsOrange: 5.00: 100:27.0: 1.800:  .000:  .000:  .000:  5.111 0
dioxat  :8010:CAsOrange: 5.00: 100:35.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :8011:CAsOrange: 5.00: 100: 4.0: 2.800:  .000:  .000:  .000:  7.836 0
dioxat  :8011:CAsOrange: 5.00: 100:10.0: 1.600:  .000:  .000:  .000:  4.556 0
dioxat  :8011:CAsOrange: 5.00: 100:38.0: 2.000:  .000:  .000:  .000:  5.662 0
dioxat  :8011:CAsOrange: 5.00: 100:46.0: 1.400:  .000:  .000:  .000:  3.998 0
dioxat  :38 1:FL Orange: 4.00: 750: 1.0:  .600:  .000:  .000:  .000:  1.733 0
```

dioxat	:38	1:FL Orange:	4.00:	750:	2.0:	.460:	.000:	.000:	.000:	 0
dioxat	:38	1:FL Orange:	4.00:	750:	5.0:	.326:	.000:	.000:	.000:	.946 0
dioxat	:38	1:FL Orange:	4.00:	750:10.0:		.250:	.000:	.000:	.000:	.726 0
dioxat	:38	1:FL Orange:	4.00:	750:20.0:		.192:	.000:	.000:	.000:	.558 0
dioxat	:38	1:FL Orange:	4.00:	750:30.0:		.164:	.000:	.000:	.000:	.477 0
dioxat	:38	2:FL Orange:	4.00:	750:	1.0:	.080:	.000:	.000:	.000:	.233 0
dioxat	:38	2:FL Orange:	4.00:	750:	2.0:	.056:	.000:	.000:	.000:	.163 0
dioxat	:38	2:FL Orange:	4.00:	750:	5.0:	.036:	.000:	.000:	.000:	.105 0
dioxat	:38	2:FL Orange:	4.00:	750:10.0:		.024:	.000:	.000:	.000:	.070 0
dioxat	:38	2:FL Orange:	4.00:	750:20.0:		.018:	.000:	.000:	.000:	.052 0
dioxat	:38	2:FL Orange:	4.00:	750:30.0:		.014:	.000:	.000:	.000:	.041 0
ethion	:27	1:CAvGrapes:	1.0:	30:	.0:	.800:	.070:	.000:	.000:	1.356 2
ethion	:27	1:CAvGrapes:	1.0:	30:	1.0:	.600:	.072:	.005:	.000:	1.057 2
ethion	:27	1:CAvGrapes:	1.0:	30:	3.0:	.200:	.078:	.020:	.000:	.466 2
ethion	:27	1:CAvGrapes:	1.0:	30:	7.0:	.065:	.055:	.048:	.000:	.263 2
ethion	:27	1:CAvGrapes:	1.0:	30:14.0:		.021:	.025:	.060:	.000:	.166 2
ethion	:27	1:CAvGrapes:	1.0:	30:21.0:		.019:	.011:	.050:	.000:	.125 2
ethion	:27	1:CAvGrapes:	1.0:	30:28.0:		.015:	.007:	.035:	.000:	.089 2
ethion	:27	2:CAvGrapes:	1.25:	200:	.0:	.900:	.080:	.004:	.000:	1.532 2
ethion	:27	2:CAvGrapes:	1.25:	200:	1.0:	.700:	.092:	.004:	.000:	1.241 2
ethion	:27	2:CAvGrapes:	1.25:	200:	3.0:	.350:	.105:	.011:	.000:	.728 2
ethion	:27	2:CAvGrapes:	1.25:	200:	7.0:	.070:	.058:	.039:	.000:	.262 2
ethion	:27	2:CAvGrapes:	1.25:	200:14.0:		.032:	.030:	.045:	.000:	.168 2
ethion	:27	2:CAvGrapes:	1.25:	200:21.0:		.020:	.019:	.039:	.000:	.122 2
ethion	:27	2:CAvGrapes:	1.25:	200:28.0:		.012:	.010:	.032:	.000:	.085 2
ethion	:47	1:CAvOrange:	3.0:	500:	2.0:	1.102:	.100:	.000:	.000:	2.710 2
ethion	:47	1:CAvOrange:	3.0:	500:	5.0:	.475:	.087:	.029:	.000:	1.340 2
ethion	:47	1:CAvOrange:	3.0:	500:	9.0:	.236:	.064:	.041:	.000:	.777 2
ethion	:47	1:CAvOrange:	3.0:	500:16.0:		.149:	.048:	.032:	.000:	.523 2
ethion	:47	1:CAvOrange:	3.0:	500:23.0:		.078:	.024:	.028:	.000:	.297 2
ethion	:47	1:CAvOrange:	3.0:	500:33.0:		.037:	.011:	.029:	.000:	.175 2
ethion	:47	2:CAvOrange:	4.0:	500:	2.0:	.516:	.028:	.008:	.000:	1.255 2
ethion	:47	2:CAvOrange:	4.0:	500:	5.0:	.754:	.054:	.012:	.000:	1.858 2
ethion	:47	2:CAvOrange:	4.0:	500:	9.0:	.342:	.034:	.011:	.000:	.881 2
ethion	:47	2:CAvOrange:	4.0:	500:16.0:		.548:	.090:	.047:	.000:	1.554 2
ethion	:47	2:CAvOrange:	4.0:	500:23.0:		.298:	.042:	.039:	.000:	.862 2
ethion	:47	2:CAvOrange:	4.0:	500:33.0:		.230:	.034:	.044:	.000:	.702 2
ethion	:47	3:CAvOrange:	4.0:	500:	2.0:	1.771:	.110:	.000:	.000:	4.207 2
ethion	:47	3:CAvOrange:	4.0:	500:	5.0:	.834:	.076:	.000:	.000:	2.058 2
ethion	:47	3:CAvOrange:	4.0:	500:	9.0:	.669:	.112:	.000:	.000:	1.769 2
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ethion	:47	3:CAvOrange:	4.0:	500:23.0:		.176:	.044:	.000:	.000:	.501 2
ethion	:47	3:CAvOrange:	4.0:	500:33.0:		.127:	.034:	.000:	.000:	.369 2
ethion	:12	1:AZ Orange:	8.00:	350:	.0:18.136:		.172:	.000:	.000:	34.195 2
ethion	:12	1:AZ Orange:	8.00:	350:	1.0:17.612:		.548:	.022:	.000:	34.005 2
ethion	:12	1:AZ Orange:	8.00:	350:	3.0:15.848:		.930:	.070:	.000:	31.962 2
ethion	:12	1:AZ Orange:	8.00:	350:	5.0:10.392:		.944:	.066:	.000:	22.942 2
ethion	:12	1:AZ Orange:	8.00:	350:	7.0:12.040:		1.220:	.106:	.000:	26.325 2
ethion	:12	1:AZ Orange:	8.00:	350:14.0:	9.420:		1.386:	.000:	.000:	21.885 2
ethion	:12	1:AZ Orange:	8.00:	350:21.0:	7.398:		1.412:	.000:	.000:	18.239 2
ethion	:12	1:AZ Orange:	8.00:	350:28.0:	4.442:		1.238:	.000:	.000:	12.175 2
ethion	:12	1:AZ Orange:	8.00:	350:42.0:	2.356:		1.006:	.000:	.000:	7.397 2
ethion	:12	2:FL Orange:	4.00:	350:	.0:10.252:		.122:	.000:	.000:	21.111 2
ethion	:12	2:FL Orange:	4.00:	350:	1.0:	9.072:	.130:	.000:	.000:	18.969 2
ethion	:12	2:FL Orange:	4.00:	350:	3.0:	7.856:	.142:	.000:	.000:	16.708 2

0391

```
ethion  :12 2:FL Orange: 4.00: 350: 5.0: 5.498:   .124:   .000:   .000:  12.059 2
ethion  :12 2:FL Orange: 4.00: 350: 7.0: 3.024:   .092:   .001:   .000:   6.876 2
ethion  :12 2:FL Orange: 4.00: 350:14.0: 1.954:   .072:   .001:   .000:   4.527 2
ethion  :12 2:FL Orange: 4.00: 350:21.0:  .844:   .076:   .008:   .000:   2.100 2
ethion  :12 2:FL Orange: 4.00: 350:28.0:  .726:   .062:   .007:   .000:   1.800 2
ethion  :12 2:FL Orange: 4.00: 350:42.0:  .368:   .044:   .006:   .000:    .952 2
ethion  :12 3:TX Orange: 4.00: 350:  .0: 6.776:   .102:   .000:   .000:  14.548 2
ethion  :12 3:TX Orange: 4.00: 350: 1.0: 4.534:   .090:   .000:   .000:  10.030 2
ethion  :12 3:TX Orange: 4.00: 350: 3.0: 3.846:   .092:   .000:   .000:   8.608 2
ethion  :12 3:TX Orange: 4.00: 350: 5.0: 2.952:   .092:   .000:   .000:   6.722 2
ethion  :12 3:TX Orange: 4.00: 350: 7.0: 1.968:   .084:   .003:   .000:   4.589 2
ethion  :12 3:TX Orange: 4.00: 350:14.0:  .420:   .062:   .007:   .000:   1.112 2
ethion  :12 3:TX Orange: 4.00: 350:21.0:  .226:   .048:   .013:   .000:    .653 2
ethion  :12 3:TX Orange: 4.00: 350:28.0:  .126:   .042:   .014:   .000:    .416 2
ethion  :12 3:TX Orange: 4.00: 350:42.0:  .030:   .012:   .007:   .000:    .111 2
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ethion  :12 4:CA Orange: 4.00: 350: 1.0: 3.900:   .110:   .000:   .000:   8.759 2
ethion  :12 4:CA Orange: 4.00: 350: 3.0: 3.504:   .106:   .000:   .000:   7.921 2
ethion  :12 4:CA Orange: 4.00: 350: 5.0: 2.894:   .126:   .005:   .000:   6.681 2
ethion  :12 4:CA Orange: 4.00: 350: 7.0: 2.274:   .116:   .006:   .000:   5.329 2
ethion  :12 4:CA Orange: 4.00: 350:14.0:  .988:   .072:   .005:   .000:   2.405 2
ethion  :12 4:CA Orange: 4.00: 350:21.0:  .476:   .082:   .015:   .000:   1.300 2
ethion  :12 4:CA Orange: 4.00: 350:28.0:  .290:   .064:   .032:   .000:    .878 2
ethion  :12 4:CA Orange: 4.00: 350:42.0:  .072:   .026:   .021:   .000:    .273 2
ethion  :34 1:FL Orange: 3.00:1200:  .0:  .199:   .008:   .000:   .000:    .472 1
ethion  :34 1:FL Orange: 3.00:1200: 1.0:  .122:   .012:   .000:   .000:    .307 1
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ethion  :34 1:FL Orange: 3.00:1200: 7.0:  .006:   .003:   .000:   .000:    .021 1
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ethion  :34 2:FL Orange: 4.50:1200: 7.0:  .034:   .010:   .000:   .000:    .101 1
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ethion  :34 2:FL Orange: 4.50:1200:35.0:  .008:   .004:   .000:   .000:    .029 1
ethion  :34 3:FL Orange: 4.50:1200:  .0:  .569:   .084:   .000:   .000:   1.483 1
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ethion  :34 4:FL Orange: 4.50:1200:  .0:  .265:   .033:   .000:   .000:    .678 1
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ethion  :34 4:FL Orange: 4.50:1200: 3.0:  .079:   .008:   .000:   .000:    .199 1
ethion  :34 4:FL Orange: 4.50:1200: 5.0:  .061:   .010:   .000:   .000:    .163 1
ethion  :34 4:FL Orange: 4.50:1200: 7.0:  .059:   .013:   .000:   .000:    .165 1
ethion  :34 4:FL Orange: 4.50:1200:14.0:  .053:   .012:   .000:   .000:    .148 1
ethion  :34 4:FL Orange: 4.50:1200:21.0:  .020:   .011:   .000:   .000:    .071 1
ethion  :34 4:FL Orange: 4.50:1200:28.0:  .015:   .010:   .000:   .000:    .057 1
ethion  :34 4:FL Orange: 4.50:1200:35.0:  .008:   .006:   .000:   .000:    .031 1
ethion  :34 5:FL Orange: 4.50:1200:  .0:  .505:   .024:   .000:   .000:   1.203 1
```

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ethion	:34 5:FL Orange:	4.50:1200:	7.0:	.022:	.009:	.000:	.000:	.071	1
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ethion	:34 6:FL Orange:	4.50:1200:	1.0:	.203:	.005:	.000:	.000:	.473	1
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ethion	:34 8:FL Orange:	4.50:1200:	28.0:	.016:	.007:	.000:	.000:	.053	1
ethion	:34 8:FL Orange:	4.50:1200:	35.0:	.009:	.006:	.000:	.000:	.033	1
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ethion	:3410:FL Orange:	9.00:1200:	14.0:	.042:	.016:	.000:	.000:	.132	1
ethion	:3410:FL Orange:	9.00:1200:	21.0:	.024:	.016:	.000:	.000:	.092	1
ethion	:3410:FL Orange:	9.00:1200:	28.0:	.024:	.016:	.000:	.000:	.092	1
ethion	:3410:FL Orange:	9.00:1200:	35.0:	.016:	.008:	.000:	.000:	.055	1
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etp	:18 1:CAsOrange:	12.50:2000:	5.0:	1.400:	.068:	.000:	.000:	44.430	0
etp	:18 1:CAsOrange:	12.50:2000:	6.0:	1.620:	.090:	.000:	.000:	51.296	0
etp	:18 1:CAsOrange:	12.50:2000:	7.0:	1.540:	.086:	.000:	.000:	49.613	0
etp	:18 1:CAsOrange:	12.50:2000:	8.0:	1.160:	.070:	.000:	.000:	41.407	0

Appendix H, page 9

```
etp    :18 1:CAsOrange:12.50:2000: 9.0: 1.040:  .076:  .000:  .000:  40.878 0
etp    :18 1:CAsOrange:12.50:2000:10.0: 1.020:  .088:  .000:  .000:  43.024 0
etp    :18 1:CAsOrange:12.50:2000:11.0:  .920:  .110:  .000:  .000:  45.909 0
etp    :18 2:CAsOrange:12.50:2000:  .5: 3.800:  .000:  .000:  .000:  61.296 0
etp    :18 2:CAsOrange:12.50:2000:  .8: 3.000:  .000:  .000:  .000:  52.734 0
etp    :18 2:CAsOrange:12.50:2000: 1.0: 1.640:  .022:  .000:  .000:  38.529 0
etp    :18 2:CAsOrange:12.50:2000: 1.5: 1.760:  .000:  .000:  .000:  35.573 0
etp    :18 2:CAsOrange:12.50:2000: 2.0: 1.800:  .046:  .000:  .000:  45.692 0
etp    :18 2:CAsOrange:12.50:2000: 3.0: 1.340:  .046:  .000:  .000:  39.079 0
etp    :18 2:CAsOrange:12.50:2000: 4.0: 1.140:  .042:  .000:  .000:  35.056 0
etp    :18 2:CAsOrange:12.50:2000: 5.0:  .920:  .036:  .000:  .000:  29.932 0
etp    :18 2:CAsOrange:12.50:2000: 6.0:  .840:  .044:  .000:  .000:  30.490 0
etp    :18 2:CAsOrange:12.50:2000: 7.0:  .660:  .036:  .000:  .000:  25.231 0
etp    :18 2:CAsOrange:12.50:2000: 8.0:  .680:  .042:  .000:  .000:  27.148 0
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etp    :18 4:CAsOrange:10.00:1600:45.0:  .040:  .000:  .000:  .000:    .994 0
etp    :23 1:CA Orange:02.00:    :  .0: 1.534:  .014:  .000:  .000:  35.089 0
etp    :23 1:CA Orange:02.00:    : 3.0: 1.012:  .022:  .000:  .000:  28.088 0
etp    :23 1:CA Orange:02.00:    : 8.0:  .708:  .028:  .000:  .000:  24.026 0
etp    :23 1:CA Orange:02.00:    :24.0:  .496:  .014:  .000:  .000:  15.874 0
etp    :23 1:CA Orange:02.00:    :34.0:  .164:  .008:  .000:  .000:   6.662 0
etp    :23 1:CA Orange:02.00:    :46.0:  .192:  .008:  .000:  .000:   7.313 0
etp    :23 1:CA Orange:02.00:    :72.0:  .044:  .000:  .000:  .000:   1.093 0
etp    :23 1:CA Orange:02.00:    :171.:  .006:  .000:  .000:  .000:    .150 0
etp    :20 1:SC tobaco:01.50:    : 1.0:  .012:  .000:  .000:  .000:?  .303?0
etp    :20 1:SC tobaco:01.50:    :10.0:  .003:  .000:  .000:  .000:?  .071?0
etp    :20 2:SC tobaco:01.50:    : 1.0:  .009:  .000:  .000:  .000:?  .213?0
etp    :20 2:SC tobaco:01.50:    : 3.0:  .002:  .000:  .000:  .000:?  .045?0
etp    :20 2:SC tobaco:01.50:    : 5.0:  .001:  .000:  .000:  .000:?  .034?0
etp    :20 2:SC tobaco:01.50:    : 9.0:  .000:  .000:  .000:  .000:?  .008?0
etp    :20 2:SC tobaco:01.50:    :15.0:  .000:  .000:  .000:  .000:?  .002?0
etp    :20 3:SC tobaco:01.50:    : 1.0:  .022:  .000:  .000:  .000:?  .549?0
etp    :20 3:SC tobaco:01.50:    : 4.0:  .013:  .000:  .000:  .000:?  .309?0
etp    :20 7:SC tobaco:01.50:    : 1.0:  .021:  .000:  .000:  .000:?  .512?0
etp    :20 7:SC tobaco:01.50:    :10.0:  .003:  .000:  .000:  .000:?  .071?0
etp    :20 8:SC tobaco:01.50:    : 1.0:  .015:  .000:  .000:  .000:?  .360?0
etp    :20 8:SC tobaco:01.50:    : 3.0:  .003:  .000:  .000:  .000:?  .078?0
etp    :20 8:SC tobaco:01.50:    : 5.0:  .001:  .000:  .000:  .000:?  .034?0
etp    :20 8:SC tobaco:01.50:    : 9.0:  .000:  .000:  .000:  .000:?  .007?0
etp    :20 8:SC tobaco:01.50:    :15.0:  .000:  .000:  .000:  .000:?  .003?0
etp    :20 9:SC tobaco:01.50:    : 1.0:  .026:  .000:  .000:  .000:?  .637?0
etp    :20 9:SC tobaco:01.50:    : 4.0:  .014:  .000:  .000:  .000:?  .339?0
etp    : 5 1:SC tobaco:0.375:    : 1.0:  .026:  .000:  .000:  .000:?  .635?0
```

```
etp    : 5 1:SC tobaco:0.375:      : 3.0:  .009:  .000:  .ouu:  .uuu.;  .___.0
etp    : 5 1:SC tobaco:0.375:      : 5.0:  .001:  .000:  .000:  .000:?  .015?0
etp    : 5 2:SC tobaco:0.375:      : 1.0:  .040:  .000:  .000:  .000:?  .965?0
etp    : 5 2:SC tobaco:0.375:      : 3.0:  .010:  .000:  .000:  .000:?  .235?0
etp    : 5 2:SC tobaco:0.375:      : 5.0:  .001:  .000:  .000:  .000:?  .034?0
etp    : 5 3:SC tobaco:0.375:      : 1.0:  .067:  .000:  .000:  .000:? 1.637?0
etp    : 5 3:SC tobaco:0.375:      : 3.0:  .005:  .000:  .000:  .000:?  .127?0
etp    : 5 3:SC tobaco:0.375:      : 5.0:  .002:  .000:  .000:  .000:?  .044?0
etp    : 5 4:SC tobaco:0.375:      : 1.0:  .031:  .000:  .000:  .000:?  .751?0
etp    : 5 4:SC tobaco:0.375:      : 3.0:  .003:  .000:  .000:  .000:?  .064?0
etp    :36 1:FL Orange: 0.75: 100: 1.0: 2.078:  .120:  .000:  .000: 60.888 0
etp    :36 1:FL Orange: 0.75: 100: 6.0:  .026:  .056:  .000:  .000: 18.318 0
etp    :36 1:FL Orange: 0.75: 100: 8.0:  .012:  .040:  .000:  .000: 13.314 0
etp    :36 2:FL Orange: 0.75: 100: 1.0: 3.624:  .074:  .000:  .000: 68.778 0
etp    :36 2:FL Orange: 0.75: 100: 2.0: 2.148:  .206:  .000:  .000: 71.549 0
etp    :36 2:FL Orange: 0.75: 100: 3.0:  .166:  .100:  .000:  .000: 32.374 0
etp    :36 2:FL Orange: 0.75: 100: 7.0:  .046:  .046:  .000:  .000: 15.832 0
etp    :36 2:FL Orange: 0.75: 100: 9.0:  .016:  .030:  .000:  .000: 10.319 0
etp    :36 3:FL Orange: 2.00: 100: 1.0: 2.244:  .052:  .000:  .000: 52.403 0
etp    :36 3:FL Orange: 2.00: 100: 3.0:  .186:  .016:  .000:  .000:  9.735 0
etp    :36 3:FL Orange: 2.00: 100: 6.0:  .012:  .004:  .000:  .000:  1.684 0
etp    :36 3:FL Orange: 2.00: 100: 8.0:  .001:  .001:  .000:  .000:   .434 0
etp    :36 4:FL Orange:  .75: 100: 1.0: 3.294:  .062:  .000:  .000: 64.642 0
etp    :36 4:FL Orange:  .75: 100: 3.0:  .486:  .034:  .000:  .000: 21.361 0
etp    :36 4:FL Orange:  .75: 100: 6.0:  .050:  .010:  .000:  .000:  4.635 0
etp    :36 4:FL Orange:  .75: 100: 8.0:  .036:  .008:  .000:  .000:  3.629 0
etp    :82 1:CAsPeach : 2.00: 400:  .0: 1.216:  .800:  .000:  .000:? 68.508 0
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etp    :82 1:CAsPeach : 2.00: 400: 7.0:  .830:  .860:  .000:  .000:? 69.811 0
etp    :82 1:CAsPeach : 2.00: 400:14.0:  .029:  .300:  .000:  .000:? 32.535 0
etp    :82 1:CAsPeach : 2.00: 400:21.0:  .010:  .000:  .000:  .000:?   .091 0
etp    :82 1:CAsPeach : 2.00: 400:28.0:  .008:  .080:  .000:  .000:?  9.968 0
etp    :82 1:CAsPeach : 2.00: 400:70.0:  .003:  .020:  .000:  .000:?  2.601 0
etp    :82 2:CAsPeach : 1.00:0400:  .0:  .294:  .000:  .000:  .000:?  2.699 0
etp    :82 2:CAsPeach : 1.00:0400: 3.0:  .053:  .000:  .000:  .000:?   .490 0
etp    :82 2:CAsPeach : 1.00:0400: 7.0:  .016:  .000:  .000:  .000:?   .152 0
etp    :82 2:CAsPeach : 1.00:0400:14.0:  .008:  .000:  .000:  .000:?   .072 0
etp    :82 2:CAsPeach : 1.00:0400:21.0:  .004:  .000:  .000:  .000:?   .040 0
etp    :82 2:CAsPeach : 1.00:0400:28.0:  .004:  .000:  .000:  .000:?   .038 0
etp    :82 2:CAsPeach : 1.00:0400:70.0:  .001:  .000:  .000:  .000:?   .011 0
etp    :82 3:CAsPeach : 1.00:0400:  .0:  .630:  .600:  .000:  .000:? 56.844 0
etp    :82 3:CAsPeach : 1.00:0400: 3.0:  .292:  .760:  .000:  .000:? 63.845 0
etp    :82 3:CAsPeach : 1.00:0400: 7.0:  .160:  .420:  .000:  .000:? 43.000 0
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etp    :82 3:CAsPeach : 1.00:0400:21.0:  .050:  .000:  .000:  .000:?   .461 0
etp    :82 3:CAsPeach : 1.00:0400:28.0:  .039:  .180:  .000:  .000:? 21.193 0
etp    :82 3:CAsPeach : 1.00:0400:70.0:  .021:  .020:  .000:  .000:?  2.759 0
etp    :74 1:AZ Cotton: 1.00:   9:  .0: 2.925:  .021:  .000:  .000:? 54.501?0
etp    :74 1:AZ Cotton: 1.00:   9:  .5:  .893:  .045:  .000:  .000:? 31.065?0
etp    :74 1:AZ Cotton: 1.00:   9: 1.0:  .535:  .038:  .000:  .000:? 22.929?0
etp    :74 1:AZ Cotton: 1.00:   9: 2.0:  .315:  .032:  .000:  .000:? 17.186?0
etp    :74 1:AZ Cotton: 1.00:   9: 3.0:  .190:  .023:  .000:  .000:? 11.709?0
etp    :74 1:AZ Cotton: 1.00:   9: 4.0:  .138:  .014:  .000:  .000:?  8.001?0
etp    :87 1:CAvplum  : 2.47: 330:  .0: 2.180:  .008:  .000:  .000:? 19.166 0
etp    :87 1:CAvplum  : 2.47: 330: 2.0:  .368:  .024:  .000:  .000:?  6.390 0
```

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etp    :87 1:CAvplum  : 2.47: 330: 5.0:  .080:  .028:  .000:  .000:? 4.297 0
etp    :87 1:CAvplum  : 2.47: 330: 7.0:  .048:  .024:  .000:  .000:? 3.510 0
etp    :87 1:CAvplum  : 2.47: 330:14.0:  .011:  .013:  .000:  .000:? 1.729 0
etp    :87 1:CAvplum  : 2.47: 330:21.0:  .005:  .006:  .000:  .000:?  .876 0
etp    :70 1:WA Apple :     :    : 1.0: 1.040:  .030:  .000:  .000:? 22.142 0
etp    :70 1:WA Apple :     :    : 7.0:  .307:  .051:  .000:  .000:? 16.057 0
etp    :70 2:WA Apple :     :    : 1.0: 1.320:  .048:  .000:  .000:? 28.929 0
etp    :70 2:WA Apple :     :    : 7.0:  .106:  .008:  .000:  .000:? 3.668 0
etp    :70 3:WA Apple :     :    : 1.0:  .166:  .022:  .000:  .000:? 7.804 0
etp    :70 3:WA Apple :     :    : 7.0:  .086:  .014:  .000:  .000:? 4.719 0
etp    :70 4:WA Apple :     :    : 1.0:  .202:  .030:  .000:  .000:? 10.114 0
etp    :70 4:WA Apple :     :    : 7.0:  .137:  .010:  .000:  .000:? 4.638 0
etp    :70 5:WA Apple :     :    : 1.0:  .405:  .021:  .000:  .000:? 11.293 0
etp    :70 5:WA Apple :     :    : 7.0:  .210:  .017:  .000:  .000:? 7.392 0
etp    :70 6:WA Apple :     :    : 1.0:  .433:  .027:  .000:  .000:? 12.980 0
etp    :70 6:WA Apple :     :    : 7.0:  .038:  .005:  .000:  .000:? 1.834 0
etp    :70 7:WA Apple :     :    : 1.0:  .478:  .013:  .000:  .000:? 10.698 0
etp    :70 7:WA Apple :     :    : 7.0:  .111:  .009:  .000:  .000:? 3.981 0
etp    :70 8:WA Apple :     :    : 1.0:  .255:  .018:  .000:  .000:? 8.324 0
etp    :70 8:WA Apple :     :    : 7.0:  .105:  .005:  .000:  .000:? 2.955 0
etp    :70 9:WA Apple :     :    : 1.0:  .637:  .022:  .000:  .000:? 14.956 0
etp    :70 9:WA Apple :     :    : 7.0:  .115:  .005:  .000:  .000:? 3.122 0
etp    :7010:WA Apple :     :    : 1.0:  .309:  .060:  .000:  .000:? 17.879 0
etp    :7010:WA Apple :     :    : 7.0:  .060:  .000:  .000:  .000:? 1.023 0
etp    :7011:WA Apple :     :    : 1.0:  .495:  .076:  .000:  .000:? 23.452 0
etp    :7011:WA Apple :     :    : 7.0:  .076:  .000:  .000:  .000:? 1.294 0
etp    :7012:WA Apple :     :    : 1.0:  .446:  .019:  .000:  .000:? 11.490 0
etp    :7013:WA Peach :     :    : 1.0:  .340:  .000:  .000:  .000:? 3.115 0
etp    :7013:WA Peach :     :    : 7.0:  .029:  .000:  .000:  .000:?  .270 0
etp    :7014:WA Peach :     :    : 1.0:  .150:  .000:  .000:  .000:? 1.386 0
etp    :7015:WA Peach :     :    : 1.0:  .452:  .015:  .000:  .000:? 5.975 0
etp    :7015:WA Peach :     :    : 7.0:  .026:  .000:  .000:  .000:?  .242 0
etp    :7016:WA Peach :     :    : 1.0:  .318:  .013:  .000:  .000:? 4.546 0
etp    :7017:WA Peach :     :    : 1.0:  .287:  .016:  .000:  .000:? 4.644 0
etp    :77 1:AZ Cotton:01.00:0009:  .0:  .950:  .008:  .000:  .000:? 22.901?0
etp    :77 1:AZ Cotton:01.00:0009: 1.0:  .124:  .015:  .000:  .000:? 7.854?0
etp    :77 1:AZ Cotton:01.00:0009: 2.0:  .051:  .010:  .000:  .000:? 4.570?0
etp    :77 1:AZ Cotton:01.00:0009: 3.0:  .028:  .005:  .000:  .000:? 2.371?0
etp    :77 1:AZ Cotton:01.00:0009: 4.0:  .017:  .004:  .000:  .000:? 1.772?0
etp    :77 2:AZ Cotton:01.00:0009:  .0: 1.450:  .001:  .000:  .000:? 30.130?0
etp    :77 2:AZ Cotton:01.00:0009: 1.0:  .209:  .019:  .000:  .000:? 10.982?0
etp    :77 2:AZ Cotton:01.00:0009: 2.0:  .071:  .011:  .000:  .000:? 5.361?0
etp    :77 2:AZ Cotton:01.00:0009: 3.0:  .037:  .009:  .000:  .000:? 3.913?0
etp    :77 2:AZ Cotton:01.00:0009: 4.0:  .020:  .005:  .000:  .000:? 2.180?0
etp    :29 1:CAvCitrus: 2.50:0500: 1.0:  .338:  .023:  .000:  .000: 15.153 0
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etp    :29 1:CAvCitrus: 2.50:0500:15.0:  .012:  .000:  .000:  .000:  .309 0
etp    :29 2:CAvCitrus: 7.50:1500:  .0: 3.162:  .049:  .000:  .000: 61.829 0
etp    :29 2:CAvCitrus: 7.50:1500: 6.0:  .078:  .034:  .000:  .000: 13.046 0
etp    :29 2:CAvCitrus: 7.50:1500:13.0:  .038:  .014:  .000:  .000: 5.607 0
etp    :29 2:CAvCitrus: 7.50:1500:21.0:  .055:  .005:  .000:  .000: 3.244 0
etp    :29 2:CAvCitrus: 7.50:1500:29.0:  .005:  .014:  .000:  .000: 4.826 0
etp    :29 3:CAvCitrus: 7.50:1500:  .0: 3.217:  .049:  .000:  .000: 62.350 0
```

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etp  :29 3:CAvCitrus: 7.50:1500: 6.0:  .095:  .043; .   .  . .         0
etp  :29 3:CAvCitrus: 7.50:1500:13.0:  .033:  .033:  .000:  .000: 11.631 0
etp  :29 3:CAvCitrus: 7.50:1500:21.0:  .018:  .014:  .000:  .000:  5.119 0
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etp  :29 4:CAvCitrus: 4.00:1600: 4.0:  .173:  .016:  .000:  .000:  9.605 0
etp  :29 4:CAvCitrus: 4.00:1600:10.0:  .014:  .014:  .000:  .000:  5.022 0
etp  :29 4:CAvCitrus: 4.00:1600:17.0:  .021:  .000:  .000:  .000:   .514 0
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etp  :29 5:CAvCitrus:10.00:1600:10.0:  .124:  .014:  .000:  .000:  7.596 0
etp  :29 5:CAvCitrus:10.00:1600:17.0:  .060:  .000:  .000:  .000:  1.500 0
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etp  :29 6:CAvCitrus:10.00:1600:10.0:  .016:  .014:  .000:  .000:  5.087 0
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etp  :29 7:CAvCitrus:10.00: 100:17.0:  .258:  .010:  .000:  .000:  9.356 0
etp  :29 7:CAvCitrus:10.00: 100:27.0:  .113:  .027:  .000:  .000: 11.692 0
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etp  :31 1:CAsOrange:10.00:1600:17.0:  .060:  .000:  .000:  .000:  1.500 0
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etp  :31 3:CAsOrange: 4.00:1600:17.0:  .021:  .000:  .000:  .000:   .514 0
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etp  :31 4:CAsOrange:10.00: 100:17.0:  .258:  .010:  .000:  .000:  9.356 0
etp  :31 4:CAsOrange:10.00: 100:27.0:  .114:  .027:  .000:  .000: 11.722 0
etp  :32 1:CAvPeach : 2.00:  50:  .5: 1.034:  .038:  .000:  .000:? 13.561 0
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etp  :32 2:CAvPeach : 1.30:  17:  .5:  .850:  .000:  .000:  .000:?  7.605 0
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etp  :32 2:CAvPeach : 1.30:  17: 7.0:  .034:  .000:  .000:  .000:?   .316 0
etp  :32 2:CAvPeach : 1.30:  17:14.0:  .024:  .000:  .000:  .000:?   .223 0
etp  :32 2:CAvPeach : 1.30:  17:21.0:  .015:  .000:  .000:  .000:?   .138 0
etp  :30 1:CAvtomato:0.375:  10:  .0:  .382:  .005:  .000:  .000:? 10.625?0
etp  :30 1:CAvtomato:0.375:  10: 1.0:  .207:  .010:  .000:  .000:?  8.219?0
etp  :30 1:CAvtomato:0.375:  10: 2.0:  .104:  .011:  .000:  .000:?  5.968?0
etp  :30 1:CAvtomato:0.375:  10: 3.0:  .046:  .005:  .000:  .000:?  2.937?0
etp  :35 1:FL Orange:  .25: 100: 1.0:  .029:  .000:  .000:  .000:    .753 0
etp  :35 1:FL Orange:  .25: 100: 3.0:  .009:  .000:  .000:  .000:    .255 0
etp  :35 1:FL Orange:  .25: 100: 5.0:  .000:  .000:  .000:  .000:    .002 0
etp  :35 2:FL Orange: .375: 100: 1.0:  .036:  .009:  .000:  .000:   3.956 0
etp  :35 2:FL Orange: .375: 100: 3.0:  .022:  .004:  .000:  .000:   2.067 0
etp  :35 2:FL Orange: .375: 100: 5.0:  .001:  .000:  .000:  .000:    .023 0
```

```
etp  :35 3:FL Orange:  .25: 100:  .0:  .440:  .022:  .000:  .000:  17.097 0
etp  :35 3:FL Orange:  .25: 100: 1.0:  .040:  .015:  .000:  .000:   5.988 0
etp  :35 3:FL Orange:  .25: 100: 3.0:  .025:  .013:  .000:  .000:   4.906 0
etp  :35 3:FL Orange:  .25: 100: 5.0:  .021:  .011:  .000:  .000:   4.272 0
etp  :35 3:FL Orange:  .25: 100: 7.0:  .011:  .005:  .000:  .000:   2.135 0
etp  :35 3:FL Orange:  .25: 100:14.0:  .008:  .002:  .000:  .000:    .821 0
etp  :35 3:FL Orange:  .25: 100:21.0:  .008:  .004:  .000:  .000:   1.517 0
etp  :35 3:FL Orange:  .25: 100:28.0:  .003:  .000:  .000:  .000:    .085 0
etp  :35 3:FL Orange:  .25: 100:35.0:  .002:  .000:  .000:  .000:    .060 0
etp  :35 4:FL Orange: .945: 100:  .0: 2.719:  .085:  .000:  .000:  62.386 0
etp  :35 4:FL Orange: .945: 100: 1.0:  .551:  .034:  .000:  .000:  22.728 0
etp  :35 4:FL Orange: .945: 100: 3.0:  .174:  .030:  .000:  .000:  13.798 0
etp  :35 4:FL Orange: .945: 100: 5.0:  .102:  .016:  .000:  .000:   7.880 0
etp  :35 4:FL Orange: .945: 100: 7.0:  .041:  .006:  .000:  .000:   3.147 0
etp  :35 4:FL Orange: .945: 100:14.0:  .023:  .006:  .000:  .000:   2.569 0
etp  :35 4:FL Orange: .945: 100:21.0:  .019:  .003:  .000:  .000:   1.640 0
etp  :35 4:FL Orange: .945: 100:28.0:  .008:  .000:  .000:  .000:    .195 0
etp  :35 4:FL Orange: .945: 100:35.0:  .002:  .000:  .000:  .000:    .055 0
etp  :12 1:CA Orange:  8.0: 350: 1.0:14.086:  .262:  .000:  .000:  98.814 0
etp  :12 1:CA Orange:  8.0: 350: 3.0: 3.604:  .170:  .000:  .000:  77.570 0
etp  :12 1:CA Orange:  8.0: 350: 5.0: 2.102:  .134:  .000:  .000:  62.979 0
etp  :12 1:CA Orange:  8.0: 350: 7.0:  .836:  .094:  .000:  .000:  41.583 0
etp  :12 1:CA Orange:  8.0: 350:14.0:  .286:  .092:  .000:  .000:  32.509 0
etp  :12 2:AZ Orange: 8.00: 350:  .0:11.246:  .038:  .000:  .000:  94.724 0
etp  :12 2:AZ Orange: 8.00: 350: 1.0: 8.590:  .134:  .000:  .000:  92.679 0
etp  :12 2:AZ Orange: 8.00: 350: 3.0: 6.126:  .222:  .000:  .000:  90.040 0
etp  :12 2:AZ Orange: 8.00: 350: 5.0: 4.130:  .228:  .000:  .000:  83.943 0
etp  :12 2:AZ Orange: 8.00: 350: 7.0: 3.832:  .302:  .000:  .000:  86.646 0
etp  :12 2:AZ Orange: 8.00: 350:14.0: 1.832:  .152:  .000:  .000:  62.812 0
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etp  :12 2:AZ Orange: 8.00: 350:28.0:  .186:  .090:  .000:  .000:  30.316 0
etp  :12 2:AZ Orange: 8.00: 350:42.0:  .086:  .090:  .000:  .000:  28.554 0
etp  :12 3:CA Orange: 8.00:1450:  .0: 3.642:  .034:  .000:  .000:  64.251 0
etp  :12 3:CA Orange: 8.00:1450: 1.0: 2.036:  .052:  .000:  .000:  49.864 0
etp  :12 3:CA Orange: 8.00:1450: 3.0:  .890:  .114:  .000:  .000:  46.259 0
etp  :12 3:CA Orange: 8.00:1450: 7.0:  .272:  .090:  .000:  .000:  31.797 0
etp  :12 3:CA Orange: 8.00:1450:14.0:  .060:  .050:  .000:  .000:  17.291 0
etp  :12 3:CA Orange: 8.00:1450:28.0:  .010:  .014:  .000:  .000:   5.016 0
etp  :12 3:CA Orange: 8.00:1450:42.0:  .004:  .006:  .000:  .000:   2.174 0
etp  :12 4:CA Orange: 8.00:1450:  .0: 3.212:  .034:  .000:  .000:  60.198 0
etp  :12 4:CA Orange: 8.00:1450: 1.0: 1.924:  .058:  .000:  .000:  49.512 0
etp  :12 4:CA Orange: 8.00:1450: 3.0:  .974:  .064:  .000:  .000:  37.319 0
etp  :12 4:CA Orange: 8.00:1450: 7.0:  .218:  .036:  .000:  .000:  16.502 0
etp  :12 4:CA Orange: 8.00:1450:14.0:  .064:  .022:  .000:  .000:   8.874 0
etp  :12 4:CA Orange: 8.00:1450:28.0:  .012:  .008:  .000:  .000:   3.050 0
etp  :12 4:CA Orange: 8.00:1450:42.0:  .006:  .006:  .000:  .000:   2.223 0
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etp  :12 5:CA Orange: 8.00:1450: 3.0:  .786:  .024:  .000:  .000:  24.442 0
etp  :12 5:CA Orange: 8.00:1450: 5.0:  .540:  .028:  .000:  .000:  20.770 0
etp  :12 5:CA Orange: 8.00:1450: 7.0:  .286:  .026:  .000:  .000:  14.987 0
etp  :12 5:CA Orange: 8.00:1450:14.0:  .112:  .008:  .000:  .000:   5.442 0
etp  :12 5:CA Orange: 8.00:1450:21.0:  .034:  .006:  .000:  .000:   2.905 0
etp  :12 5:CA Orange: 8.00:1450:28.0:  .026:  .012:  .000:  .000:   4.730 0
etp  :12 5:CA Orange: 8.00:1450:42.0:  .004:  .004:  .000:  .000:   1.488 0
```

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etp   :12 6:CA Orange: 8.00: 350:  .0: 7.440:  .030:  .000:  .000:  85.962 0
etp   :12 6:CA Orange: 8.00: 350: 1.0: 5.396:  .118:  .000:  .000:  82.805 0
etp   :12 6:CA Orange: 8.00: 350: 3.0: 2.102:  .050:  .000:  .000:  50.338 0
etp   :12 6:CA Orange: 8.00: 350: 5.0: 1.346:  .060:  .000:  .000:  42.077 0
etp   :12 6:CA Orange: 8.00: 350: 7.0:  .792:  .038:  .000:  .000:  28.160 0
etp   :12 6:CA Orange: 8.00: 350:14.0:  .202:  .010:  .000:  .000:   8.188 0
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etp   :12 6:CA Orange: 8.00: 350:28.0:  .024:  .008:  .000:  .000:   3.340 0
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etp   :12 7:AZ Orange: 8.00: 350:28.0:  .156:  .080:  .000:  .000:  27.294 0
etp   :12 7:AZ Orange: 8.00: 350:42.0:  .040:  .034:  .000:  .000:  12.093 0
etp   :12 8:CA Grapes: 8.00: 350:  .0:15.378:  .188:  .000:  .000:  95.438 0
etp   :12 8:CA Grapes: 8.00: 350: 1.0:14.086:  .262:  .000:  .000:  95.233 0
etp   :12 8:CA Grapes: 8.00: 350: 3.0: 3.604:  .170:  .000:  .000:  64.150 0
etp   :12 8:CA Grapes: 8.00: 350: 5.0: 2.102:  .134:  .000:  .000:  49.437 0
etp   :12 8:CA Grapes: 8.00: 350: 7.0:  .836:  .094:  .000:  .000:  30.852 0
etp   :12 8:CA Grapes: 8.00: 350:14.0:  .286:  .092:  .000:  .000:  23.649 0
etp   :12 8:CA Grapes: 8.00: 350:28.0:  .052:  .030:  .000:  .000:   7.773 0
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etp   :12 9:CA Apple : 8.00: 350:  .0:18.690:  .162:  .000:  .000:? 97.248 0
etp   :12 9:CA Apple : 8.00: 350: 1.0:11.970:  .292:  .000:  .000:? 93.625 0
etp   :12 9:CA Apple : 8.00: 350: 3.0: 3.892:  .382:  .000:  .000:? 79.485 0
etp   :12 9:CA Apple : 8.00: 350: 5.0: 1.636:  .230:  .000:  .000:? 56.502 0
etp   :12 9:CA Apple : 8.00: 350: 7.0: 1.286:  .176:  .000:  .000:? 47.421 0
etp   :12 9:CA Apple : 8.00: 350:14.0:  .056:  .040:  .000:  .000:? 10.022 0
etp   :12 9:CA Apple : 8.00: 350:42.0:  .010:  .012:  .000:  .000:?  3.005 0
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etp   :1210:FL Orange: 8.00: 350: 3.0: 3.342:  .058:  .000:  .000:  64.571 0
etp   :1210:FL Orange: 8.00: 350: 5.0: 2.624:  .072:  .000:  .000:  59.637 0
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etp   :1211:TX Orange: 8.00: 350: 5.0: 2.668:  .104:  .000:  .000:  64.305 0
etp   :1211:TX Orange: 8.00: 350: 7.0: 1.166:  .060:  .000:  .000:  39.413 0
etp   :1211:TX Orange: 8.00: 350:14.0:  .098:  .016:  .000:  .000:   7.728 0
etp   :1211:TX Orange: 8.00: 350:21.0:  .024:  .008:  .000:  .000:   3.340 0
etp   :1211:TX Orange: 8.00: 350:28.0:  .010:  .006:  .000:  .000:   2.321 0
etp   :1211:TX Orange: 8.00: 350:42.0:  .004:  .002:  .000:  .000:    .796 0
etp   :75 1:AZ Cotton:  .50:   5:  .0: 4.020:  .020:  .000:  .000:? 65.113?0
etp   :75 1:AZ Cotton:  .50:   5:  .5: 2.750:  .040:  .000:  .000:? 55.541?0
etp   :75 1:AZ Cotton:  .50:   5: 1.0: 2.580:  .040:  .000:  .000:? 53.651?0
etp   :75 1:AZ Cotton:  .50:   5: 2.0: 1.960:  .050:  .000:  .000:? 47.870?0
```

```
etp   :75 1:AZ Cotton:  .50:   5: 3.0: 1.240:  .040:  .000:  .000:? 35.649?0
etp   :75 2:AZ Cotton:  .50:   5:  .0:  .920:  .000:  .000:  .000:? 20.173?0
etp   :75 2:AZ Cotton:  .50:   5:  .5:  .760:  .010:  .000:  .000:? 19.781?0
etp   :75 2:AZ Cotton:  .50:   5: 1.0:  .590:  .010:  .000:  .000:? 16.371?0
etp   :75 2:AZ Cotton:  .50:   5: 2.0:  .440:  .010:  .000:  .000:? 13.241?0
etp   :75 2:AZ Cotton:  .50:   5: 3.0:  .380:  .010:  .000:  .000:? 11.957?0
etp   :76 1:AZ Cotton: 1.00:   9: 1.0:  .350:  .004:  .000:  .000:?  9.465?0
etp   :76 1:AZ Cotton: 1.00:   9: 1.5:  .370:  .002:  .000:  .000:?  9.225?0
etp   :79 1:AZ Cotton: 1.00:   9:  .0: 2.330:  .000:  .000:  .000:? 43.482?0
etp   :79 1:AZ Cotton: 1.00:   9: 1.0:  .270:  .017:  .000:  .000:? 11.698?0
etp   :79 1:AZ Cotton: 1.00:   9: 2.0:  .150:  .012:  .000:  .000:?  7.492?0
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etp   :84 1:CAvCitrus: 8.00: 100: 1.0:  .000:  .380:  .000:  .000:  73.524 0
etp   :84 1:CAvCitrus: 8.00: 100: 2.0: 3.200:  .000:  .000:  .000:  55.038 0
etp   :84 1:CAvCitrus: 8.00: 100: 3.0: 1.400:  .300:  .000:  .000:  75.312 0
etp   :84 1:CAvCitrus: 8.00: 100: 7.0:  .000:  .340:  .000:  .000:  69.548 0
etp   :84 1:CAvCitrus: 8.00: 100:10.0:  .360:  .320:  .000:  .000:  70.151 0
etp   :84 1:CAvCitrus: 8.00: 100:14.0:  .120:  .200:  .000:  .000:  51.780 0
etp   :84 1:CAvCitrus: 8.00: 100:21.0:  .060:  .140:  .000:  .000:  39.625 0
etp   :84 1:CAvCitrus: 8.00: 100:28.0:  .036:  .104:  .000:  .000:  31.113 0
etp   :84 2:CAvCitrus: 8.00: 100:  .0: 8.000:  .044:  .000:  .000:  88.378 0
etp   :84 2:CAvCitrus: 8.00: 100: 1.0:  .000:  .200:  .000:  .000:  50.313 0
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```

```
etp   :84 5:CAvCitrus:  8.00: 100: 5.0:  .500:  .000:  .000:  .000:  11.---  0
etp   :84 5:CAvCitrus:  8.00: 100: 7.0:  .300:  .000:  .000:  .000:   7.220  0
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etp   :84 6:CAvCitrus:  8.00: 100:  .0: 5.000:  .000:  .000:  .000:  71.320  0
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etp   :84 6:CAvCitrus:  8.00: 100: 3.0: 1.200:  .000:  .000:  .000:  25.900  0
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etp   :84 6:CAvCitrus:  8.00: 100: 7.0:  .420:  .000:  .000:  .000:   9.960  0
etp   :84 6:CAvCitrus:  8.00: 100: 9.0:  .130:  .000:  .000:  .000:   3.195  0
etp   :84 6:CAvCitrus:  8.00: 100:13.0:  .120:  .000:  .000:  .000:   2.953  0
etp   :84 6:CAvCitrus:  8.00: 100:20.0:  .040:  .000:  .000:  .000:    .994  0
etp   :84 6:CAvCitrus:  8.00: 100:34.0:  .036:  .000:  .000:  .000:    .895  0
etp   :67 1:CAvOrange:  6.0:1200: 2.0:  .264:  .019:  .000:  .000:  12.289  0
etp   :67 1:CAvOrange:  6.0:1200: 9.0:  .030:  .013:  .000:  .000:   5.027  0
etp   :67 1:CAvOrange:  6.0:1200:16.0:  .010:  .007:  .000:  .000:   2.635  0
etp   :67 2:CAvOrange:  5.0:1000: 2.0:  .398:  .032:  .000:  .000:  19.079  0
etp   :67 2:CAvOrange:  5.0:1000: 9.0:  .055:  .033:  .000:  .000:  12.122  0
etp   :67 2:CAvOrange:  5.0:1000:16.0:  .025:  .009:  .000:  .000:   3.684  0
etp   :67 2:CAvOrange:  5.0:1000:23.0:  .008:  .006:  .000:  .000:   2.316  0
etp   :67 3:CAvOrange:  5.0:1000: 2.0:  .413:  .030:  .000:  .000:  18.695  0
etp   :67 3:CAvOrange:  5.0:1000: 9.0:  .095:  .012:  .000:  .000:   6.262  0
etp   :67 3:CAvOrange:  5.0:1000:16.0:  .050:  .010:  .000:  .000:   4.669  0
etp   :67 3:CAvOrange:  5.0:1000:23.0:  .011:  .006:  .000:  .000:   2.250  0
etp   :67 4:CAvOrange:  2.25: 900: 2.0: 1.434:  .109:  .000:  .000:  52.293  0
etp   :67 4:CAvOrange:  2.25: 900: 9.0:  .311:  .065:  .000:  .000:  26.250  0
etp   :67 4:CAvOrange:  2.25: 900:16.0:  .114:  .050:  .000:  .000:  18.395  0
etp   :67 4:CAvOrange:  2.25: 900:23.0:  .042:  .020:  .000:  .000:   7.650  0
etp   :67 5:CAvOrange:  2.0: 300: 2.0:  .181:  .090:  .000:  .000:  30.128  0
etp   :67 5:CAvOrange:  2.0: 300: 9.0:  .023:  .025:  .000:  .000:   9.040  0
etp   :67 5:CAvOrange:  2.0: 300:16.0:  .007:  .007:  .000:  .000:   2.698  0
etp   :67 6:CAvOrange:  2.0: 300: 2.0:  .171:  .071:  .000:  .000:  25.362  0
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etp   :67 7:CAvOrange:  2.5:1000: 9.0:  .006:  .026:  .000:  .000:   8.816  0
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etp   :67 8:CAvOrange:  1.5: 750: 2.0:  .191:  .011:  .000:  .000:   8.102  0
etp   :67 8:CAvOrange:  1.5: 750: 9.0:  .013:  .003:  .000:  .000:   1.293  0
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etp   :6710:CAvOrange:  1.3: 500: 2.0:  .252:  .034:  .000:  .000:  16.552  0
etp   :6710:CAvOrange:  1.3: 500: 9.0:  .027:  .020:  .000:  .000:   7.348  0
etp   :6710:CAvOrange:  1.3: 500:16.0:  .010:  .010:  .000:  .000:   3.703  0
etp   :6711:CAvOrange:  2.0: 200: 2.0:  .187:  .053:  .000:  .000:  20.654  0
etp   :6711:CAvOrange:  2.0: 200: 9.0:  .021:  .017:  .000:  .000:   6.253  0
etp   :6711:CAvOrange:  2.0: 200:16.0:  .007:  .007:  .000:  .000:   2.425  0
etp   :6711:CAvOrange:  2.0: 200:22.0:  .003:  .005:  .000:  .000:   1.830  0
etp   :6712:CAvOrange:  3.1:1250: 2.0:  .104:  .021:  .000:  .000:   9.582  0
etp   :6712:CAvOrange:  3.1:1250: 9.0:  .023:  .009:  .000:  .000:   3.745  0
etp   :6712:CAvOrange:  3.1:1250:16.0:  .008:  .007:  .000:  .000:   2.717  0
```

etp	:6713:CAvOrange:	1.9:	750:	2.0:	.175:	.035:	.000:	.000:	15.337 0
etp	:6713:CAvOrange:	1.9:	750:	9.0:	.028:	.014:	.000:	.000:	5.449 0
etp	:6713:CAvOrange:	1.9:	750:	16.0:	.011:	.009:	.000:	.000:	3.491 0
etp	:6714:CAvOrange:	2.5:	300:	2.0:	.295:	.034:	.000:	.000:	17.431 0
etp	:6714:CAvOrange:	2.5:	300:	9.0:	.033:	.012:	.000:	.000:	5.034 0
etp	:6714:CAvOrange:	2.5:	300:	16.0:	.006:	.007:	.000:	.000:	2.467 0
etp	:6715:CAvOrange:	3.0:	1200:	2.0:	.089:	.023:	.000:	.000:	9.779 0
etp	:6715:CAvOrange:	3.0:	1200:	9.0:	.020:	.006:	.000:	.000:	2.624 0
etp	:6715:CAvOrange:	3.0:	1200:	16.0:	.013:	.002:	.000:	.000:	.977 0
etp	:6716:CAvOrange:	2.0:	500:	2.0:	.241:	.021:	.000:	.000:	12.471 0
etp	:6716:CAvOrange:	2.0:	500:	9.0:	.044:	.018:	.000:	.000:	7.161 0
etp	:6716:CAvOrange:	2.0:	500:	16.0:	.008:	.007:	.000:	.000:	2.691 0
etp	:6717:CAvOrange:	1.9:	750:	2.0:	.688:	.025:	.000:	.000:	22.974 0
etp	:6717:CAvOrange:	1.9:	750:	9.0:	.048:	.011:	.000:	.000:	4.972 0
etp	:6717:CAvOrange:	1.9:	750:	16.0:	.011:	.007:	.000:	.000:	2.731 0
etp	:6718:CAvOrange:	1.9:	750:	2.0:	.229:	.052:	.000:	.000:	21.168 0
etp	:6718:CAvOrange:	1.9:	750:	9.0:	.058:	.025:	.000:	.000:	9.681 0
etp	:6718:CAvOrange:	1.9:	750:	16.0:	.012:	.012:	.000:	.000:	4.232 0
etp	:6719:CAvOrange:	2.0:	300:	2.0:	.483:	.167:	.000:	.000:	50.491 0
etp	:6719:CAvOrange:	2.0:	300:	9.0:	.012:	.054:	.000:	.000:	17.388 0
etp	:6719:CAvOrange:	2.0:	300:	16.0:	.005:	.021:	.000:	.000:	7.338 0
etp	:6720:CAvOrange:	7.5:	1800:	2.0:	1.297:	.227:	.000:	.000:	67.336 0
etp	:6720:CAvOrange:	7.5:	1800:	9.0:	.120:	.135:	.000:	.000:	39.492 0
etp	:6720:CAvOrange:	7.5:	1800:	16.0:	.039:	.021:	.000:	.000:	8.011 0
etp	:6720:CAvOrange:	7.5:	1800:	21.0:	.009:	.017:	.000:	.000:	6.095 0
etp	:6721:CAvOrange:	2.0:	300:	2.0:	.173:	.328:	.000:	.000:	69.551 0
etp	:6721:CAvOrange:	2.0:	300:	9.0:	.021:	.066:	.000:	.000:	20.967 0
etp	:6721:CAvOrange:	2.0:	300:	16.0:	.033:	.021:	.000:	.000:	7.698 0
etp	:6722:CAvOrange:	2.0:	300:	2.0:	.439:	.396:	.000:	.000:	77.570 0
etp	:6722:CAvOrange:	2.0:	300:	9.0:	.043:	.072:	.000:	.000:	23.060 0
etp	:6722:CAvOrange:	2.0:	300:	16.0:	.002:	.018:	.000:	.000:	6.146 0
etp	:6723:CAvOrange:	1.9:	750:	3.0:	.170:	.001:	.000:	.000:	4.582 0
etp	:6723:CAvOrange:	1.9:	750:	10.0:	.015:	.004:	.000:	.000:	1.660 0
etp	:6723:CAvOrange:	1.9:	750:	17.0:	.005:	.003:	.000:	.000:	1.139 0
etp	:6724:CAvOrange:	1.9:	750:	2.0:	.153:	.016:	.000:	.000:	8.875 0
etp	:6724:CAvOrange:	1.9:	750:	9.0:	.008:	.005:	.000:	.000:	1.768 0
etp	:6724:CAvOrange:	1.9:	750:	16.0:	.004:	.002:	.000:	.000:	.965 0
etp	:6725:CAvOrange:	2.5:	1000:	2.0:	.417:	.025:	.000:	.000:	17.439 0
etp	:6725:CAvOrange:	2.5:	1000:	9.0:	.038:	.016:	.000:	.000:	6.474 0
etp	:6725:CAvOrange:	2.5:	1000:	16.0:	.004:	.005:	.000:	.000:	1.806 0
etp	:6726:CAvOrange:	2.0:	250:	2.0:	.771:	.366:	.000:	.000:	77.026 0
etp	:6726:CAvOrange:	2.0:	250:	9.0:	.069:	.051:	.000:	.000:	17.821 0
etp	:6726:CAvOrange:	2.0:	250:	16.0:	.021:	.025:	.000:	.000:	8.994 0
etp	:6727:CAvOrange:	4.6:	1850:	2.0:	.387:	.011:	.000:	.000:	12.768 0
etp	:6727:CAvOrange:	4.6:	1850:	9.0:	.043:	.016:	.000:	.000:	6.289 0
etp	:6727:CAvOrange:	4.6:	1850:	16.0:	.012:	.005:	.000:	.000:	1.928 0
etp	:6728:CAvOrange:	7.5:	1500:	2.0:	.618:	.321:	.000:	.000:	72.081 0
etp	:6728:CAvOrange:	7.5:	1500:	9.0:	.067:	.115:	.000:	.000:	34.296 0
etp	:6728:CAvOrange:	7.5:	1500:	16.0:	.024:	.058:	.000:	.000:	18.848 0
etp	:6728:CAvOrange:	7.5:	1500:	22.0:	.010:	.018:	.000:	.000:	6.373 0
etp	:6729:CAvOrange:	2.3:	900:	2.0:	.363:	.032:	.000:	.000:	18.360 0
etp	:6729:CAvOrange:	2.3:	900:	9.0:	.020:	.013:	.000:	.000:	4.981 0
etp	:6729:CAvOrange:	2.3:	900:	16.0:	.004:	.007:	.000:	.000:	2.535 0
etp	:6730:CAvOrange:	1.9:	750:	2.0:	.200:	.145:	.000:	.000:	42.706 0
etp	:6730:CAvOrange:	1.9:	750:	9.0:	.024:	.022:	.000:	.000:	8.088 0

etp	:6730:CAvOrange:	1.9: 750:16.0:	.009:	.013:	.000:	.000:		0
etp	:45 0:CAvOrange:	7.5:1800: 2.0:	.483:	.326:	.000:	.000:	71.624	0
etp	:45 0:CAvOrange:	7.5:1800: 8.0:	.048:	.235:	.000:	.000:	56.547	0
etp	:45 0:CAvOrange:	7.5:1800: 9.0:	.016:	.065:	.000:	.000:	20.727	0
etp	:45 0:CAvOrange:	7.5:1800:16.0:	.013:	.090:	.000:	.000:	27.288	0
etp	:45 0:CAvOrange:	7.5:1800:21.0:	.008:	.033:	.000:	.000:	11.117	0
etp	:45 0:CAvOrange:	7.5:1800:22.0:	.006:	.036:	.000:	.000:	11.910	0
etp	:45 0:CAvOrange:	7.5:1800:23.0:	.003:	.026:	.000:	.000:	8.864	0
etp	:45 0:CAvOrange:	7.5:1800:24.0:	.006:	.037:	.000:	.000:	12.306	0
etp	:45 0:CAvOrange:	7.5:1800:25.0:	.005:	.035:	.000:	.000:	11.716	0
etp	:45 0:CAvOrange:	7.5:1800:28.0:	.002:	.035:	.000:	.000:	11.604	0
etp	:45 0:CAvOrange:	7.5:1800:29.0:	.002:	.018:	.000:	.000:	5.983	0
etp	:45 0:CAvOrange:	7.5:1800:30.0:	.005:	.041:	.000:	.000:	13.609	0
etp	:45 0:CAvOrange:	7.5:1800:36.0:	.007:	.027:	.000:	.000:	9.210	0
etp	:45 0:CAvOrange:	7.5:1800:46.0:	.003:	.024:	.000:	.000:	8.104	0
etp	:46 1:CAvOrange:	2.0: 250: 5.0:	.304:	.111:	.000:	.000:	37.081	0
etp	:46 1:CAvOrange:	2.0: 250: 8.0:	.107:	.062:	.000:	.000:	21.662	0
etp	:46 1:CAvOrange:	2.0: 250:15.0:	.040:	.029:	.000:	.000:	10.432	0
etp	:46 1:CAvOrange:	2.0: 250:22.0:	.026:	.021:	.000:	.000:	7.751	0
etp	:46 1:CAvOrange:	2.0: 250:33.0:	.010:	.007:	.000:	.000:	2.752	0
etp	:46 2:CAvOrange:	5.0:1000: 2.0:	.893:	.277:	.000:	.000:	69.611	0
etp	:46 2:CAvOrange:	5.0:1000: 5.0:	.216:	.127:	.000:	.000:	39.167	0
etp	:46 2:CAvOrange:	5.0:1000: 9.0:	.045:	.096:	.000:	.000:	29.272	0
etp	:46 2:CAvOrange:	5.0:1000:16.0:	.010:	.020:	.000:	.000:	6.850	0
etp	:46 2:CAvOrange:	5.0:1000:23.0:	.005:	.003:	.000:	.000:	1.028	0
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etp	:46 3:CAvOrange:	2.5: 500: 2.0:	.563:	.038:	.000:	.000:	23.934	0
etp	:46 3:CAvOrange:	2.5: 500: 5.0:	.146:	.011:	.000:	.000:	7.244	0
etp	:46 3:CAvOrange:	2.5: 500:10.0:	.054:	.004:	.000:	.000:	2.614	0
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etp	:46 3:CAvOrange:	2.5: 500:24.0:	.009:	.003:	.000:	.000:	1.162	0
etp	:46 3:CAvOrange:	2.5: 500:33.0:	.004:	.002:	.000:	.000:	.757	0
etp	:46 4:CAvOrange:	2.5: 500: 2.0:	.216:	.025:	.000:	.000:	13.093	0
etp	:46 4:CAvOrange:	2.5: 500: 9.0:	.016:	.010:	.000:	.000:	3.660	0
etp	:46 4:CAvOrange:	2.5: 500:16.0:	.004:	.004:	.000:	.000:	1.607	0
etp	:46 4:CAvOrange:	2.5: 500:23.0:	.002:	.001:	.000:	.000:	.549	0
etp	:46 4:CAvOrange:	2.5: 500:33.0:	.003:	.002:	.000:	.000:	.686	0
etp	:46 5:CAvOrange:	2.0: 250: 2.0:	1.724:	.093:	.000:	.000:	52.966	0
etp	:46 5:CAvOrange:	2.0: 250: 5.0:	.475:	.062:	.000:	.000:	28.611	0
etp	:46 5:CAvOrange:	2.0: 250: 9.0:	.093:	.028:	.000:	.000:	11.289	0
etp	:46 5:CAvOrange:	2.0: 250:16.0:	.018:	.020:	.000:	.000:	7.320	0
etp	:46 5:CAvOrange:	2.0: 250:23.0:	.008:	.009:	.000:	.000:	3.359	0
etp	:46 5:CAvOrange:	2.0: 250:33.0:	.005:	.003:	.000:	.000:	1.332	0
etp	:46 6:CAvOrange:	6.3:1200: .0:	2.272:	.198:	.000:	.000:	71.673	0
etp	:46 6:CAvOrange:	6.3:1200: 1.0:	.634:	.225:	.000:	.000:	61.165	0
etp	:46 6:CAvOrange:	6.3:1200: 2.0:	.304:	.160:	.000:	.000:	46.971	0
etp	:46 6:CAvOrange:	6.3:1200: 6.0:	.080:	.148:	.000:	.000:	41.692	0
etp	:46 6:CAvOrange:	6.3:1200:12.0:	.023:	.047:	.000:	.000:	15.768	0
etp	:46 6:CAvOrange:	6.3:1200:19.0:	.020:	.035:	.000:	.000:	12.083	0
etp	:46 6:CAvOrange:	6.3:1200:35.0:	.007:	.012:	.000:	.000:	4.291	0
etp	:46 7:CAvOrange:	6.3:1200: .0:	2.149:	.336:	.000:	.000:	81.947	0
etp	:46 7:CAvOrange:	6.3:1200: 1.0:	.757:	.315:	.000:	.000:	72.534	0
etp	:46 7:CAvOrange:	6.3:1200: 2.0:	.327:	.263:	.000:	.000:	63.215	0
etp	:46 7:CAvOrange:	6.3:1200: 6.0:	.074:	.172:	.000:	.000:	46.284	0
etp	:46 7:CAvOrange:	6.3:1200:12.0:	.019:	.083:	.000:	.000:	25.580	0

etp	:46 7:CAvOrange:	6.3:1200:19.0:	.009:	.035:	.000:	.000:	11.825	0
etp	:46 7:CAvOrange:	6.3:1200:35.0:	.004:	.012:	.000:	.000:	4.223	0
etp	:46 8:CAvOrange:	7.5:1200: 2.0:	.419:	.062:	.000:	.000:	27.532	0
etp	:46 8:CAvOrange:	7.5:1200: 9.0:	.081:	.041:	.000:	.000:	14.990	0
etp	:46 8:CAvOrange:	7.5:1200:16.0:	.036:	.026:	.000:	.000:	9.581	0
etp	:46 8:CAvOrange:	7.5:1200:23.0:	.031:	.023:	.000:	.000:	8.333	0
etp	:46 8:CAvOrange:	7.5:1200:40.0:	.014:	.012:	.000:	.000:	4.378	0
etp	:46 9:CAvOrange:	2.0: 500: .0:	1.704:	.012:	.000:	.000:	37.454	0
etp	:46 9:CAvOrange:	2.0: 500: 2.0:	.194:	.090:	.000:	.000:	30.570	0
etp	:46 9:CAvOrange:	2.0: 500: 6.0:	.046:	.055:	.000:	.000:	18.465	0
etp	:46 9:CAvOrange:	2.0: 500:10.0:	.027:	.027:	.000:	.000:	9.568	0
etp	:46 9:CAvOrange:	2.0: 500:15.0:	.026:	.027:	.000:	.000:	9.599	0
etp	:46 9:CAvOrange:	2.0: 500:33.0:	.005:	.007:	.000:	.000:	2.568	0
etp	:4610:CAvOrange:	4.0:1000: .0:	2.797:	.023:	.000:	.000:	54.122	0
etp	:4610:CAvOrange:	4.0:1000: 2.0:	.235:	.096:	.000:	.000:	32.606	0
etp	:4610:CAvOrange:	4.0:1000: 6.0:	.053:	.109:	.000:	.000:	32.670	0
etp	:4610:CAvOrange:	4.0:1000:10.0:	.041:	.050:	.000:	.000:	16.920	0
etp	:4610:CAvOrange:	4.0:1000:16.0:	.025:	.030:	.000:	.000:	10.442	0
etp	:4610:CAvOrange:	4.0:1000:21.5:	.017:	.042:	.000:	.000:	14.026	0
etp	:4610:CAvOrange:	4.0:1000:33.0:	.007:	.013:	.000:	.000:	4.482	0
etp	:4611:CAvOrange:	8.0:1500: .0:	4.067:	.011:	.000:	.000:	65.134	0
etp	:4611:CAvOrange:	8.0:1500: 2.0:	.607:	.211:	.000:	.000:	58.873	0
etp	:4611:CAvOrange:	8.0:1500: 6.0:	.216:	.161:	.000:	.000:	46.029	0
etp	:4611:CAvOrange:	8.0:1500:10.0:	.083:	.086:	.000:	.000:	27.505	0
etp	:4611:CAvOrange:	8.0:1500:17.0:	.048:	.080:	.000:	.000:	25.267	0
etp	:4611:CAvOrange:	8.0:1500:25.0:	.030:	.083:	.000:	.000:	25.752	0
etp	:4611:CAvOrange:	8.0:1500:27.0:	.031:	.056:	.000:	.000:	18.327	0
etp	:4611:CAvOrange:	8.0:1500:44.0:	.014:	.035:	.000:	.000:	11.712	0
etp	:4611:CAvOrange:	8.0:1500:82.0:	.006:	.007:	.000:	.000:	2.709	0
etp	:4612:CAvOrange:	7.5:1500: .0:	2.098:	.044:	.000:	.000:	49.252	0
etp	:4612:CAvOrange:	7.5:1500: 1.0:	.415:	.046:	.000:	.000:	23.244	0
etp	:4612:CAvOrange:	7.5:1500: 3.0:	.512:	.154:	.000:	.000:	48.647	0
etp	:4612:CAvOrange:	7.5:1500: 7.0:	.128:	.115:	.000:	.000:	35.218	0
etp	:4612:CAvOrange:	7.5:1500:14.0:	.048:	.085:	.000:	.000:	26.600	0
etp	:4612:CAvOrange:	7.5:1500:28.0:	.008:	.032:	.000:	.000:	10.697	0
etp	:4612:CAvOrange:	7.5:1500:42.0:	.005:	.013:	.000:	.000:	4.456	0
etp	:4613:CAvOrange:	7.5:1500: .0:	3.000:	.096:	.000:	.000:	66.214	0
etp	:4613:CAvOrange:	7.5:1500: 1.0:	1.614:	.083:	.000:	.000:	50.014	0
etp	:4613:CAvOrange:	7.5:1500: 3.0:	.750:	.170:	.000:	.000:	54.245	0
etp	:4613:CAvOrange:	7.5:1500: 7.0:	.252:	.112:	.000:	.000:	36.532	0
etp	:4613:CAvOrange:	7.5:1500:14.0:	.079:	.065:	.000:	.000:	21.890	0
etp	:4613:CAvOrange:	7.5:1500:28.0:	.007:	.019:	.000:	.000:	6.699	0
etp	:4613:CAvOrange:	7.5:1500:42.0:	.008:	.021:	.000:	.000:	7.266	0
etp	:4614:CAvOrange:	7.5:1500: .0:	2.481:	.034:	.000:	.000:	52.224	0
etp	:4614:CAvOrange:	7.5:1500: 1.0:	1.713:	.104:	.000:	.000:	54.688	0
etp	:4614:CAvOrange:	7.5:1500: 3.0:	.480:	.130:	.000:	.000:	43.703	0
etp	:4614:CAvOrange:	7.5:1500: 7.0:	.120:	.082:	.000:	.000:	27.148	0
etp	:4614:CAvOrange:	7.5:1500:14.0:	.034:	.070:	.000:	.000:	22.376	0
etp	:4614:CAvOrange:	7.5:1500:28.0:	.008:	.019:	.000:	.000:	6.618	0
etp	:4614:CAvOrange:	7.5:1500:42.0:	.005:	.009:	.000:	.000:	3.050	0
etp	:4615:CAvOrange:	7.5:1500: .0:	2.850:	.072:	.000:	.000:	61.919	0
etp	:4615:CAvOrange:	7.5:1500: 1.0:	.880:	.041:	.000:	.000:	30.455	0
etp	:4615:CAvOrange:	7.5:1500: 3.0:	.810:	.097:	.000:	.000:	41.816	0
etp	:4615:CAvOrange:	7.5:1500: 7.0:	.140:	.058:	.000:	.000:	21.164	0
etp	:4615:CAvOrange:	7.5:1500:14.0:	.050:	.036:	.000:	.000:	12.924	0

```
etp     :4615:CAvOrange: 7.5:1500:28.0:  .017:  .019:  .000:  .000:   6.825 0
etp     :4615:CAvOrange: 7.5:1500:42.0:  .009:  .032:  .000:  .000:  10.788 0
etp     :4616:CAvOrange: 7.5:1500:  .0: 1.880:  .069:  .000:  .000:  50.881 0
etp     :4616:CAvOrange: 7.5:1500: 1.0: 2.200:  .114:  .000:  .000:  61.257 0
etp     :4616:CAvOrange: 7.5:1500: 3.0: 1.100:  .120:  .000:  .000:  50.064 0
etp     :4616:CAvOrange: 7.5:1500: 7.0:  .237:  .116:  .000:  .000:  37.178 0
etp     :4616:CAvOrange: 7.5:1500:14.0:  .060:  .045:  .000:  .000:  15.832 0
etp     :4616:CAvOrange: 7.5:1500:28.0:  .013:  .024:  .000:  .000:   8.349 0
etp     :4616:CAvOrange: 7.5:1500:42.0:  .009:  .021:  .000:  .000:   7.301 0
etp     :4617:CAvOrange: 7.5:1500:  .0: 2.074:  .030:  .000:  .000:  46.366 0
etp     :4617:CAvOrange: 7.5:1500: 1.0: 1.560:  .051:  .000:  .000:  43.237 0
etp     :4617:CAvOrange: 7.5:1500: 3.0:  .141:  .032:  .000:  .000:  13.742 0
etp     :4617:CAvOrange: 7.5:1500: 7.0:  .147:  .049:  .000:  .000:  18.928 0
etp     :4617:CAvOrange: 7.5:1500:14.0:  .043:  .034:  .000:  .000:  12.150 0
etp     :4617:CAvOrange: 7.5:1500:28.0:  .010:  .011:  .000:  .000:   3.904 0
etp     :4617:CAvOrange: 7.5:1500:42.0:  .009:  .007:  .000:  .000:   2.642 0
malat   :38 1:FL Orange: 4.00: 750: 1.0: 1.000:  .000:  .000:  .000:    .079 0
malat   :38 1:FL Orange: 4.00: 750: 2.0:  .444:  .000:  .000:  .000:    .035 0
malat   :38 1:FL Orange: 4.00: 750: 5.0:  .152:  .000:  .000:  .000:    .012 0
malat   :38 1:FL Orange: 4.00: 750:10.0:  .068:  .000:  .000:  .000:    .005 0
malat   :38 1:FL Orange: 4.00: 750:20.0:  .030:  .000:  .000:  .000:    .002 0
malat   :38 1:FL Orange: 4.00: 750:30.0:  .018:  .000:  .000:  .000:    .001 0
malat   :38 2:FL Orange: 4.00: 750: 1.0:  .012:  .000:  .000:  .000:    .001 0
malat   :38 2:FL Orange: 4.00: 750: 2.0:  .006:  .000:  .000:  .000:    .000 0
malat   :38 2:FL Orange: 4.00: 750: 5.0:  .018:  .000:  .000:  .000:    .001 0
malat   :38 2:FL Orange: 4.00: 750:10.0:  .001:  .000:  .000:  .000:    .000 0
mep     :22 1:CA Grapes:  .75: 100:  .0:  .342:  .002:  .000:  .000:   1.219 0
mep     :22 1:CA Grapes:  .75: 100: 1.0:  .034:  .022:  .000:  .000:    .120 0
mep     :22 1:CA Grapes:  .75: 100: 2.0:  .015:  .028:  .000:  .000:    .053 0
mep     :22 1:CA Grapes:  .75: 100: 5.0:  .002:  .012:  .000:  .000:    .008 0
mep     :22 2:CA Grapes:  .75: 100:  .0:  .246:  .000:  .000:  .000:    .876 0
mep     :22 2:CA Grapes:  .75: 100: 1.0:  .008:  .000:  .000:  .000:    .030 0
mep     :22 2:CA Grapes:  .75: 100: 2.0:  .006:  .000:  .000:  .000:    .023 0
mep     :22 3:CA Grapes:  .75:  25:  .0:  .477:  .000:  .000:  .000:   1.693 0
mep     :22 3:CA Grapes:  .75:  25: 1.0:  .103:  .000:  .000:  .000:    .368 0
mep     :22 3:CA Grapes:  .75:  25: 3.0:  .017:  .000:  .000:  .000:    .060 0
mep     :22 3:CA Grapes:  .75:  25: 7.0:  .006:  .000:  .000:  .000:    .023 0
mep     :22 4:CA Grapes:  .75: 100:  .0:  .269:  .000:  .000:  .000:    .958 0
mep     :22 4:CA Grapes:  .75: 100: 1.0:  .046:  .000:  .000:  .000:    .165 0
mep     :22 4:CA Grapes:  .75: 100: 3.0:  .015:  .000:  .000:  .000:    .053 0
mep     :22 4:CA Grapes:  .75: 100: 7.0:  .006:  .000:  .000:  .000:    .023 0
mep     :22 5:CA Grapes:  .75:  25:  .0:  .233:  .000:  .000:  .000:    .832 0
mep     :22 5:CA Grapes:  .75:  25: 1.0:  .065:  .000:  .000:  .000:    .233 0
mep     :22 5:CA Grapes:  .75:  25: 2.0:  .017:  .000:  .000:  .000:    .060 0
mep     :22 5:CA Grapes:  .75:  25: 3.0:  .010:  .000:  .000:  .000:    .038 0
mep     :22 5:CA Grapes:  .75:  25: 7.0:  .002:  .008:  .000:  .000:    .008 0
mep     :22 6:CA Grapes:  .75: 100:  .0:  .191:  .000:  .000:  .000:    .682 0
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mep     :22 6:CA Grapes:  .75: 100: 2.0:  .013:  .000:  .000:  .000:    .045 0
mep     :22 6:CA Grapes:  .75: 100: 3.0:  .017:  .000:  .000:  .000:    .060 0
mep     :22 7:CA Grapes:  .75:  25:  .0:  .359:  .000:  .000:  .000:   1.278 0
mep     :22 7:CA Grapes:  .75:  25: 1.0:  .076:  .000:  .000:  .000:    .270 0
mep     :22 7:CA Grapes:  .75:  25: 3.0:  .010:  .000:  .000:  .000:    .038 0
mep     :22 7:CA Grapes:  .75:  25: 4.0:  .004:  .000:  .000:  .000:    .015 0
mep     :22 7:CA Grapes:  .75:  25: 7.0:  .002:  .000:  .000:  .000:    .008 0
```

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mep    :22 8:CA Grapes:  .75: 100:  .0:  .187:  .000:  .000:  .000:    .667 0
mep    :22 8:CA Grapes:  .75: 100: 1.0:  .034:  .000:  .000:  .000:    .120 0
mep    :22 8:CA Grapes:  .75: 100: 3.0:  .010:  .000:  .000:  .000:    .038 0
mep    :22 8:CA Grapes:  .75: 100: 7.0:  .002:  .000:  .000:  .000:    .008 0
mep    :22 9:CA Grapes:  .75:  25:  .0:  .416:  .000:  .000:  .000:   1.478 0
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mep    :22 9:CA Grapes:  .75:  25: 3.0:  .029:  .000:  .000:  .000:    .105 0
mep    :22 9:CA Grapes:  .75:  25: 7.0:  .013:  .000:  .000:  .000:    .045 0
mep    :22 9:CA Grapes:  .75:  25:14.0:  .010:  .000:  .000:  .000:    .038 0
mep    :2210:CA Grapes:  .75: 100:  .0:  .155:  .000:  .000:  .000:    .555 0
mep    :2210:CA Grapes:  .75: 100: 1.0:  .055:  .000:  .000:  .000:    .195 0
mep    :2210:CA Grapes:  .75: 100: 3.0:  .015:  .000:  .000:  .000:    .053 0
mep    :2210:CA Grapes:  .75: 100: 7.0:  .004:  .000:  .000:  .000:    .015 0
mep    :74 1:AZ Cotton: 1.00:   9:  .0: 2.650:  .014:  .000:  .000:? 12.743?1
mep    :74 1:AZ Cotton: 1.00:   9:  .5:  .498:  .015:  .000:  .000:?  2.589?1
mep    :74 1:AZ Cotton: 1.00:   9: 1.0:  .250:  .007:  .000:  .000:?  1.308?1
mep    :74 1:AZ Cotton: 1.00:   9: 2.0:  .153:  .002:  .000:  .000:?   .790?1
mep    :74 1:AZ Cotton: 1.00:   9: 3.0:  .127:  .002:  .000:  .000:?   .658?1
mep    :74 1:AZ Cotton: 1.00:   9: 4.0:  .098:  .000:  .000:  .000:?   .499?1
mep    :30 1:CAvtomato: .019:  10:  .0:  .242:  .000:  .000:  .000:?  1.232?1
mep    :30 1:CAvtomato: .019:  10: 1.0:  .151:  .004:  .000:  .000:?   .789?1
mep    :30 1:CAvtomato: .019:  10: 2.0:  .064:  .000:  .000:  .000:?   .329?1
mep    :30 1:CAvtomato: .019:  10: 3.0:  .010:  .000:  .000:  .000:?   .052?1
mep    :12 1:AZ Orange: 8.00: 350:  .0:18.162:  .072:  .000:  .000:  61.393 1
mep    :12 1:AZ Orange: 8.00: 350: 1.0:14.550:  .186:  .000:  .000:  53.660 1
mep    :12 1:AZ Orange: 8.00: 350: 3.0: 9.208:  .244:  .000:  .000:  38.943 1
mep    :12 1:AZ Orange: 8.00: 350: 5.0: 6.158:  .238:  .000:  .000:  28.384 1
mep    :12 1:AZ Orange: 8.00: 350: 7.0: 4.392:  .226:  .000:  .000:  21.419 1
mep    :12 1:AZ Orange: 8.00: 350:14.0:  .846:  .192:  .000:  .000:   5.274 1
mep    :12 1:AZ Orange: 8.00: 350:21.0:  .204:  .128:  .000:  .000:   1.718 1
mep    :12 1:AZ Orange: 8.00: 350:28.0:  .070:  .096:  .000:  .000:    .863 1
mep    :12 1:AZ Orange: 8.00: 350:42.0:  .014:  .014:  .000:  .000:    .146 1
mep    :75 1:AZ Cotton:  .50:   5:  .0: 5.610:  .050:  .000:  .000:? 25.147?1
mep    :75 1:AZ Cotton:  .50:   5:  .5: 3.310:  .120:  .000:  .000:? 16.098?1
mep    :75 1:AZ Cotton:  .50:   5: 1.0: 2.840:  .070:  .000:  .000:? 13.836?1
mep    :75 1:AZ Cotton:  .50:   5: 2.0: 1.890:  .060:  .000:  .000:?  9.497?1
mep    :75 1:AZ Cotton:  .50:   5: 3.0: 1.090:  .050:  .000:  .000:?  5.667?1
mep    :75 2:AZ Cotton:  .50:   5:  .0: 1.370:  .020:  .000:  .000:?  6.866?1
mep    :75 2:AZ Cotton:  .50:   5:  .5: 1.090:  .020:  .000:  .000:?  5.522?1
mep    :75 2:AZ Cotton:  .50:   5: 1.0:  .810:  .010:  .000:  .000:?  4.109?1
mep    :75 2:AZ Cotton:  .50:   5: 2.0:  .560:  .010:  .000:  .000:?  2.875?1
mep    :75 2:AZ Cotton:  .50:   5: 3.0:  .490:  .010:  .000:  .000:?  2.526?1
mep    :78 1:AZ Cotton: 1.00:   9: 1.0:  .150:  .004:  .000:  .000:?   .785?1
mep    :78 1:AZ Cotton: 1.00:   9: 1.5:  .060:  .002:  .000:  .000:?   .317?1
mep    :79 1:AZ Cotton: 1.00:   9:  .0: 2.370:  .000:  .000:  .000:? 11.421?0
mep    :79 1:AZ Cotton: 1.00:   9:  .5: 1.630:  .000:  .000:  .000:?  8.003?0
mep    : 6 1:WA Apple :01.50:0400:  .0: 4.740:  .000:  .000:  .000:? 15.616 0
mep    : 6 1:WA Apple :01.50:0400: 1.0: 1.704:  .000:  .000:  .000:?  5.921 0
mep    : 6 1:WA Apple :01.50:0400: 2.0: 1.042:  .000:  .000:  .000:?  3.664 0
mep    : 6 1:WA Apple :01.50:0400: 3.0:  .710:  .000:  .000:  .000:?  2.511 0
mep    : 6 1:WA Apple :01.50:0400: 7.0:  .284:  .000:  .000:  .000:?  1.012 0
mep    : 6 2:WA Apple :01.50:0400:  .0: 5.600:  .000:  .000:  .000:? 18.176 0
mep    : 6 2:WA Apple :01.50:0400: 1.0: 4.396:  .000:  .000:  .000:? 14.570 0
mep    : 6 2:WA Apple :01.50:0400: 2.0: 3.136:  .000:  .000:  .000:? 10.625 0
mep    : 6 2:WA Apple :01.50:0400: 3.0: 3.080:  .000:  .000:  .000:? 10.446 0
```

```
mep     : 6 2:WA Apple :01.50:0400: 7.0: 1.400:  .000:  .000:  .000:7  4.891 0
metion  :17 1:CAsOrange: 3.75:1500:  .0: 1.060:  .000:  .000:  .000:   4.951 0
metion  :17 1:CAsOrange: 3.75:1500: 3.0:  .520:  .024:  .000:  .000:   2.869 0
metion  :17 1:CAsOrange: 3.75:1500:10.0:  .044:  .004:  .000:  .000:    .280 0
metion  :17 1:CAsOrange: 3.75:1500:17.0:  .022:  .016:  .000:  .000:    .384 0
metion  :17 2:CAsOrange: 7.50:1500:  .0: 2.000:  .000:  .000:  .000:   9.137 0
metion  :17 2:CAsOrange: 7.50:1500: 3.0: 1.240:  .030:  .000:  .000:   6.260 0
metion  :17 2:CAsOrange: 7.50:1500:10.0:  .138:  .004:  .000:  .000:    .728 0
metion  :17 2:CAsOrange: 7.50:1500:17.0:  .066:  .000:  .000:  .000:    .316 0
metion  :17 2:CAsOrange: 7.50:1500:31.0:  .020:  .000:  .000:  .000:    .096 0
metion  :17 2:CAsOrange: 7.50:1500:45.0:  .004:  .000:  .000:  .000:    .019 0
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metion  :17 3:CAsOrange: 3.75: 100: 3.0: 3.600:  .036:  .000:  .000:  16.369 0
metion  :17 3:CAsOrange: 3.75: 100:10.0:  .600:  .012:  .000:  .000:   3.037 0
metion  :17 3:CAsOrange: 3.75: 100:17.0:  .120:  .004:  .000:  .000:    .643 0
metion  :17 3:CAsOrange: 3.75: 100:31.0:  .056:  .000:  .000:  .000:    .268 0
metion  :17 3:CAsOrange: 3.75: 100:45.0:  .026:  .000:  .000:  .000:    .124 0
metion  :17 3:CAsOrange: 3.75: 100:60.0:  .020:  .000:  .000:  .000:    .096 0
metion  :17 4:CAsOrange: 3.75:1500:  .0: 1.000:  .000:  .000:  .000:   4.678 0
metion  :17 4:CAsOrange: 3.75:1500: 3.0:  .420:  .000:  .000:  .000:   1.992 0
metion  :17 4:CAsOrange: 3.75:1500:10.0:  .074:  .000:  .000:  .000:    .354 0
metion  :17 4:CAsOrange: 3.75:1500:17.0:  .024:  .000:  .000:  .000:    .115 0
metion  :17 5:CAsOrange: 7.00:1500:  .0: 2.200:  .000:  .000:  .000:  10.003 0
metion  :17 5:CAsOrange: 7.00:1500: 3.0:  .860:  .004:  .000:  .000:   4.103 0
metion  :17 5:CAsOrange: 7.00:1500:10.0:  .160:  .000:  .000:  .000:    .764 0
metion  :17 5:CAsOrange: 7.00:1500:17.0:  .062:  .000:  .000:  .000:    .297 0
metion  :17 5:CAsOrange: 7.00:1500:31.0:  .008:  .000:  .000:  .000:    .038 0
metion  :17 6:CAsOrange: 3.75: 100:  .0: 6.000:  .000:  .000:  .000:  24.982 0
metion  :17 6:CAsOrange: 3.75: 100: 3.0: 2.600:  .000:  .000:  .000:  11.711 0
metion  :17 6:CAsOrange: 3.75: 100:10.0:  .260:  .000:  .000:  .000:   1.238 0
metion  :17 6:CAsOrange: 3.75: 100:17.0:  .124:  .000:  .000:  .000:    .592 0
metion  :17 6:CAsOrange: 3.75: 100:31.0:  .026:  .000:  .000:  .000:    .124 0
metion  :17 6:CAsOrange: 3.75: 100:45.0:  .020:  .000:  .000:  .000:    .096 0
metion  :17 6:CAsOrange: 3.75: 100:59.0:  .008:  .000:  .000:  .000:    .038 0
metion  :17 7:CAsOrange: 3.75:1500:  .0:  .980:  .000:  .000:  .000:   4.586 0
metion  :17 7:CAsOrange: 3.75:1500: 3.0:  .500:  .022:  .000:  .000:   2.742 0
metion  :17 7:CAsOrange: 3.75:1500:10.0:  .124:  .040:  .000:  .000:   1.285 0
metion  :17 7:CAsOrange: 3.75:1500:17.0:  .060:  .044:  .000:  .000:   1.051 0
metion  :17 7:CAsOrange: 3.75:1500:31.0:  .014:  .022:  .000:  .000:    .451 0
metion  :17 8:CAsOrange: 7.00:1500:  .0: 1.800:  .000:  .000:  .000:   8.262 0
metion  :17 8:CAsOrange: 7.00:1500: 3.0:  .960:  .032:  .000:  .000:   5.028 0
metion  :17 8:CAsOrange: 7.00:1500:10.0:  .200:  .052:  .000:  .000:   1.850 0
metion  :17 8:CAsOrange: 7.00:1500:17.0:  .100:  .052:  .000:  .000:   1.379 0
metion  :17 8:CAsOrange: 7.00:1500:31.0:  .028:  .032:  .000:  .000:    .691 0
metion  :17 9:CAsOrange: 3.75: 100:  .0: 4.200:  .004:  .000:  .000:  18.283 0
metion  :17 9:CAsOrange: 3.75: 100: 3.0: 1.580:  .042:  .000:  .000:   7.968 0
metion  :17 9:CAsOrange: 3.75: 100:10.0:  .220:  .060:  .000:  .000:   2.081 0
metion  :17 9:CAsOrange: 3.75: 100:17.0:  .120:  .060:  .000:  .000:   1.611 0
metion  :17 9:CAsOrange: 3.75: 100:31.0:  .050:  .032:  .000:  .000:    .796 0
metion  :17 9:CAsOrange: 3.75: 100:45.0:  .022:  .000:  .000:  .000:    .105 0
metion  :17 9:CAsOrange: 3.75: 100:59.0:  .024:  .000:  .000:  .000:    .115 0
metion  :1710:CAsOrange: 3.75:1500:  .0: 1.180:  .000:  .000:  .000:   5.496 0
metion  :1710:CAsOrange: 3.75:1500: 3.0:  .440:  .012:  .000:  .000:   2.291 0
metion  :1710:CAsOrange: 3.75:1500:10.0:  .150:  .024:  .000:  .000:   1.132 0
metion  :1710:CAsOrange: 3.75:1500:17.0:  .068:  .024:  .000:  .000:    .743 0
```

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metion  :1710:CAsOrange: 3.75:1500:31.0:  .016:  .012:  .000:  .000:    .286 0
metion  :1711:CAsOrange: 7.00:1500:  .0: 2.200:  .012:  .000:  .000:  10.192 0
metion  :1711:CAsOrange: 7.00:1500: 3.0:  .900:  .020:  .000:  .000:   4.554 0
metion  :1711:CAsOrange: 7.00:1500:10.0:  .340:  .038:  .000:  .000:   2.267 0
metion  :1711:CAsOrange: 7.00:1500:17.0:  .120:  .036:  .000:  .000:   1.197 0
metion  :1711:CAsOrange: 7.00:1500:31.0:  .034:  .020:  .000:  .000:    .511 0
metion  :1711:CAsOrange: 7.00:1500:45.0:  .022:  .012:  .000:  .000:    .315 0
metion  :1711:CAsOrange: 7.00:1500:60.0:  .020:  .000:  .000:  .000:    .096 0
metion  :1712:CAsOrange: 3.75: 100:  .0: 4.200:  .034:  .000:  .000:  18.710 0
metion  :1712:CAsOrange: 3.75: 100: 3.0: 1.700:  .024:  .000:  .000:   8.207 0
metion  :1712:CAsOrange: 3.75: 100:10.0:  .460:  .042:  .000:  .000:   2.895 0
metion  :1712:CAsOrange: 3.75: 100:17.0:  .140:  .042:  .000:  .000:   1.395 0
metion  :1712:CAsOrange: 3.75: 100:31.0:  .078:  .034:  .000:  .000:    .964 0
metion  :1712:CAsOrange: 3.75: 100:45.0:  .058:  .000:  .000:  .000:    .277 0
metion  :1712:CAsOrange: 3.75: 100:60.0:  .036:  .000:  .000:  .000:    .172 0
metion  :1713:CAvOrange: 5.63:2250:  .0: 1.980:  .008:  .000:  .000:   9.177 0
metion  :1713:CAvOrange: 5.63:2250: 3.0: 1.080:  .028:  .000:  .000:   5.506 0
metion  :1713:CAvOrange: 5.63:2250:10.0:  .260:  .070:  .000:  .000:   2.439 0
metion  :1713:CAvOrange: 5.63:2250:17.0:  .108:  .078:  .000:  .000:   1.864 0
metion  :1713:CAvOrange: 5.63:2250:31.0:  .050:  .090:  .000:  .000:   1.797 0
metion  :1713:CAvOrange: 5.63:2250:45.0:  .000:  .012:  .000:  .000:    .210 0
metion  :1714:CAvOrange:11.30:2250:  .0: 2.600:  .004:  .000:  .000:  11.773 0
metion  :1714:CAvOrange:11.30:2250: 3.0: 2.000:  .038:  .000:  .000:   9.738 0
metion  :1714:CAvOrange:11.30:2250:10.0:  .440:  .078:  .000:  .000:   3.412 0
metion  :1714:CAvOrange:11.30:2250:17.0:  .200:  .084:  .000:  .000:   2.398 0
metion  :1714:CAvOrange:11.30:2250:31.0:  .140:  .122:  .000:  .000:   2.765 0
metion  :1714:CAvOrange:11.30:2250:45.0:  .010:  .024:  .000:  .000:    .466 0
metion  :1715:CAvOrange: 5.63: 100:  .0: 8.800:  .030:  .000:  .000:  34.742 0
metion  :1715:CAvOrange: 5.63: 100: 3.0: 6.800:  .100:  .000:  .000:  29.054 0
metion  :1715:CAvOrange: 5.63: 100:10.0: 1.540:  .142:  .000:  .000:   9.390 0
metion  :1715:CAvOrange: 5.63: 100:17.0:  .620:  .136:  .000:  .000:   5.208 0
metion  :1715:CAvOrange: 5.63: 100:31.0:  .200:  .160:  .000:  .000:   3.686 0
metion  :1715:CAvOrange: 5.63: 100:45.0:  .060:  .032:  .000:  .000:    .843 0
metion  :1715:CAvOrange: 5.63: 100:60.0:  .020:  .000:  .000:  .000:    .096 0
metion  :1716:CAvOrange: 5.63:2250:  .0:  .800:  .004:  .000:  .000:   3.827 0
metion  :1716:CAvOrange: 5.63:2250: 3.0:  .340:  .024:  .000:  .000:   2.028 0
metion  :1716:CAvOrange: 5.63:2250:10.0:  .120:  .024:  .000:  .000:    .990 0
metion  :1716:CAvOrange: 5.63:2250:17.0:  .042:  .016:  .000:  .000:    .480 0
metion  :1716:CAvOrange: 5.63:2250:31.0:  .016:  .000:  .000:  .000:    .077 0
metion  :1717:CAvOrange:11.30:2250:  .0: 1.500:  .004:  .000:  .000:   6.999 0
metion  :1717:CAvOrange:11.30:2250: 3.0:  .640:  .022:  .000:  .000:   3.392 0
metion  :1717:CAvOrange:11.30:2250:10.0:  .220:  .036:  .000:  .000:   1.669 0
metion  :1717:CAvOrange:11.30:2250:17.0:  .102:  .030:  .000:  .000:   1.008 0
metion  :1717:CAvOrange:11.30:2250:31.0:  .034:  .006:  .000:  .000:    .267 0
metion  :1717:CAvOrange:11.30:2250:45.0:  .024:  .000:  .000:  .000:    .115 0
metion  :1717:CAvOrange:11.30:2250:60.0:  .024:  .000:  .000:  .000:    .115 0
metion  :1718:CAvOrange: 5.63: 100:  .0: 4.200:  .004:  .000:  .000:  18.283 0
metion  :1718:CAvOrange: 5.63: 100: 3.0: 1.820:  .022:  .000:  .000:   8.702 0
metion  :1718:CAvOrange: 5.63: 100:10.0:  .440:  .036:  .000:  .000:   2.700 0
metion  :1718:CAvOrange: 5.63: 100:17.0:  .178:  .024:  .000:  .000:   1.264 0
metion  :1718:CAvOrange: 5.63: 100:31.0:  .068:  .020:  .000:  .000:    .673 0
metion  :1718:CAvOrange: 5.63: 100:45.0:  .046:  .008:  .000:  .000:    .360 0
metion  :1718:CAvOrange: 5.63: 100:60.0:  .042:  .000:  .000:  .000:    .201 0
metion  :1719:CAvOrange: 5.63:2250:  .0:  .340:  .000:  .000:  .000:   1.616 0
metion  :1719:CAvOrange: 5.63:2250: 3.0:  .420:  .022:  .000:  .000:   2.368 0
```

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metion :1719:CAvOrange: 5.63:2250:10.0:  .120:  .040:  .000:  .000:  1.266 0
metion :1719:CAvOrange: 5.63:2250:17.0:  .044:  .044:  .000:  .000:   .975 0
metion :1719:CAvOrange: 5.63:2250:31.0:  .012:  .042:  .000:  .000:   .789 0
metion :1719:CAvOrange: 5.63:2250:45.0:  .000:  .002:  .000:  .000:   .035 0
metion :1720:CAvOrange:11.30:2250:  .0: 3.400:  .016:  .000:  .000: 15.268 0
metion :1720:CAvOrange:11.30:2250: 3.0:  .820:  .020:  .000:  .000:  4.188 0
metion :1720:CAvOrange:11.30:2250:10.0:  .180:  .040:  .000:  .000:  1.550 0
metion :1720:CAvOrange:11.30:2250:17.0:  .104:  .060:  .000:  .000:  1.535 0
metion :1720:CAvOrange:11.30:2250:31.0:  .036:  .066:  .000:  .000:  1.318 0
metion :1720:CAvOrange:11.30:2250:45.0:  .016:  .006:  .000:  .000:   .181 0
metion :1721:CAvOrange: 5.63: 100:  .0: 9.000:  .048:  .000:  .000: 35.567 0
metion :1721:CAvOrange: 5.63: 100: 3.0: 2.600:  .038:  .000:  .000: 12.296 0
metion :1721:CAvOrange: 5.63: 100:10.0:  .560:  .096:  .000:  .000:  4.268 0
metion :1721:CAvOrange: 5.63: 100:17.0:  .340:  .120:  .000:  .000:  3.658 0
metion :1721:CAvOrange: 5.63: 100:31.0:  .086:  .104:  .000:  .000:  2.206 0
metion :1721:CAvOrange: 5.63: 100:45.0:  .018:  .022:  .000:  .000:   .470 0
metion :1721:CAvOrange: 5.63: 100:60.0:  .028:  .020:  .000:  .000:   .483 0
metion :1722:CAvOrange: 5.63:2250:  .0: 1.140:  .000:  .000:  .000:  5.315 0
metion :1722:CAvOrange: 5.63:2250: 3.0:  .540:  .022:  .000:  .000:  2.928 0
metion :1722:CAvOrange: 5.63:2250:10.0:  .160:  .056:  .000:  .000:  1.731 0
metion :1722:CAvOrange: 5.63:2250:17.0:  .078:  .048:  .000:  .000:  1.206 0
metion :1722:CAvOrange: 5.63:2250:31.0:  .026:  .054:  .000:  .000:  1.063 0
metion :1722:CAvOrange: 5.63:2250:45.0:  .002:  .036:  .000:  .000:   .637 0
metion :1722:CAvOrange: 5.63:2250:60.0:  .000:  .032:  .000:  .000:   .558 0
metion :1723:CAvOrange:11.30:2250:  .0: 1.860:  .000:  .000:  .000:  8.525 0
metion :1723:CAvOrange:11.30:2250: 3.0:  .720:  .022:  .000:  .000:  3.761 0
metion :1723:CAvOrange:11.30:2250:10.0:  .240:  .064:  .000:  .000:  2.243 0
metion :1723:CAvOrange:11.30:2250:17.0:  .126:  .066:  .000:  .000:  1.742 0
metion :1723:CAvOrange:11.30:2250:31.0:  .054:  .080:  .000:  .000:  1.644 0
metion :1723:CAvOrange:11.30:2250:45.0:  .016:  .040:  .000:  .000:   .773 0
metion :1723:CAvOrange:11.30:2250:60.0:  .000:  .036:  .000:  .000:   .628 0
metion :1724:CAvOrange: 5.63: 100:  .0: 8.000:  .000:  .000:  .000: 31.836 0
metion :1724:CAvOrange: 5.63: 100: 3.0: 3.800:  .078:  .000:  .000: 17.773 0
metion :1724:CAvOrange: 5.63: 100:10.0: 1.060:  .136:  .000:  .000:  7.185 0
metion :1724:CAvOrange: 5.63: 100:17.0:  .420:  .126:  .000:  .000:  4.128 0
metion :1724:CAvOrange: 5.63: 100:31.0:  .100:  .100:  .000:  .000:  2.203 0
metion :1724:CAvOrange: 5.63: 100:45.0:  .080:  .080:  .000:  .000:  1.766 0
metion :1724:CAvOrange: 5.63: 100:60.0:  .048:  .048:  .000:  .000:  1.064 0
metion :1725:CAvOrange: 3.63:1450:  .0: 1.340:  .022:  .000:  .000:  6.578 0
metion :1725:CAvOrange: 3.63:1450: 3.0:  .240:  .086:  .000:  .000:  2.619 0
metion :1725:CAvOrange: 3.63:1450:10.0:  .040:  .044:  .000:  .000:   .956 0
metion :1725:CAvOrange: 3.63:1450:17.0:  .032:  .056:  .000:  .000:  1.126 0
metion :1725:CAvOrange: 3.63:1450:31.0:  .000:  .028:  .000:  .000:   .488 0
metion :1725:CAvOrange: 3.63:1450:45.0:  .000:  .004:  .000:  .000:   .070 0
metion :1726:CAvOrange: 7.25:1450:  .0: 2.400:  .016:  .000:  .000: 11.110 0
metion :1726:CAvOrange: 7.25:1450: 3.0:  .360:  .140:  .000:  .000:  4.087 0
metion :1726:CAvOrange: 7.25:1450:10.0:  .056:  .086:  .000:  .000:  1.756 0
metion :1726:CAvOrange: 7.25:1450:17.0:  .032:  .078:  .000:  .000:  1.506 0
metion :1726:CAvOrange: 7.25:1450:31.0:  .016:  .028:  .000:  .000:   .565 0
metion :1726:CAvOrange: 7.25:1450:45.0:  .000:  .012:  .000:  .000:   .210 0
metion :1727:CAvOrange: 3.63: 100:  .0: 4.600:  .054:  .000:  .000: 20.532 0
metion :1727:CAvOrange: 3.63: 100: 3.0:  .980:  .140:  .000:  .000:  6.894 0
metion :1727:CAvOrange: 3.63: 100:10.0:  .102:  .128:  .000:  .000:  2.690 0
metion :1727:CAvOrange: 3.63: 100:17.0:  .078:  .126:  .000:  .000:  2.544 0
metion :1727:CAvOrange: 3.63: 100:31.0:  .030:  .056:  .000:  .000:  1.117 0
```

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metion  :1727:CAvOrange: 3.63: 100:45.0:  .022:  .030:  .000:  .000:    .628 0
metion  :1727:CAvOrange: 3.63: 100:60.0:  .022:  .006:  .000:  .000:    .210 0
metion  :1728:CAsOrange: 1.88:1500:  .0:  .800:  .000:  .000:  .000:   3.760 0
metion  :1728:CAsOrange: 1.88:1500: 3.0:  .170:  .020:  .000:  .000:   1.157 0
metion  :1728:CAsOrange: 1.88:1500:10.0:  .040:  .060:  .000:  .000:   1.233 0
metion  :1728:CAsOrange: 1.88:1500:17.0:  .022:  .020:  .000:  .000:    .454 0
metion  :1728:CAsOrange: 1.88:1500:31.0:  .006:  .000:  .000:  .000:    .029 0
metion  :1729:CAsOrange: 3.75:1500:  .0:  .980:  .000:  .000:  .000:   4.586 0
metion  :1729:CAsOrange: 3.75:1500: 3.0:  .200:  .004:  .000:  .000:   1.023 0
metion  :1729:CAsOrange: 3.75:1500:10.0:  .058:  .040:  .000:  .000:    .973 0
metion  :1729:CAsOrange: 3.75:1500:17.0:  .026:  .040:  .000:  .000:    .821 0
metion  :1729:CAsOrange: 3.75:1500:45.0:  .016:  .000:  .000:  .000:    .077 0
metion  :82 1:FL Orange: 2.30:1200:  .0:  .158:  .000:  .000:  .000:    .754 0
metion  :82 1:FL Orange: 2.30:1200: 1.0:  .100:  .000:  .000:  .000:    .478 0
metion  :82 1:FL Orange: 2.30:1200: 3.0:  .100:  .000:  .000:  .000:    .478 0
metion  :82 1:FL Orange: 2.30:1200: 5.0:  .032:  .000:  .000:  .000:    .153 0
metion  :82 1:FL Orange: 2.30:1200: 7.0:  .006:  .000:  .000:  .000:    .030 0
metion  :82 1:FL Orange: 2.30:1200:14.0:  .012:  .000:  .000:  .000:    .056 0
metion  :82 1:FL Orange: 2.30:1200:21.0:  .004:  .000:  .000:  .000:    .020 0
metion  :82 2:FL Orange: 4.60:1200:  .0:  .280:  .000:  .000:  .000:   1.332 0
metion  :82 2:FL Orange: 4.60:1200: 1.0:  .160:  .000:  .000:  .000:    .764 0
metion  :82 2:FL Orange: 4.60:1200: 3.0:  .112:  .000:  .000:  .000:    .535 0
metion  :82 2:FL Orange: 4.60:1200: 5.0:  .068:  .000:  .000:  .000:    .325 0
metion  :82 2:FL Orange: 4.60:1200: 7.0:  .024:  .000:  .000:  .000:    .115 0
metion  :82 2:FL Orange: 4.60:1200:14.0:  .006:  .000:  .000:  .000:    .030 0
metion  :82 2:FL Orange: 4.60:1200:21.0:  .007:  .000:  .000:  .000:    .034 0
metion  :82 3:FL Orange: 6.90:1200:  .0:  .560:  .000:  .000:  .000:   2.647 0
metion  :82 3:FL Orange: 6.90:1200: 1.0:  .380:  .000:  .000:  .000:   1.804 0
metion  :82 3:FL Orange: 6.90:1200: 3.0:  .240:  .000:  .000:  .000:   1.143 0
metion  :82 3:FL Orange: 6.90:1200: 5.0:  .174:  .000:  .000:  .000:    .830 0
metion  :82 3:FL Orange: 6.90:1200: 7.0:  .028:  .000:  .000:  .000:    .134 0
metion  :82 3:FL Orange: 6.90:1200:14.0:  .012:  .000:  .000:  .000:    .059 0
metion  :82 3:FL Orange: 6.90:1200:21.0:  .009:  .000:  .000:  .000:    .041 0
metion  :82 4:FL Orange: 2.30:1200:  .0:  .300:  .000:  .000:  .000:   1.427 0
metion  :82 4:FL Orange: 2.30:1200: 1.0:  .074:  .000:  .000:  .000:    .354 0
metion  :82 4:FL Orange: 2.30:1200: 3.0:  .020:  .000:  .000:  .000:    .096 0
metion  :82 4:FL Orange: 2.30:1200: 5.0:  .016:  .000:  .000:  .000:    .077 0
metion  :82 4:FL Orange: 2.30:1200: 7.0:  .014:  .000:  .000:  .000:    .066 0
metion  :82 4:FL Orange: 2.30:1200:14.0:  .008:  .000:  .000:  .000:    .040 0
metion  :82 4:FL Orange: 2.30:1200:21.0:  .012:  .000:  .000:  .000:    .057 0
metion  :82 5:FL Orange: 4.60:1200:  .0:  .280:  .000:  .000:  .000:   1.332 0
metion  :82 5:FL Orange: 4.60:1200: 1.0:  .066:  .000:  .000:  .000:    .316 0
metion  :82 5:FL Orange: 4.60:1200: 3.0:  .016:  .000:  .000:  .000:    .079 0
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metion  :82 6:FL Orange: 6.90:1200:21.0:  .026:  .005:  .000:  .000:    .205 0
metion  :82 7:FL Orange: 2.30:1200:  .0:  .050:  .000:  .000:  .000:    .239 0
```

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```
metion  :82 7:FL Orange: 2.30:1200: 1.0:  .010:  .000:  .000:  .000:  .050 0
metion  :82 7:FL Orange: 2.30:1200: 3.0:  .015:  .000:  .000:  .000:  .072 0
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pholon  :48 2:CAvPeach : 4.  :  375:  .0:10.906:  .000:  .000:  .000:?  .924 0
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```
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phosmet : 3 3:AR Peach :0.716:0150: 4.0:    .059:  .000:  .000:  .000:?   .005 0
phosmet : 3 3:AR Peach :0.716:0150: 5.0:    .034:  .000:  .000:  .000:?   .003 0
tric    :16 1:CAsOrange: 4.00: 500:  .0: 5.400:  .000:  .000:  .000:    .940 0
tric    :16 1:CAsOrange: 4.00: 500: 3.0:  .980:  .000:  .000:  .000:    .171 0
tric    :16 1:CAsOrange: 4.00: 500:11.0:  .034:  .000:  .000:  .000:    .006 0
tric    :16 1:CAsOrange: 4.00: 500:17.0:  .056:  .000:  .000:  .000:    .010 0
tric    :16 2:CAsCitrus: 4.00: 500:  .0: 5.400:  .000:  .000:  .000:    .940 0
tric    :16 2:CAsCitrus: 4.00: 500: 3.0:  .980:  .000:  .000:  .000:    .171 0
tric    :16 2:CAsCitrus: 4.00: 500:11.0:  .034:  .000:  .000:  .000:    .006 0
tric    :16 2:CAsCitrus: 4.00: 500:17.0:  .056:  .000:  .000:  .000:    .010 0
dial2   :25 1:CAvGrapes:01.00:0025:  .0: 3.800:  .000:  .000:  .000:   7.091 0
dial2   :25 1:CAvGrapes:01.00:0025: 1.0: 3.200:  .000:  .000:  .000:   6.006 0
dial2   :25 1:CAvGrapes:01.00:0025: 3.0: 3.140:  .000:  .000:  .000:   5.896 0
dial2   :25 1:CAvGrapes:01.00:0025: 7.0: 2.540:  .000:  .000:  .000:   4.797 0
dial2   :25 1:CAvGrapes:01.00:0025:14.0: 1.860:  .000:  .000:  .000:   3.536 0
dial2   :25 1:CAvGrapes:01.00:0025:21.0: 1.260:  .000:  .000:  .000:   2.409 0
dial2   :25 1:CAvGrapes:01.00:0025:28.0:  .740:  .000:  .000:  .000:   1.422 0
dial2   :25 2:CAvGrapes:01.00:0100:  .0: 4.200:  .000:  .000:  .000:   7.807 0
dial2   :25 2:CAvGrapes:01.00:0100: 1.0: 2.540:  .000:  .000:  .000:   4.797 0
dial2   :25 2:CAvGrapes:01.00:0100: 3.0: 2.660:  .000:  .000:  .000:   5.018 0
dial2   :25 2:CAvGrapes:01.00:0100: 7.0: 2.260:  .000:  .000:  .000:   4.280 0
dial2   :25 2:CAvGrapes:01.00:0100:14.0: 1.340:  .000:  .000:  .000:   2.560 0
dial2   :25 2:CAvGrapes:01.00:0100:21.0:  .660:  .000:  .000:  .000:   1.269 0
dial2   :25 2:CAvGrapes:01.00:0100:28.0:  .400:  .000:  .000:  .000:    .771 0
dial2   :83 1:CAvGrapes:   . :    :59.0:  .214:  .043:  .000:  .000:   1.266 0
dial2   :83 1:CAvGrapes:   . :    :59.0:  .199:  .052:  .000:  .000:   1.415 0
dial2   :83 1:CAvGrapes:   . :    :60.0:  .121:  .045:  .000:  .000:   1.128 0
dial2   :38 1:FL Orange: 4.00: 750: 1.0: 1.200:  .000:  .000:  .000:   3.328 0
dial2   :38 1:FL Orange: 4.00: 750: 2.0:  .922:  .000:  .000:  .000:   2.567 0
dial2   :38 1:FL Orange: 4.00: 750: 5.0:  .650:  .000:  .000:  .000:   1.816 0
dial2   :38 1:FL Orange: 4.00: 750:10.0:  .500:  .000:  .000:  .000:   1.400 0
dial2   :38 1:FL Orange: 4.00: 750:20.0:  .384:  .000:  .000:  .000:   1.077 0
dial2   :38 1:FL Orange: 4.00: 750:30.0:  .330:  .000:  .000:  .000:    .926 0
dial2   :38 2:FL Orange: 4.00: 750: 1.0:  .200:  .000:  .000:  .000:    .562 0
dial2   :38 2:FL Orange: 4.00: 750: 2.0:  .134:  .000:  .000:  .000:    .377 0
dial2   :38 2:FL Orange: 4.00: 750: 5.0:  .080:  .000:  .000:  .000:    .225 0
dial2   :38 2:FL Orange: 4.00: 750:10.0:  .054:  .000:  .000:  .000:    .152 0
dial2   :38 2:FL Orange: 4.00: 750:20.0:  .036:  .000:  .000:  .000:    .101 0
ethio2  :27 1:CAvGrapes:  1.0:  30:  .0:  .800:  .070:  .000:  .000:   2.347 0
ethio2  :27 1:CAvGrapes:  1.0:  30: 1.0:  .600:  .072:  .005:  .000:   2.239 0
ethio2  :27 1:CAvGrapes:  1.0:  30: 3.0:  .200:  .078:  .020:  .000:   2.222 0
ethio2  :27 1:CAvGrapes:  1.0:  30: 7.0:  .065:  .055:  .048:  .000:   2.593 0
ethio2  :27 1:CAvGrapes:  1.0:  30:14.0:  .021:  .025:  .060:  .000:   2.459 0
ethio2  :27 1:CAvGrapes:  1.0:  30:21.0:  .019:  .011:  .050:  .000:   1.902 0
ethio2  :27 1:CAvGrapes:  1.0:  30:28.0:  .015:  .007:  .035:  .000:   1.327 0
ethio2  :27 2:CAvGrapes: 1.25: 200:  .0:  .900:  .080:  .004:  .000:   2.789 0
ethio2  :27 2:CAvGrapes: 1.25: 200: 1.0:  .700:  .092:  .004:  .000:   2.671 0
ethio2  :27 2:CAvGrapes: 1.25: 200: 3.0:  .350:  .105:  .011:  .000:   2.572 0
ethio2  :27 2:CAvGrapes: 1.25: 200: 7.0:  .070:  .058:  .039:  .000:   2.347 0
ethio2  :27 2:CAvGrapes: 1.25: 200:14.0:  .032:  .030:  .045:  .000:   2.052 0
ethio2  :27 2:CAvGrapes: 1.25: 200:21.0:  .020:  .019:  .039:  .000:   1.659 0
ethio2  :27 2:CAvGrapes: 1.25: 200:28.0:  .012:  .010:  .032:  .000:   1.268 0
ethio2  :47 1:CAvOrange:  3.0: 500: 2.0: 1.102:  .100:  .000:  .000:   4.735 0
ethio2  :47 1:CAvOrange:  3.0: 500: 5.0:  .475:  .087:  .029:  .000:   4.460 0
```

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ethio2  :47 1:CAvOrange:  3.0: 500: 9.0:  .236:  .064:  .041:  .000:   3.998 0
ethio2  :47 1:CAvOrange:  3.0: 500:16.0:  .149:  .048:  .032:  .000:   3.012 0
ethio2  :47 1:CAvOrange:  3.0: 500:23.0:  .078:  .024:  .028:  .000:   2.114 0
ethio2  :47 1:CAvOrange:  3.0: 500:33.0:  .037:  .011:  .029:  .000:   1.774 0
ethio2  :47 2:CAvOrange:  4.0: 500: 2.0:  .516:  .028:  .008:  .000:   2.207 0
ethio2  :47 2:CAvOrange:  4.0: 500: 5.0:  .754:  .054:  .012:  .000:   3.519 0
ethio2  :47 2:CAvOrange:  4.0: 500: 9.0:  .342:  .034:  .011:  .000:   2.102 0
ethio2  :47 2:CAvOrange:  4.0: 500:16.0:  .548:  .090:  .047:  .000:   5.540 0
ethio2  :47 2:CAvOrange:  4.0: 50C:23.0:  .298:  .042:  .039:  .000:   3.544 0
ethio2  :47 2:CAvOrange:  4.0: 500:33.0:  .230:  .034:  .044:  .000:   3.455 0
ethio2  :47 3:CAvOrange:  4.0: 500: 2.0: 1.771:  .110:  .000:  .000:   6.399 0
ethio2  :47 3:CAvOrange:  4.0: 500: 5.0:  .834:  .076:  .000:  .000:   3.611 0
ethio2  :47 3:CAvOrange:  4.0: 500: 9.0:  .669:  .112:  .000:  .000:   4.056 0
ethio2  :47 3:CAvOrange:  4.0: 500:16.0:  .268:  .063:  .000:  .000:   2.060 0
ethio2  :47 3:CAvOrange:  4.0: 500:23.0:  .176:  .044:  .000:  .000:   1.418 0
ethio2  :47 3:CAvOrange:  4.0: 500:33.0:  .127:  .034:  .000:  .000:   1.077 0
ethio2  :12 1:AZ Orange: 8.00: 350:  .0:18.136:  .172:  .000:  .0C0:  36.532 0
ethio2  :12 1:AZ Orange: 8.00: 350: 1.0:17.612:  .548:  .022:  .000:  41.802 0
ethio2  :12 1:AZ Orange: 8.00: 350: 3.0:15.848:  .930:  .070:  .000:  45.884 0
ethio2  :12 1:AZ Orange: 8.00: 350: 5.0:10.392:  .944:  .066:  .000:  38.774 0
ethio2  :12 1:AZ Orange: 8.00: 350: 7.0:12.040: 1.220:  .106:  .000:  45.306 0
ethio2  :12 1:AZ Orange: 8.00: 350:14.0: 9.420: 1.386:  .000:  .000:  41.635 0
ethio2  :12 1:AZ Orange: 8.00: 350:21.0: 7.398: 1.412:  .000:  .000:  39.243 0
ethio2  :12 1:AZ Orange: 8.00: 350:28.0: 4.442: 1.238:  .000:  .000:  32.305 0
ethio2  :12 1:AZ Orange: 8.00: 350:42.0: 2.356: 1.006:  .000:  .000:  25.053 0
ethio2  :12 2:FL Orange: 4.00: 350:  .0:10.252:  .122:  .000:  .000:  23.108 0
ethio2  :12 2:FL Orange: 4.00: 350: 1.0: 9.072:  .130:  .000:  .000:  21.154 0
ethio2  :12 2:FL Orange: 4.00: 350: 3.0: 7.856:  .142:  .000:  .000:  19.158 0
ethio2  :12 2:FL Orange: 4.00: 350: 5.0: 5.498:  .124:  .000:  .000:  14.322 0
ethio2  :12 2:FL Orange: 4.00: 350: 7.0: 3.024:  .092:  .001:  .000:   8.705 0
ethio2  :12 2:FL Orange: 4.00: 350:14.0: 1.954:  .072:  .001:  .000:   6.007 0
ethio2  :12 2:FL Orange: 4.00: 350:21.0:  .844:  .076:  .008:  .000:   4.018 0
ethio2  :12 2:FL Orange: 4.00: 350:28.0:  .726:  .062:  .007:  .000:   3.396 0
ethio2  :12 2:FL Orange: 4.00: 350:42.0:  .368:  .044:  .006:  .000:   2.143 0
ethio2  :12 3:TX Orange: 4.00: 350:  .0: 6.776:  .102:  .000:  .000:  16.361 0
ethio2  :12 3:TX Orange: 4.00: 350: 1.0: 4.534:  .090:  .000:  .000:  11.717 0
ethio2  :12 3:TX Orange: 4.00: 350: 3.0: 3.846:  .092:  .000:  .000:  10.359 0
ethio2  :12 3:TX Orange: 4.00: 350: 5.0: 2.952:  .092:  .000:  .000:   8.508 0
ethio2  :12 3:TX Orange: 4.00: 350: 7.0: 1.968:  .084:  .003:  .000:   6.393 0
ethio2  :12 3:TX Orange: 4.00: 350:14.0:  .420:  .062:  .007:  .000:   2.718 0
ethio2  :12 3:TX Orange: 4.00: 350:21.0:  .226:  .048:  .013:  .000:   2.259 0
ethio2  :12 3:TX Orange: 4.00: 350:28.0:  .126:  .042:  .014:  .000:   1.947 0
ethio2  :12 3:TX Orange: 4.00: 350:42.0:  .030:  .012:  .007:  .000:    .696 0
ethio2  :12 4:CA Orange: 4.00: 350:  .0: 4.336:  .104:  .000:  .000:  11.605 0
ethio2  :12 4:CA Orange: 4.00: 350: 1.0: 3.900:  .110:  .000:  .000:  10.845 0
ethio2  :12 4:CA Orange: 4.00: 350: 3.0: 3.504:  .106:  .000:  .000:   9.950 0
ethio2  :12 4:CA Orange: 4.00: 350: 5.0: 2.894:  .126:  .005:  .000:   9.337 0
ethio2  :12 4:CA Orange: 4.00: 350: 7.0: 2.274:  .116:  .006:  .000:   7.875 0
ethio2  :12 4:CA Orange: 4.00: 350:14.0:  .988:  .072:  .005:  .000:   4.100 0
ethio2  :12 4:CA Orange: 4.00: 350:21.0:  .476:  .082:  .015:  .000:   3.680 0
ethio2  :12 4:CA Orange: 4.00: 350:28.0:  .290:  .064:  .032:  .000:   3.684 0
ethio2  :12 4:CA Orange: 4.00: 350:42.0:  .072:  .026:  .021:  .000:   1.803 0
ethio2  :34 1:FL Orange: 3.00:1200:  .0:  .199:  .008:  .000:  .000:    .639 0
ethio2  :34 1:FL Orange: 3.00:1200: 1.0:  .122:  .012:  .000:  .000:    .557 0
ethio2  :34 1:FL Orange: 3.00:1200: 3.0:  .015:  .008:  .000:  .000:    .221 0
```

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ethio2  :34 1:FL Orange: 3.00:1200: 5.0:  .006:  .005:  .000:  .000:   .130 0
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ethio2  :34 1:FL Orange: 3.00:1200:14.0:  .004:  .003:  .000:  .000:   .079 0
ethio2  :34 2:FL Orange: 4.50:1200:  .0:  .283:  .024:  .000:  .000:  1.199 0
ethio2  :34 2:FL Orange: 4.50:1200: 1.0:  .066:  .005:  .000:  .000:   .267 0
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ethio2  :34 2:FL Orange: 4.50:1200: 5.0:  .033:  .008:  .000:  .000:   .262 0
ethio2  :34 2:FL Orange: 4.50:1200: 7.0:  .034:  .010:  .000:  .000:   .310 0
ethio2  :34 2:FL Orange: 4.50:1200:14.0:  .033:  .010:  .000:  .000:   .308 0
ethio2  :34 2:FL Orange: 4.50:1200:21.0:  .010:  .008:  .000:  .000:   .209 0
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ethio2  :34 2:FL Orange: 4.50:1200:35.0:  .008:  .004:  .000:  .000:   .111 0
ethio2  :34 3:FL Orange: 4.50:1200:  .0:  .569:  .084:  .000:  .000:  3.206 0
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ethio2  :34 3:FL Orange: 4.50:1200: 3.0:  .050:  .010:  .000:  .000:   .347 0
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ethio2  :34 3:FL Orange: 4.50:1200: 7.0:  .003:  .005:  .000:  .000:   .123 0
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ethio2  :34 4:FL Orange: 4.50:1200: 1.0:  .116:  .005:  .000:  .000:   .381 0
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ethio2  :34 4:FL Orange: 4.50:1200:14.0:  .053:  .012:  .000:  .000:   .400 0
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ethio2  :34 4:FL Orange: 4.50:1200:28.0:  .015:  .010:  .000:  .000:   .267 0
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ethio2  :34 5:FL Orange: 4.50:1200: 1.0:  .126:  .014:  .000:  .000:   .613 0
ethio2  :34 5:FL Orange: 4.50:1200: 3.0:  .034:  .006:  .000:  .000:   .217 0
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ethio2  :34 6:FL Orange: 4.50:1200: 7.0:  .021:  .008:  .000:  .000:   .234 0
ethio2  :34 6:FL Orange: 4.50:1200:14.0:  .044:  .011:  .000:  .000:   .356 0
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ethio2  :34 7:FL Orange: 4.50:1200: 3.0:  .048:  .016:  .000:  .000:   .482 0
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ethio2  :34 7:FL Orange: 4.50:1200:14.0:  .011:  .006:  .000:  .000:   .165 0
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ethio2  :34 8:FL Orange: 4.50:1200: 1.0:  .190:  .003:  .000:  .000:   .503 0
ethio2  :34 8:FL Orange: 4.50:1200: 3.0:  .222:  .016:  .000:  .000:   .877 0
ethio2  :34 8:FL Orange: 4.50:1200: 5.0:  .108:  .014:  .000:  .000:   .572 0
ethio2  :34 8:FL Orange: 4.50:1200: 7.0:  .041:  .009:  .000:  .000:   .303 0
ethio2  :34 8:FL Orange: 4.50:1200:14.0:  .028:  .009:  .000:  .000:   .273 0
ethio2  :34 8:FL Orange: 4.50:1200:21.0:  .014:  .009:  .000:  .000:   .242 0
```

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ethio2  :34 8:FL Orange: 4.50:1200:28.0:  .016:  .007:  .000:  .000:   .200 0
ethio2  :34 8:FL Orange: 4.50:1200:35.0:  .009:  .006:  .000:  .000:   .160 0
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ethio2  :34 9:FL Orange: 9.00:1200: 7.0:  .016:  .005:  .000:  .000:   .153 0
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ethio2  :3410:FL Orange: 9.00:1200:14.0:  .042:  .016:  .000:  .000:   .468 0
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ethio2  :3410:FL Orange: 9.00:1200:35.0:  .016:  .008:  .000:  .000:   .223 0
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The Effects of Organophosphate Pesticide
Residue Variability Upon Reentry Intervals

Preliminary Phase II Report
July 1986

by
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The Effects of Organophosphate Pesticide Residue Variability Upon Reentry Intervals

Abstract:

A stochastic simulation program was written to study the importance of residue variability in preventing anti-cholinesterase overexposure, excessive chronic AChE inhibition, or acute illness. A range of daily inhibitions and residue variability were explored, and the simulated cohort response was compared to the historical record of chronic and acute data. The resulting chronic and acute AChE response patterns are largely displayed in Tables IV and V, respectively.

It was concluded that residue variability has only a slight effect on the mean AChE health status of a working cohort, in comparison to mean daily inhibition. Residue variability has a slightly stronger although still secondary effect upon the overall variability of the cohort's AChE activity. The fraction of the cohort whose seasonal AChE inhibition exceeded a relatively arbitrary chronic threshold of 50% was again largely controlled by the daily mean inhibition, but at 4% per day and above virtually the entire cohort exceeded that limit and below 4% per day residue variability had an increasing important role.

On the other hand, residue variability appears to have a very strong effect upon the uniformity of the AChE activity within the cohort. This nonuniformity has both chronic and acute AChE implications. For instance, for residue variability even below a geometric deviation of 2.0, the crews seasonal AChE inhibitions are not expected to be statistically uniform (with 99% confidence) until half way through a season; and for variability of 3.0 and above, the crews will be dissimilar throughout the season. Thus, it is possible to have several crews below an administrative AChE inhibition threshold (or even potentially with clinical symptoms) while the cohort mean is only marginally different from normal. This pattern has similar implications to both the design and interpretation of epidemiologic surveys among this population.

Acute responses, in terms of individual and group AChE responses in excess of potential clinical symptoms, exhibit a fairly clear boundary as a function of both residue mean and variation. In the low mean range of 1% to 2% per day, no acute individual or group incidents were predicted for geometric variations below 2.5; however, a set of random parathion commercial application residues collected on days 2, 9, and 16 all showed variations of around 2.6, just sufficient to induce sporatic acute responses.

This pattern of acute effects under conditions of low chronic response and the practical boundary of a geometric deviation of 2.5 (+ 150%), suggest that consideration to both the mean anti-cholinesterase effect and the variability of the foliar residues should be considered when setting administrative reentry intervals.

Introduction:

The 35 year history of harvesters being poisoned while working in a field "recently" sprayed with an organophosphate (OP) insecticide has been sporatically documented from scattered case reports during their earliest use beginning circa 1950 [1-4] to whole summaries in the last 10 years [5-10]. The consensus of opinion is that these poisonings have resulted from excessive field residues, most likely on the foliage of the plants being harvested rather than on the crop, per se. The focus of interest for the control of this occupational health hazard has been to require an adequate time period between insecticide application and crop harvest (or other activity) for the residue to "decay" to levels not harmful to the harvest workers. This time period has come to be referred to as the "reentry interval".

One particular review of the history and development of reentry intervals for OP pesticides [9] resulted in a conceptual and quantitative model which will be the basis for the study described herein. This "Unified Field Model" could predict short-term anti-cholinesterase effects from either single exposures or a series of uniform exposures to insecticides of known dermal toxicity, and was proposed to be used to set a foliar residue limit or "reentry interval" associated with a preselected and acceptable anti-cholinesterase threshold. One of the key limitations of this original proposal was the uncertainty of setting an "acceptable" administrative threshold for daily cholinesterase inhibitions, given the fact that real exposures are neither daily nor uniform.

This report describes a study using this Unified Field Model to explore the effects of variations in both the levels and frequencies of OP exposure upon the cholinesterase activity of a harvesting cohort throughout a harvest season. The method used in this exploration has been Monte Carlo simulation. This report first reviews the background of the model; then the methods used in these explorations; and finally their findings and implications.

Background:

A comprehensive report describing the reentry problem and integrating or "unifying" the major factors controlling it, was first published in 1982 as the Unified Field Model [9]. This basic model originally had three submodels [9 p.132], as shown below. Later elaborations and clarifications of this model [11] broke out a fourth submodel [9 p.180, 11], essentially Equation 3 as follows:

Residue Decay: $$R = R_o \exp^{-k_r T} \qquad (1)$$

Dose Deposition: $$D' = k_d R t \qquad (2)$$

Dose Absorption-Distribution: $$D = k_a D' / m \qquad (3)$$

Toxic Response: $$delAChE = 1 - \exp^{-k_e \operatorname{sum}(D_i / LD_{50:i})} \qquad (4)$$

where R = foliar residue, ug/cm^2 or ng/cm^2, at some point in time T after application.

R_o = initial foliar residue, ug/cm^2 or ng/cm^2 at the time of application.

k_r = pesticide exponential decay coefficient, day^{-1}; in practice, multiple coefficients may be used [12], or other than exponential submodels or a non-mathematical (e.g. graphical) method may be used [9].

T = the time (usually in days) after application of the pesticide; viz. the reentry interval.

D' = topical dermal dose, ug of pesticide (which in a mixture would be subscripted i).

k_d = a crop (and possibly activity) dependent dosing coefficient, whose units are dependent upon those of R, D, and t; e.g. if units of R were ug/cm^2, D were ug, and t were hours, then k_d would be cm^2/hr [see ref. 11].

t = the length of exposure, hours (assumed herein to be a nominal 8-hour workday).

k_a = a dermal absorption coefficient presented in most pesticide literature as a percent of deposited dose [9] but is toxicologically more related to a permeation rate coefficient [13]; however, use of the latter would require a more detailed scenario of the total time the dose would remain unwashed upon the skin. Use of the model herein (with submodel Equation 4 and k_e=6) assumes k_a=1.

m = the mass of the exposed person, kg (nominally 70 kg).

D = the toxicological, dermally deposited dose, mg/kg.

k_e = an enzyme coefficient relating the degree of red blood cell (RBC) acetylcholinesterase (AChE) activity to the LD$_{50}$ of an OP. This submodel is an extension of an original finding by Grob and Harvey [14]. K_e = 6 was used herein with a rat dermal LD$_{50}$.

LD_{50} = the dose (mg/kg) of chemical necessary [or sufficient] to kill 50% of the exposed animals; this submodel expects the use of a <u>dermal</u> LD$_{50}$; the subscript i for LD$_{50}$ and dose D implies that the AChE response to multiple, simultaneous OPs is additive in this fashion.

delAChE = the fractional, acute change in AChE enzymatic activity relative to a pre-exposure baseline, i.e.

$$delAChE = (E_{n-1} - E_n) / E_{n-1} \qquad (5a)$$

$$= (E_{n-1} / E_{n-1}) - (E_n / E_{n-1}) \qquad (5b)$$

$$delAChE = 1 - (E_n / E_{n-1}) \qquad (5c)$$

and

$$E_n/E_{n-1} = 1 - delAChE \qquad (5d)$$

where E = the measurable AChE enzyme activity on post-exposure day n and the pre-exposure activity on day n-1. Note also that the previous day (n-1) may or may not necessarily be the person's unexposed baseline (see later discussion circa Equations 12-16).

While not essential to the development of this particular study, a number of alternative submodels were discussed in the original document [9] and its later elaboration [11]. For instance, exponential decay (submodel 1) is a very common temporal pattern of environmental decay for pesticides, but it may not always apply; procedures were in fact outlined therein for dealing with graphical or even tabular decay data. A more complex (and potentially far-reaching) variation upon submodel 4 may be necessary to deal with non-cholinergic effects; one suggestion to extend the Unified Field Model to non-cholinesterase pesticides was to use the allowable absorbed daily or chronic dose which is typically established for all pesticides [11 p.337]. While the quantitative Dose-Response submodel for risk assessment might employ any of several criteria, such as a carcinogenic extrapolation risk assessment, a generalized submodel for acceptability (replacing Equation 4) could be viewed as follows:

$$\text{Toxic Response: acceptability} = \frac{D_{\text{dermally absorbed}}}{D_{\text{allowable}}} \qquad (6)$$

where acceptability is simply the ratio of actual to allowable daily dose (e.g. its NOEL) for each pesticide (or analogue subscripted i as above); this approach is equivalent to the ACGIH TLV and OSHA's PEL procedure for mixtures [15,16].

Of more direct relevance herein are the consequences of repeated variable residues upon AChE and the associated incidents of clinical poisoning. The consequences of daily repeated equal residues and of variability in single daily residues upon AChE were originally discussed separately on pages 137-140 and 186-191 [9]. A later manuscript [11] described the temporal pattern of chronic (seasonal) AChE response in more detail but was still restricted to constant residues and doses. As it is the purpose of this report to describe the effects of repeated, variable residues and doses, the mathematical description of the methods used herein shall begin with the model and terminology as developed in the original report and presented above.

<u>Methods</u>:

The historical focal point of health studies on people exposed to anti-cholinesterase chemicals has been the enzymatic activity of AChE in the body, which is most conveniently and routinely measured in the blood by various laboratory procedures [17]. In health research settings, the effect on a person's AChE is commonly expressed as a change relative to the study subject's individual baseline activity, viz. <u>delAChE</u> as shown in Equation 5a or 100 x delAChE expressed as a percent [6-8]. This concept reflects the fact that individuals differ in their enzymatic activity but that health effects accrue from changes in their activity relative to either their normal (unexposed E_o) or pre-exposure baseline (E_{n-1}). Note also that a "pre-exposure baseline" implies that there may have been exposures with some enzyme inhibition prior to the exposure in question and that normal and pre-exposure levels are only equal for the first exposure (dose) of the season.

An alternative to <u>delAChE</u> which is mathematically and biochemically more convenient, is to look directly at the individual's relative activity E_n/E_{n-1} or E_n/E_o where E_n, E_{n-1}, and E_o are the person's current, pre-

exposure, and personal normal baseline activities, respectively [14,17]. One might think of this ratio as the person's health status (in fact this shall later be called "H"). The relationship defined in Equation 5d permits the direct use of the basic Unified Field Model Equations 1-4 to also predict E_n/E_{n-1}. Thus, Equations 2 through 5 may be combined into one complete equation, as follows:

$$E_n/E_{n-1} = \exp^{-k_d k_e t} \, sum(R_i/m\ LD_{50,i}) = 1 - delAChE \tag{7}$$

It may be convenient at this time to introduce the fact that values of many of the model's variables and coefficients will differ among the chemical components within a residue (i), among the people within the cohort (j), and from day to day (n). These values are subscripted in the following rewrite of Equation 7:

$$E_{j,n}/E_{j,n-1} = \exp^{-k_{d:j} k_{e:j} t_n} \, sum(R_{i,n} \, / \, m_j \, LD_{50:i}) \tag{8}$$

where the following subscripts when used with subscripted coefficients, follow a colon:
 i = chemical component of the residue,
 j = person within the cohort,
 n = day within the season

As noted above in Equations 5d, 7 and 8, the enzyme "health" status ratio $E_{j,n}/E_{j,n-1}$ is relative to a generalized pre-exposure E_{n-1} enzyme activity value which may be either a true "baseline" (E_o) or an already partially inhibited level of activity. Clinical health effects are often related to this acute change in activity [14,17], but focus for standards requiring infrequent biological monitoring of AChE is chronic or cumulative seasonal changes relative to a person's unexposed baseline, E_o [9]. As a notational convenience to aid the reader, the <u>acute</u> fraction $E_{j,n}/E_{j,n-1}$ for a given person "j" on a given day "n" as defined by Equation 8 will hereafter be noted by $K_{j,n}$ (similar to a K notation without subscripts used in the original report [9]), as follows:

$$K_{j,n} = E_{j,n}/E_{j,n-1} = \exp^{-k_{d:j} k_{e:j} t_n} sum(R_{i,n} \, / \, m_j \, LD_{50:i}) \tag{9}$$

Thus,

$$E_{j,n} = K_{j,n} \, E_{j,n-1} \tag{10}$$

And as another notational convenience, the fractional activity relative to a normal baseline $E_{j,n}/E_{j,o}$ will be noted by $H_{j,n}$ which can easily be related to the acute pre-exposure effect $K_{j,n}$ via Equation 10, as follows:

$$H_{j,n} = E_{j,n}/E_{j,o} = (K_{j,n} \, E_{j,n-1})/E_{j,o} = K_{j,n} \, (E_{j,n-1}/E_{j,o}) \tag{11}$$

But before using Equations 9-11 to predict long-term (i.e. cumulative seasonal) changes in E, two biochemical and physiologic processes must be included within the model. These are (a) reversible inhibition or reversion, the fact that recently inhibited enzymes are bound somewhat reversibly, and that over a few hours a generally small fraction of the enzymes will revert or return to their active state; and (b) regeneration, the normal process of erythropoiesis (red blood cell production) which will result in the generation of new RBC AChE and the accompanying process of

removal of a proportional fraction of inhibited RBC AChE. In the original report [9], these two processes were termed ρ' and ρ, respectively.

Although the detailed process and temporal pattern of reversion is not completely understood, it may proceed for 6 to 30 hours or so after exposure. Values for ρ' range from 0 to 10% for the strong inhibitors such as TEPP and Sarin studied by Grob [14], to circa 15 to 20% for parathion [9], to nearly 100% for most carbamates [15]. The modeled effect of reversion is that the post-exposure enzyme activity E_n/E_o is increased after one day (24 hours) to a new fraction E_n'/E_o by the reversion of a certain fraction of the recent acute inhibition:

$$\text{reversion} = \rho' \, (1 - K_n) = \rho' \; \text{delAChE} \qquad (12)$$

where ρ' = the fraction of <u>recently</u> inhibited enzymes which becomes unbound.

The process of regeneration of RBCs is believed to be independent of exposure and inhibition, as is the accompanying process of removal of old RBC by the liver which is assumed to remove cells with both active and inactive AChE indiscriminately. Values of ρ for man range from 0.008 to 0.012 per day (average RBC life times of 85 to 130 days) [18]. In the context of enzyme activity, the overall effect is one of replacement of <u>some</u> old, inhibited enzymes with fresh, uninhibited enzymes. The net effect on the long-term model is that each day a fraction (ρ) of new RBC and associated AChE are produced and an equal fraction of old RBC are removed along with a somewhat lesser amount of active AChE proportional to the bulk blood activity (or $\rho \times E_n/E_o$). Here a mathematical approximation is made to the model to account for the fact that E_n/E_o may be changing throughout the day due to the on-going process of reversion of recently inhibited enzymes. As a convenient first-order approximation, the linear average relative enzymatic activity over this period is assumed. Thus,

$$\text{regeneration} = \rho - (\rho/2 \; (E_n/E_o + E_n'/E_o)) \qquad (13)$$

where $E_n' = E_n$ + a slight improvement after 24 hours by virtue of reversion, see Equation 12.

These processes were modeled within the original report only to predict the net effect of repeated equal exposures [9 p.137-140]. Herein, they are used to predict the entire pattern of the cumulative seasonal response $(E_{i,n}/E_{i,o})$ which would result from a random series of variable residues $(R_{i,n})$. To predict the cumulative effect of variations in repeated unequal occupational exposures, one begins with responses $(K_{i,n})$ predicted from Equation 9 and the post-exposure enzyme health status predicted by Equation 11. Subsequent to each exposure and predicted acute response, the body will undergo a level of recovery so that the next day's "pre-exposure" baseline is slightly improved over that at (or shortly after) the end of the previous day's work. This improved enzyme activity shall be defined as $H'_{j,n}$ (or $E'_{j,n}/E_{j,o}$). Therefore, to the initial post-exposure health status predicted by Equation 11 shall be added the effects of reversion (Equation 12) and regeneration (Equation 13) with the appropriate person subscripts "j" inserted as needed:

$$E'_{j,n}/E_{j,o} = E_{j,n}/E_{j,o} + \rho'_j(1 - K_{j,n}) + \rho_j$$
$$- (\rho_j/2 \, (E_{j,n}/E_{j,o} + E'_{j,n}/E_{j,o})) \quad (14a)$$

Or,

$$E'_{j,n}/E_{j,o} = E_{j,n}/E_{j,o}(1 - \rho/2) + \rho'_j(1 - K_{j,n})$$
$$+ \rho_j - \rho_j/2 \, (E'_{j,n}/E_{j,o}) \quad (14b)$$

And now solving for $E'_{j,n}/E_{j,o}$ which appears on both sides of Equation 14:

$$E'_{j,n}/E_{j,o}(1 + \rho/2) = E_{j,n}/E_{j,o}(1 - \rho/2) + \rho'_j(1 - K_{j,n}) + \rho_j \quad (15)$$

$$E'_{j,n}/E_{j,o} = \frac{E_{j,n}/E_{j,o}(1 - \rho/2) + \rho'_j(1 - K_{j,n}) + \rho_j}{(1 + \rho/2)} \quad (16)$$

As indicated circa Equation 5d, it is this slightly recovered enzyme activity level of Equation 16 which becomes the pre-exposure value for succeeding exposures ($E_{j,n-1}/E_{j,o}$ in Equation 11), or

$$H_{j,n-1} = E_{j,n-1}/E_{j,o} = E'_{j,n}/E_{j,o} = H'_{n-1} \quad (17)$$

The above iterative sequence of daily inhibition (Equation 9-11) and partial recovery (Equation 16) lends itself nicely to a digital program which re-iterates this calculation, day-by-day throughout the season. A stochastic or Monte Carlo simulation computer program was written to permit the parametric random variation of many of the factors described above (see Appendices A-C). In principle, the Monte Carlo simulation process could create a heterogeneous population of values for any model parameter distributed about a mean value with virtually any specified variability [19]. Table I summarizes the terms within this study which are varied and fixed, their notation within the text, and the subscripts assigned to those parameters permitted to vary during this study.

A number of modeled factors were either not varied or not used at all, in particular, the residue application and decay coefficients. The initial plan for this project intended to begin these variations from the point of residue application, i.e. to randomize R_o and the decay coefficients (k_r) as used in a multicomponent decay model [12]. The intended decay model for paraoxon follows:

$$R_{paraoxon} = \frac{k_1 R_{1,o}}{k_5 - k_1} \exp\text{-k1T} + \frac{k_4 R_{2,o}}{k_5 - k_3} \exp\text{-k3T} +$$
$$(R_{3,o} - \frac{k_1 R_{1,o}}{k_5 - k_1} - \frac{k_4 R_{2,o}}{k_5 - k_3}) \exp\text{-k5T} \quad (18)$$

where the subscripts # to

$k_{\#}$ indicate one of five k_r coefficients used in this particular model [12], and

$R_{\#,o}$ indicate one of two portions of the initial paraoxon residue [12].

Considerable difficulty with this approach resulted from the existence of a "pole" in these equations (i.e. when the denominator approaches zero, the value of the residue becomes impossibly large). When the residue at selected points in time was calculated using the above decay submodel with randomly varying coefficients based on field data [12], such impossibly and unrealistically high values sporadically resulted. To avoid this difficulty, the residue at initial reentry R was randomized directly; therefore neither k_r nor T was used within this simulation, as noted in Table I.

For other reasons k_a was also not used within this simulation (since a dermal LD_{50} value was assumed, the absorption coefficient k_a would have been set to unity as intended by the original Unified Field Model. Various other parameters in the Unified Field Model were used but not permitted to vary. For example, Values for dermal toxicity were not varied since only one generic OP was examined and variations in interpersonal susceptibility was already accounted for by $k_{e,i}$, m_i, ρ', and ρ. As a first approximation and to obtain a more clear understanding of the effects of variability caused only by people and their daily residue, the length of the workday was assumed constant. Later elaborations of this study could include more daily variations or even an interaction as from a hypothetical effect of decreased enzyme activity upon the harvester's physical ability to sustain an 8-hour workday (t) and a uniform work-rate (equivalent here to the dosing coefficient k_d).

The concept of Monte Carlo simulation is that any factor can be varied at random in any of a wide range of possible distributions [19]. This particular study assumed that the factors listed as "varied" in Table I were assumed to be either normally or log-normally distributed (the logarithms of log-normally distributed values are themselves normally distributed). The mean and variability of each of the varied terms is listed in Table II. Most of these factors are assumed to be log-normal, although for small deviations (equivalent coefficients of variation less than 50%) it makes little difference whether normal or log-normal variability is assumed.

The particular form and magnitude of the parametric characterization of R was selected from experimental experience with environmental samples generally and foliar residue samples in particular [9]. Such samples are invariably distributed in a skewed manner approximating a log-normal distribution. The largest available set of multiple foliar residue samples collected on the same day(s) post-application but from a variety of commercial applications is listed in Table III. It is clear from the relative size of the standard deviations compared to the arithmetic mean values, that these data are not normally distributed. The acceptability of fit of these data to a log-normal distribution was confirmed by a Univariate Analysis on the pooled data. The pooled geometric deviation for all six sets of samples is 2.6 or 160%, a point of reference for later comparisons.

Two versions of the simulation program (Appendices A and B) were utilized during this study. Version A was designed to run on a large mainframe computer (viz. an IBM 370/168 (with VM/CMS operating system)) and utilized two commercially available subroutines (IMSL). This version can only be operated in the batch mode and generates its model parameters by randomly drawing separate sets of personal characteristics and field residues for each crew from pseudo-infinite, parametrically distributed universes for each respective model parameter. The benchmark runs were made with Version A, primarily because of its earlier availability.

To expand portability to other computers and add further flexibility to the exposure patterns which could be simulated, a second version was written for Fortran-77 which can be (and was) run on an IBM - PC. It utilizes two published subroutines [20-21] to create parametrically distributed sets of personal characteristics for the entire cohort and all field residues, then randomly distributes this cohort and field residues among the crews.

There are a number of differences between these two approaches: the latter version consistently creates an entire study population of harvesters or residues which fits the desired parametric distribution virtually exactly (versus an $F(\infty, n)$ sampling error in the cohort created by the former version which is a function of the cohort size, n; for 216 harvesters the 99% confidence limit on achieving the parameter variability requested is $\pm$ 15% and for 916 field residues is $\pm$ 6%). At the same time, the variability of each crew created by the latter method is only slightly larger than the former (a sampling error which is a function of both the cohort and crew sizes; for the population cohort of 216 and crew size of 12 used within this study, the crew sampling error for both approaches is about 2-fold ($\pm$ 98% versus $\pm$ 99%, respectively)).

Operationally, the simulation program (Appendix B) first creates a cohort of harvesters. Each harvester is randomly characterized in terms of work habits (k_d), weight (m), enzyme susceptibility (k_e), and reversion-regeneration coefficients. This population is then distributed among "ncrews" with "npersons" per crew. An array of parametrically distributed residues at reentry is also created and randomly assigned to each field. For this series of simulations, each harvest crew works alternately two or three days for 8 hours within two fields each week (five days per week). Initially $H_{j,n} = H_{j,o} = 1$. Each day the acute $K_{i,n}$ is determined by Equation 9, and $H_{j,o}$ by Equation 11. At the start of the next exposure day, $H'_{j,n}$ is determined by Equation 16; and the process, beginning with acute inhibition, is repeated. Non-exposure days are handled in much the same manner (except of course $K_n = 1.0$ for all j). The program records the enzyme health status (H) for each harvester within each crew from field to field for a 26 week (six month) harvest season.

Finally a second program (Appendix C) was written to analyze this detailed personal health history to determine the following:

OAM and OGM = the overall arithmetic and geometric mean delAChE of the cohort, respectively.

PSD and PGD = the pooled standard and geometric deviations of the cohort, respectively.

F = an analysis of variance F test statistic characterizing the uniformity or dispersion of delAChE within the crews versus among

the crews. It was expected that the crews will be significantly different from each other as a function of residue variability but will become more uniform with passing time.

Poi# = the daily incidence of individual OP "poisoning" cases based on one of four threshold criteria:

(1) acute response, a delAChE of at least 50% in 1 day,
(2) " " " " " at least 65% " 2 days,
(3) " " " " " at least 75% " 3 days,
(4) chronic " " " " at least 50% versus $E_{j,o}$.

An example of the print-out from this program is shown in Appendix D. The first three of the above poisoning counters are also summarized by the total number of poisoning cases, the number of days (nominal number of fields) in which the above cases occurred, and the number of potentially reportable incidents (assumed here to require at least one-half of the crew to have exceeded one of the above criteria in one day). In practice the 1-day acute and seasonal chronic "poisoning" will be the primary focus of discussion.

Results and Discussion:

A depiction of the cohort mean delAChE response throughout the season is presented in Figures 1-5 grouped by daily mean inhibition (with residue variability as a co-factor) and in Figure 6 grouped by variability equal to 1.0 (with daily mean inhibition as a co-factor). A summary of the end-of-season (chronic) AChE conditions are tabulated in Table IV. By comparing the vertical spread in the cohort mean response lines within Figures 1-5 with those in Figure 6, it can be stated that variations in the daily mean inhibition $(1-K_n)$ have a greater impact on the chronic state of inhibition than does residue variation, per se. The rate at which these simulated cohorts approached their seasonal lows varied from "half-response" times of about 2 months for low daily inhibitions (1%) to about 2 weeks for high daily inhibitions (16%).

These chronic response patterns are similar to earlier predictions [11, p. 330] except that they assumed uniform exposures 7-days per week. Another feature not seen before is the weekly cycle of inhibition and partial recovery as the level of inhibition approaches 60% or greater; for relatively high daily inhibitions (circa 8 to 16%), the combination of reversion and regeneration results in recoveries of as much as 4% of the baseline normal over a weekend, which becomes more visible on the expanded scale near the bottom of these figures.

Based on the first row of data in Table IV, it appears that the only practical daily inhibition (i.e. residues with any variability at all) for which seasonal inhibition will be less than 50% is 1% per day. This is similar to the prediction in reference 9 (p. 140) of 1 to 2% per day for 40% seasonal inhibition given a 7-day per week exposure pattern. The variability in the seasonal inhibition is indicated by the second row of data, the geometric deviation. It appears that the relative variability in the seasonal low AChE activity is reduced primarily as the daily inhibitions increase and secondarily as the variability in the residues increases. This pattern is explainable by the overwhelming importance of the magnitude of the daily inhibition in relationship to the speed of enzyme reversion and replacement. The impact of variability on the fraction of the cohort whose seasonal inhibition exceeds 50% is indicated

by the third row of data in this table: the trade-off between low levels of daily inhibition and relatively high levels of variability causes there to be some fraction of the cohort which exceeds 50% under all conditions, although again this fraction increases primarily with increasing levels of daily inhibition.

As it will be discussed in relation to acute responses, the significance of these simulated chronic responses in relation to future human experience is best judged in relation to past experience. Unfortunately the history of past chronic cholinesterase studies among harvesters has hardly been reported. One rather unique study of one East coast migrant crew by Owens and Owens [24] was referenced in the elaboration of the Unified Field Model [11] showed seasonal inhibitions of 30 to 40%, but the more detailed analyses of their data has not been accomplished. Another known report was a student master's thesis of some 822 California central valley harvesters in 1970 which showed seasonal inhibition of 5 to 8% [25]. In both studies neither the intensity nor frequency of residue exposure was known; therefore, direct comparisons of the chronic response between this simulation and human experience is barely possible.

In general, such chronic longitudinal studies are difficult to initiate, organize, maintain and analyze. Of practical importance is the effect on data analysis of the relative size (and numbers) of individual crews into which the whole cohort is distributed. Included in the results printed by the data summary program is the analysis of variance F statistic indicating the uniformity between the crews versus within the crews (and the cohort as a whole). Initially these test statistics are quite large, indicating statistically greater variation between crews than within crews (except of course, when the variability in the residues is 0 (geometric deviation of 1.0). Over time, the crews become more and more consistent, and the daily F statistic decreases. A value of about 2.0 indicates statistical uniformity with 99% confidence. The fourth row of Table IV indicates the number of days into the season necessary for such inter-crew uniformity to be established. From this data it is clear that residue variability is the dominant factor characterizing inter-crew uniformity and that statistical uniformity is not achieved within a six-month season for levels of variability of 3 or more. This conclusion implies that an adequate interpretation of harvester cholinesterase survey data must take into account the grouping of that data by crew; similarly, some crews should be expected to be significantly more inhibited than others or than the group as a whole.

The preceding discussion of chronic response variability is directly relatable to acute "clinical" responses which represent the high "tails" of the daily statistical distribution. A summary of acute response data are depicted in Table V only (rather than in figures). The first row of this table indicates the frequency with which individual harvesters might have RBC AChE shifts sufficient to induce clinical symptoms. It appears that while the incidence of chronic seasonal inhibition is high under many of the scenarios investigated, the incidence of clinically acute responses is undetectable under a much broader range of residue conditions. Practical conditions without incidents begin at 8% per day if the variability can be kept at or below 1.5; at 4% per day, below 1.5; 2% per day of at or below 2.0; and 1% per day if variability approaches 3.0. It also appears that

once conditions of daily mean or residue variability are sufficiently high
to cause one individual acute case, multiple cases (the second row) and
incidents involving at least half the crew (the third row) begin to occur;
this pattern is relatable to the inter-crew versus intra-crew uniformity
discussed above. Therefore, a reasonable administrative target is to
prevent any individual cases of anti-cholinesterase poisoning sufficient to
cause clinical symptoms.

Fortunately the significance of these simulated acute responses in
relation to future human experience is more readily judged in relation to
past experience than was true for chronic cholinesterase effects. Several
tabulations of "reported" poisoning incidents from the literature are
available to provide a first estimate of past field experience [3,6,8].
These data indicate an incidence of about 25 harvesters and 1 "incident"
reported in California per year from 1948 to 1977; although two other
independent reports indicate the above values "represent perhaps 1% of of
the persons who suffered less severe symptoms, received medical treatment,
but remained unreported" [9]. Most (but not all) of these reported cases
involved parathion.

The denominator for these cases can be estimated from the roughly
74,000 acres of valencia oranges in California [26] (the variety harvested
during the April-September prime parathion application period; see Table VI)
and reported individual harvest rate data [27], which indicate about 7400
harvesters are actively engaged in harvesting the seasonal crop most
commonly involved in reported residue poisoning incidents [3,6,8]. The
denominator for these incidents can be closely approximated from California
Pesticide Use Reports, Table VI, which for the early 1970s was about 2000
fields and circa 60,000 acres of oranges (of which about 50% was summer
valencias) sprayed per year [28]. Thus, on an annual average over the
thirty year history, about 25/7400 = 0.34% of the orange harvesters in
California have been involved in a reported residue poisoning per year and
1/1000 = 0.1% of the field applications have resulted in reported incidents.

Recall also that the variability in parathion residues on citrus was
2.6 (Table III); furthermore, the equivalent anti-cholinesterase power of
the residues on day 9 was about 8% and on day 16, about 4%. Since
California had, prior to 1970, an administrative harvest - reentry interval
for parathion of 14 days, a mean daily inhibition of 4% is the worst
expected scenario to simulate historical experience. Although it is
unlikely that every field was harvested as soon as its reentry interval had
elapsed, it is possible that a great many of these fields could have been
harvested between that time and 2 weeks later (or about 2 half lives and
1/4th the AChE effect later).

Locating these conditions in Table V indicates a reasonably good
agreement between the simulation and historical record. The simulation
indicates a somewhat higher incidence of individual overexposures than the
historical record shows, but well within the higher range estimated by the
"critics" of the established reporting system. On the other hand, the
simulation indicates an incidence of "potentially reportable" group
incidents somewhat lower than reported. There are many possible
explanations for this latter difference, among them are (1) a difference in
the ratio of number of crews and crew size from that modeled, (2) an overly
conservative definition of "incident" (i.e. at least 50% of the crew having

an AChE shift of 50% or more), and (3) other than a log-normal distribution of foliar residues (i.e. a bimodal distribution with unexpectedly more frequent high residues under some relatively unique combination of environmental and/or application conditions, or possibly some combination of the above. Whatever the reason, the differences are relatively slight; proving the value of this stochastic simulation procedure.

Conclusion:

A stochastic simulation program was written to study the importance of residue variability in preventing anti-cholinesterase overexposure, excessive chronic AChE inhibition, or acute illness. A range of daily inhibitions and residue variability were explored, and the simulated cohort response was compared to the historical record of chronic and acute data. The resulting chronic and acute AChE response patterns are largely displayed in Tables IV and V, respectively.

It was concluded that residue variability has only a slight effect on the mean AChE health status of a working cohort, in comparison to mean daily inhibition. Residue variability has a slightly stronger although still secondary effect upon the overall variability of the cohort's AChE activity. The fraction of the cohort whose seasonal AChE inhibition exceeded a relatively arbitrary chronic threshold of 50% was again largely controlled by the daily mean inhibition, but at 4% per day and above virtually the entire cohort exceeded that limit and below 4% per day residue variability had an increasing important role.

On the other hand, residue variability appears to have a very strong effect upon the uniformity of the AChE activity within the cohort. This nonuniformity has both chronic and acute AChE implications. For instance, for residue variability even below a geometric deviation of 2.0, the crews seasonal AChE inhibitions are not expected to be statistically uniform (with 99% confidence) until half way through a season; and for variability of 3.0 and above, the crews will be dissimilar throughout the season. Thus, it is possible to have several crews below an administrative AChE inhibition threshold (or even potentially with clinical symptoms) while the cohort mean is only marginally different from normal. This pattern has similar implications to both the design and interpretation of epidemiologic surveys among this population.

Acute responses, in terms of individual and group AChE responses in excess of potential clinical symptoms, exhibit a fairly clear boundary as a function of both residue mean and variation. In the low mean range of 1% to 2% per day, no acute individual or group incidents were predicted for geometric variations below 2.5; however, a set of random parathion commercial application residues collected on days 2, 9, and 16 all showed variations of around 2.6, just sufficient to induce sporatic acute responses.

This pattern of acute effects under conditions of low chronic response and the practical boundary of a geometric deviation of 2.5 (or $\pm$ 150%), suggest that consideration to both the mean anti-cholinesterase effect and the variability of the foliar residues should be considered when setting administrative reentry intervals.

References:

1. Abrams, H.K., and A.R. Leonard: Toxicology of Organic Phosphate Insecticides. Calif. Med. 73:183-186, 1950.
2. Ingram, F.R.: Health Hazards Associated with Use of Airplanes for Dusting Crops with Parathion. Amer. Ind. Hyg. Assoc. Quart. 12:165-170, 1951.
3. Quinby, G.E., and A.B. Lemmon: Parathion Residues as a Cause of Poisoning in Crop Workers. J. Amer. Med. Assoc. 166:740-746, 1958.
4. Milby, T.H., F. Ottoboni, and H. Mitchell: Parathion Residue Poisoning Among Orchard Workers. J. Amer. Med. Assoc. 189:351-356, 1964.
5. Milby et al.: Occupational Exposure to Pesticides. A Report of the Federal Working Group on Pest Management, Washington DC, 1974.
6. Spear, R.C., W.J. Popendorf, J.T. Leffingwell, and D. Jenkins: Parathion on Citrus Foliage: Decay and Composition as Related to Worker Hazard. J. Agr. Food Chem. 23:808-810, 1975.
7. NIOSH: Proceedings: Pesticide Residue Hazards to Farm Workers. U.S. Dept. HEW Pub. No. (NIOSH) 76-191, 1976.
8. Gunther, F.A., Y. Iwata, G.E. Carman, C.A. Smith: The Citrus Reentry Problem: Research on its Causes and Effects, and Approaches to its Minimization. Residue Reviews 67:1-139, 1977.
9. Popendorf, W. and J.T. Leffingwell: Regulating OP Pesticide Residues for Farmworker Protection. Residue Reviews 82, 125-201, 1982.
10. Dermal Exposure Related to Pesticide Use: Discussion of Risk Assessment. ed. by R.C. Honeycutt, G. Zweig, N.C. Ragsdale. American Chemical Society, Washington DC, 1985.
11. Popendorf, W.P.: Advances in the Unified Field Model for Reentry Hazards. p. 323-341, op cit., 1985.
12 Popendorf, W. and J.T. Leffingwell: Natural Variations in the Decay and Oxidation of Parathion Foliar Residues. J. Agric. Food Chem. 26:437-441, 1978.
13. Scheuplein, R.J.: Percutaneous Absorption After Twenty-five Years: or "Old Wine in New Wine Skins." J. Invest. Dermat. 67:31-38, 1976. (not his latest).
14. Grob, D. and A.M. Harvey: Effects in Man of the Anti-cholinesterase Compound Sarin (Isopropyl Methyl Phosphonofluoridate). J. Clin. Inv. 37:350-368, 1958.
15. ACGIH Threshold Limit Values and Biological Exposure Indices for 1985-86. TLV for Mixtures, p. 47, Amer. Conf. Governmental Industr. Hyg. Cincinnati, OH, 1986.
16. OSHA Safety and Health Standards (29 CFR 1910.1000) U.S. Dept. Labor Pub. No. (OSHA) 2206, Washington DC, 1983.
17. Wills, J.H., and K.P. Dubois: The Measurement and Significance of Changes in the Cholinesterase Activities of Erythrocytes and Plasma in Man and Animals. CRC Critical Reviews in Toxicol. 1:153-202,1972.
18. Geigy Scientific Tables Vol. 3, 8th Ed., edited by C. Lentner, Ciba-Geigy, W. Caldwell NJ, 1984.
19. Rubinstein, R.Y.: Simulation and the Monte Carlo Method. John Wiley & Sons, New York, 1981.
20. Odeh, R.E. and J.O Evans: The Percentage Points for the Normal Distribution, AS 70. Appl. Statist. 23:96-97, 1974.

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21. Wichmann, B.A. and I.D. Hill: An Efficient and Portable Pseudo-random Number Generator, AS 183. Appl. Statist. 31:188-190, 1982.
22. Gage, J.G.: The Significance of Blood Cholinesterase Activity Measurements. Residue Reviews 18:159-173, 1967.
23. Gaines, T.B.: Acute Toxicity of Pesticides. Toxicol. Appl. Pharmacol. 14:515-534, 1969.
24. Owens, E.W. and S.Y. Owens. Science, submitted 1984.
25. Ray, R. Occupational Exposure to Organophosphate Pesticides among Agricultural Workers and their Families. MS Thesis, University of California, Berkeley CA, 1972.
26. California Crop and Livestock Reporting Service, 1981.
27. Popendorf, W. and R.C. Spear: Preliminary Survey of Factors Affecting the Exposure of Harvesters to Pesticide Residues. Amer. Industr. Hyg. Assoc. J. 36:374-380, 1974.
28. Pesticide Use Reports, California Dept. Food and Agriculture, Sacramento CA, for the years noted (1972-1982).

Table I. Equivalence of the terms and notation used in the text of this report versus the notation used in the programs listed in Appendix B and C. Terms are listed according to the subscript by which they were varied (or if in parentheses, by which they could have been varied).

text subscript text notation	chem. i	crew	person j	day n	program notation
terms varied:					
reentry residue $R_{i,n}$	(x)	x		x	res
daily field residue		x		xa	r
dosing coef. $k_{d:j}$			x	(x)	kd
body weight m_j			x		wt
enzyme coef. $k_{e:j}$			x		ke
reversion coef. ρ			x		pp
regeneration rate			x		p
terms not varied:					
residue decay coef.[b] k_r	(x)[a]				half
work day t			(x)	(x)	hwpd
dermal tox. $LD_{50:i}$	(x)				ld50
enzyme measurement			(x)	xb	vlab
Terms not used:					
initial residue R^o	(x)[a]				
reentry interval T				(x)a	
absorption coef. k_a	(x)		(x)		
program subscript	mm chem.	i crew	j person	k day	program notation

footnote:
a) term effectively varied by variations in R_n above.
b) capability to vary laboratory measurement technique was built in to program, but unused throughout the majority of the study.

Table II. A summary of the mean and deviation for each model parameter used within this study. Deviations followed by "x" denote geometric deviations (multipliers and dividers of the mean); those with units are geometric deviations (the normal distribution).

		mean	deviation	reference
terms varied:				
reentry residue	$R_{i,n}$	a	1.0 to 4.0 x	[6,12]
dosing coef.	$k_{d:j}$	5.1 cm	1.41 x	[9]
body weight	m_j	70 kg	$\pm$ 7 kg	[9]
enzyme coef.	$k^j_{e:j}$	6.0	1.3 x	[9]
reversion coef.	ρ	0.15 day-1	1.01 x	[9,14,15]
regeneration rate	ϕ	.893 %/day	1.046 x	[18]
terms not varied:				
residue decay coef.[b]	k_r	7 days		[12]
work day	t^r	8 hours		[15,16]
dermal tox.	$LD_{50:i}$	10. mg/kg		[9,22]
enzyme measurement				[9,17,23]

===

footnote:
   a) initial mean reentry residue levels were determined from the Unified
      Field Model based upon the mean daily delAChE response specified by
      the user of the program; each of the following combinations of mean
      residue and residue variability were investigated:

	mean delAChE				
	1%	2%	4%	8%	16%
geometric deviation 1.0					
1.5					
2.0					
3.0					
4.0					

Table III . Summary of foliar dislodgeable parathion (thion) and paraoxon (poxon) concentrations, ng/cm^2 from commercial citrus groves sampled on the same day post-application [reference 6].

day	thion	poxon	day	thion	poxon	day	thion	poxon
2	264.1	18.63	9	29.94	12.61	16	9.526	6.956
2	398.5	32.07	9	55.17	33.01	16	24.52	8.983
2	412.6	29.71	9	95.49	11.67	16	49.75	10.12
2	1434.	109.2	9	311.2	64.84	16	113.9	49.99
2	180.8	89.60	9	22.85	25.46	16	7.474	7.286
2	170.9	71.44	9	17.38	20.42	16	9.148	7.875
2	149.7	108.9	9	6.319	25.94	16	5.965	9.974
2	190.7	10.54	9	13.49	2.759	16	3.466	1.582
2	49.75	6.272	9	7.451	1.252	16	1.250	.6413
2	252.3	33.72	9	26.64	19.92	16	9.785	10.09
2	186.7	52.82	9	20.77	16.98	16	7.144	6.508
2	103.5	21.41	9	22.73	9.290	16	7.946	7.309
2	174.7	35.13	9	27.59	14.05	16	10.87	9.384
2	294.7	33.72	9	32.77	12.43	16	6.272	6.696
2	89.13	23.06	9	19.64	6.201	16	13.46	1.846
2	240.5	20.91	9	43.62	18.13	16	8.205	7.215
2	688.5	25.46	9	48.34	11.13	16	11.48	7.097
2	229.2	51.64	9	57.77	24.99	16	11.95	11.51
2	483.4	166.5	9	12.05	53.76	16	5.376	21.41
2	1297.	227.3	9	119.8	135.1	16	39.14	21.08
2	172.6	327.7	9	21.06	65.78	16	32.54	20.58
2	438.6	396.1	9	42.68	71.91	16	2.358	17.97
2	152.8	15.66	9	7.710	4.551	16	3.843	2.499
2	417.3	24.99	9	38.20	16.41	16	3.631	4.951
2	771.0	365.5	9	69.32	51.17	16	20.84	25.46
2	386.7	11.44	9	42.91	15.51	16	11.93	4.716
2	617.8	320.7	9	67.20	115.3	16	24.05	58.00
2	363.1	32.07	9	20.30	13.16	16	4.409	7.026
2	199.7	145.0	9	24.05	22.40	16	8.583	13.16
2	482.8	325.7	9	15.51	65.31	16	13.03	90.19
2	893.0	276.8	9	45.39	95.79	16	10.49	19.54
2	562.9	38.02	9	15.59	9.549	16	3.773	4.362
2	216.0	24.70	9	92.84	27.62	16	18.04	20.45
2	1724.	92.55	9	80.76	40.67	16	35.96	26.23
2	303.6	159.7				16	24.73	29.77
2	327.2	262.6						
2	418.5	62.19						
2	193.9	90.48						
2	234.6	96.08						
2	607.1	210.7						
arth.mean =	419.3	111.2		46.31	33.38		16.42	15.96
std. dev. =	365.1	114.6		54.40	32.75		20.44	18.04
N =	40	40		34	34		35	35
geom.mean =	316.0	63.31		31.65	21.16		10.51	10.00
geom.dev. =	2.12	3.08		2.33	2.83		2.52	2.76

Pooled geometric deviation = 2.61

Table IV. Chronic Response to exposures 5 days per week distributed among 18 crews of 12 persons each working alternately 2 and 3 days per field (see also Figures 1-6):

1) The typical mean pseudo-equilibrium AChE activity expressed as a percent of normal baseline of each individual for the harvester cohort as a whole in mid- to late in the last week of the season.

2) The geometric deviation for the above data, expressed as a percent $\pm$ of the mean.

3) The prevalence (expressed as percent) of harvesters who have exceeded 50% inhibition of RBC AChE by the end of the season.

4) The number of days into the 182 day (26 week) season necessary for the analysis of variance F statistic to decrease to or below 2.00 (the critical $F_{17,198}$ test statistic for 99% confidence of uniformity).

		Daily	Mean	delAChE	
	1%	2%	4%	8%	16%
Geometric **1.0**	35	50	65	75	82
	$\pm$30%	$\pm$20%	$\pm$12%	$\pm$7%	$\pm$4%
Deviation	6-7%	53-56%	97-99%	100%	100%
	0	0	0	0	0
1.5	37	52	66	76	82
	$\pm$29%	$\pm$19%	$\pm$11%	$\pm$6%	$\pm$3%
	6-8%	58-63%	98-99%	100%	100%
	38	39	38	37[a]	35[b]
2.0	40	55	68	77	83
	$\pm$27%	$\pm$17%	$\pm$10%	$\pm$6%	$\pm$3%
	12-18%	69-74%	> 99 %	100%	100%
	117	119	140[b]	>182	>182
3.0	47	61	71	78	84
	$\pm$22%	$\pm$13%	$\pm$8%	$\pm$5%	$\pm$3%
	41-46%	90-94%	> 98 %	100%	100%
	175	>182	>182	>182	>182
4.0	54	66	74	80	85
	$\pm$17%	$\pm$10%	$\pm$6%	$\pm$4%	$\pm$3%
	69-74%	95-97%	99-100%	100%	100%
	>182	>182	>182	>182	>182

==

footnotes:
   a) not consistently uniform thereafter.
   b) infrequently uniform thereafter.

Table Va. Acute Response (in absolute numbers) to exposures 5 days per week distributed among 18 crews of 12 persons each working alternately 2 and 3 days per field:

1) The number of harvesters experiencing a 1-day AChE inhibition of >50% (believed capable of inducing clinical symptoms); values in excess of 216 indicate individuals multiply exposed to high levels of residue.
2) The number of days throughout the season in which the above inhibitions occurred (this will be between 1 and 2 times the number of fields, depending upon the frequency and severity of the "poisoning").
3) The number of sprayed fields per season in which the above inhibitions were clustered into potentially reportable "incidents" (involving at least one-half of the crew).

		Daily	Mean	delAChE		
		1%	2%	4%	8%	16%
Geometric	1.0	0	0	0	0	0
		0	0	0	0	0
Deviation		0	0	0	0	0
	1.5	0	0	0	0	46
		0	0	0	0	22
		0	0	0	0	3
	2.0	0	0	1	39	317
		0	0	1	16	79
		0	0	0	2	5
	3.0	1	12	84	383	*
		0	5	26	48	*
		0	1	6	32	~76
	4.0	20	82	288	*	*
		5	22	36	*	*
		2	5	18	~42	*

==

	2.6	0	2	28
		0	2	10
		0	0	1

Table Vb. Acute Responses (in rates per hundred) to exposures 5 days per week distributed among 18 crews of 12 persons each working alternately 2 and 3 days per field:

1) The incidence (percent of 216) of harvesters experiencing a 1-day AChE inhibition of >50% (believed capable of inducing clinical symptoms); values in excess of 100% indicate individuals multiply exposed to high levels of residue.
2) The percent of 182 days throughout the season in which the above inhibitions occurred (this will be between 1 and 2 times the number of fields, depending upon the frequency and severity of the "poisoning").
3) The percent of the 916 sprayed fields per season in which the above inhibitions were clustered into potentially reportable "incidents" (involving at least one-half of the crew).

		Daily 1%	Mean 2%	delAChE 4%	8%	16%
Geometric	1.0	0	0	0	0	0
		0	0	0	0	0
Deviation		0	0	0	0	0
	1.5	0	0	0	0	21%
		0	0	0	0	12%
		0	0	0	0	.3%
	2.0	0	0	.5%	18%	147%
		0	0	.5%	9%	43%
		0	0	0	.2%	.5%
	2.6	0	.9%	13%		
		0	1%	5%		
		0	0	.1%		
	3.0	.1%	6%	39%	177%	*
		0	3%	14%	26%	*
		0	.1%	.7%	3.5%	~8.3%
	4.0	9%	38%	133%	*	*
		3%	12%	20%	*	*
		.2%	.5%	2.0%	~4.6%	*

footnote *) frequencies become unreliably too high to be representative.

Table VI. Reported use history of parathion on oranges in California
[Source Pesticide Use Reports, California Dept. Food and Agriculture, for the years noted].

Year	Number of Applications	Pounds	Acres	Pounds/Acre
1972	1982	160 377	52 855	3.03
1973	2206	194 061	65 777	2.95
1974	2135	161 233	63 574	2.54
1975	1554	124 049	45 189	2.75
1976	921	77 956	30 742	2.54
1977	1000	90 240	29 106	3.10
1978	744	57 111	21 765	2.62
1979	638	69 722	23 314	2.99
1980	443	50 051	14 199	3.52
1981	476	55 677	14 446	3.85
1982	681	54 171	21 845	2.48
1983				
1984	548	49 848	17 579	2.84

Tulare County Use Report, Oranges, 1972.

Jan	0	0	0	
Feb	1	1	1	
Mar	271	22 045	9 905	2.23
Apr	128	6 867	3 092	2.22
May	165	15 640	4 662	3.35
Jun	260	25 335	7 086	3.58
Jul	182	11 975	4 357	2.75
Aug	158	11 174	3 682	3.03
Sep	83	20 778	2 919	7.12
Oct	67	6 462	1 900	3.40
Nov	21	1 520	1 520	3.55
Dec	5	559	155	3.60
totals	1444	122 737	38 199	3.21
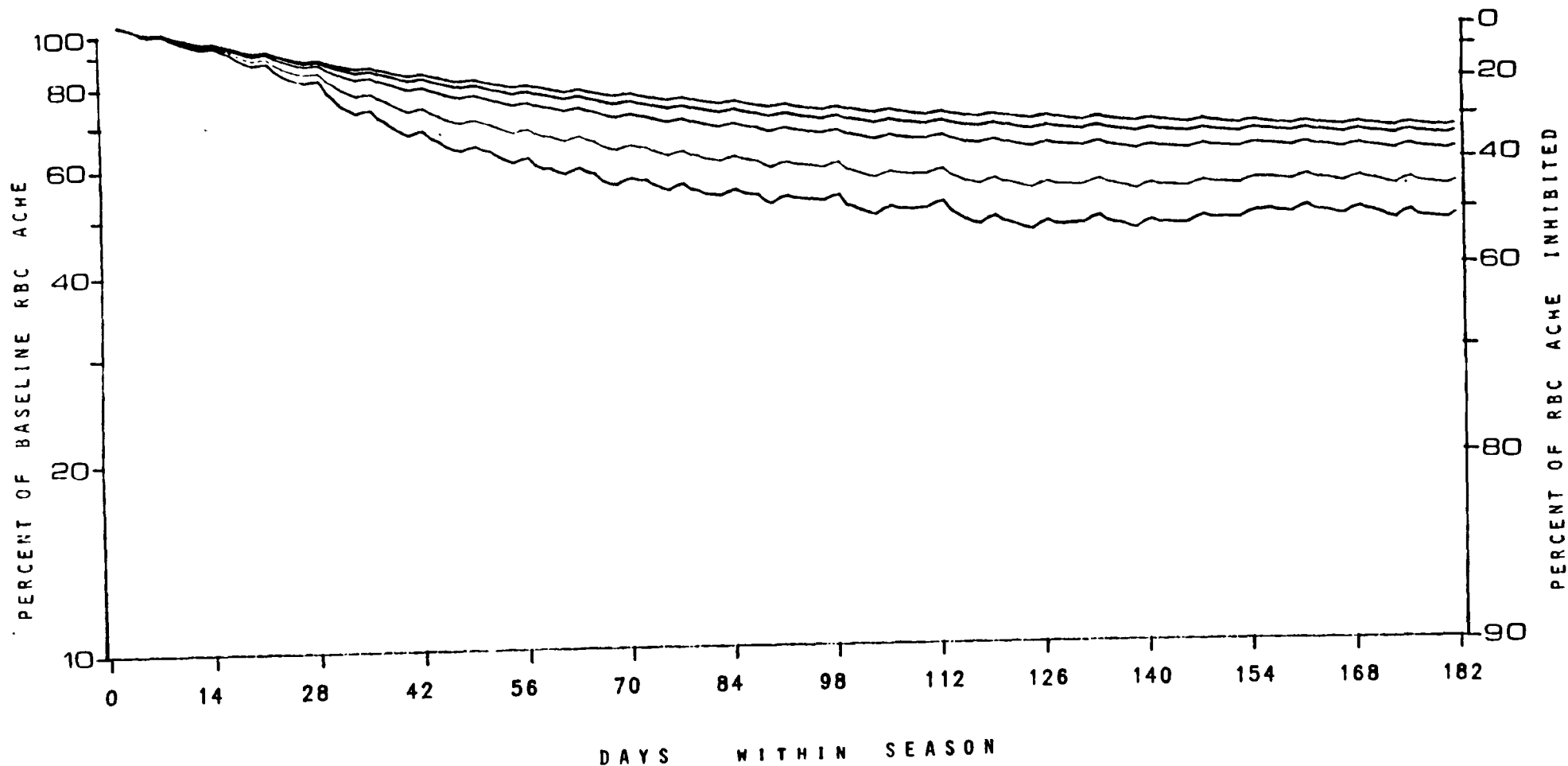
Figure 1. Plot of AChE activity on the Y axis versus seasonal time in
days on the X axis for 1% daily delAChE, with residue geometric
deviation increasing progressively from the top to bottom line
from 1.0 to 1.5, 2.0, 3.0, and 4.0, respectively.

Figure 2. Plot of AChE activity on the Y axis versus seasonal time in days on the X axis for 2% daily delAChE, with residue geometric deviation increasing progressively from the top to bottom line from 1.0 to 1.5, 2.0, 3.0, and 4.0, respectively.

Figure 3. Plot of AChE activity on the Y axis versus seasonal time in days on the X axis for 4% daily delAChE, with residue geometric deviation increasing progressively from the top to bottom line from 1.0 to 1.5, 2.0, 3.0, and 4.0 respectively.

Figure 4. Plot of AChE activity on the Y axis versus seasonal time in days on the X axis for 8% daily delAChE, with residue geometric deviation increasing progressively from the top to bottom line from 1.0 to 1.5, 2.0, 3.0, and 4.0, respectively.

Figure 5.   Plot of AChE activity on the Y axis versus seasonal time in
days on the X axis for 16% daily delAChE, with residue geomtric
deviation increasing progressively from the top to bottom line
from 1.0 to 1.5, 2.0, 3.0, and 4.0, respectively.
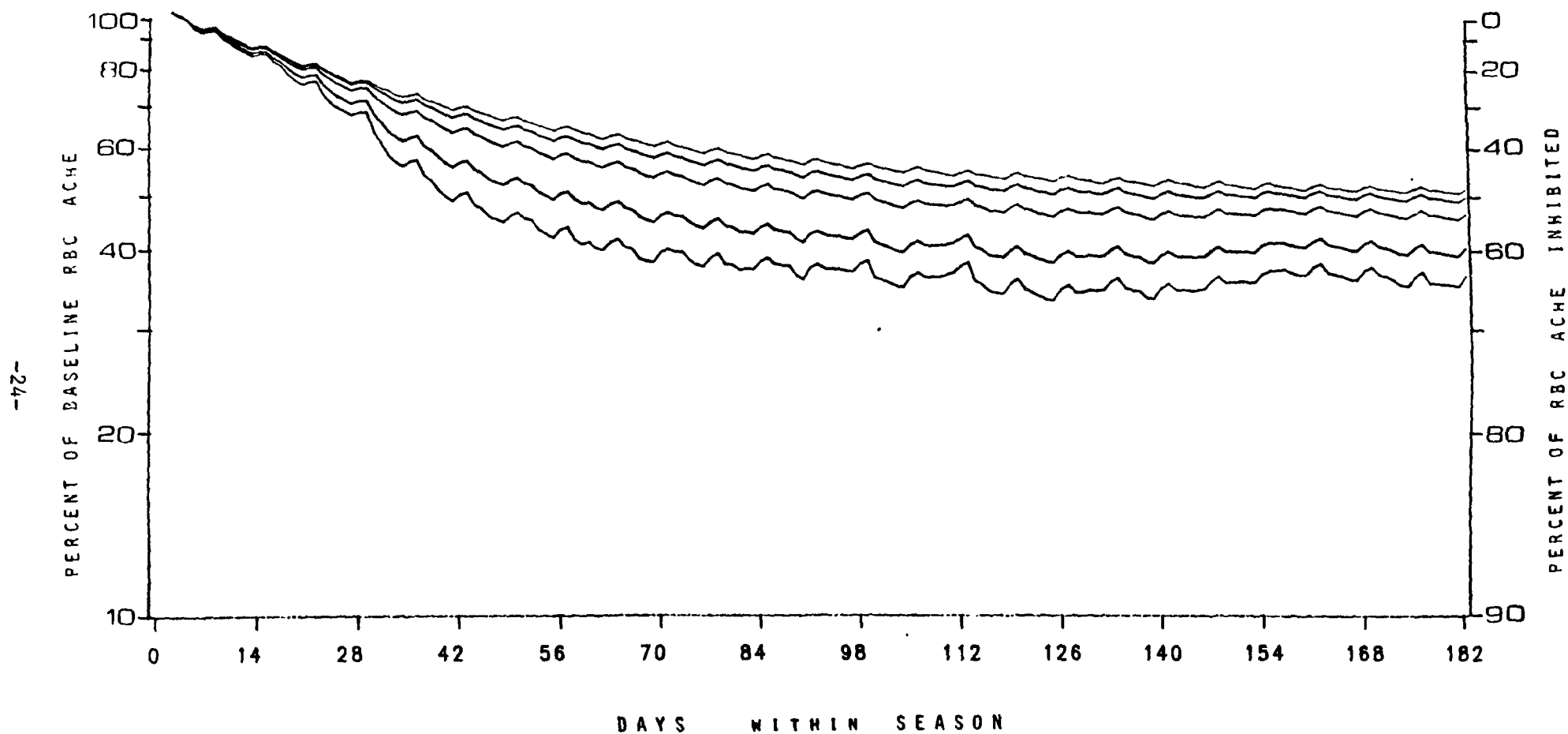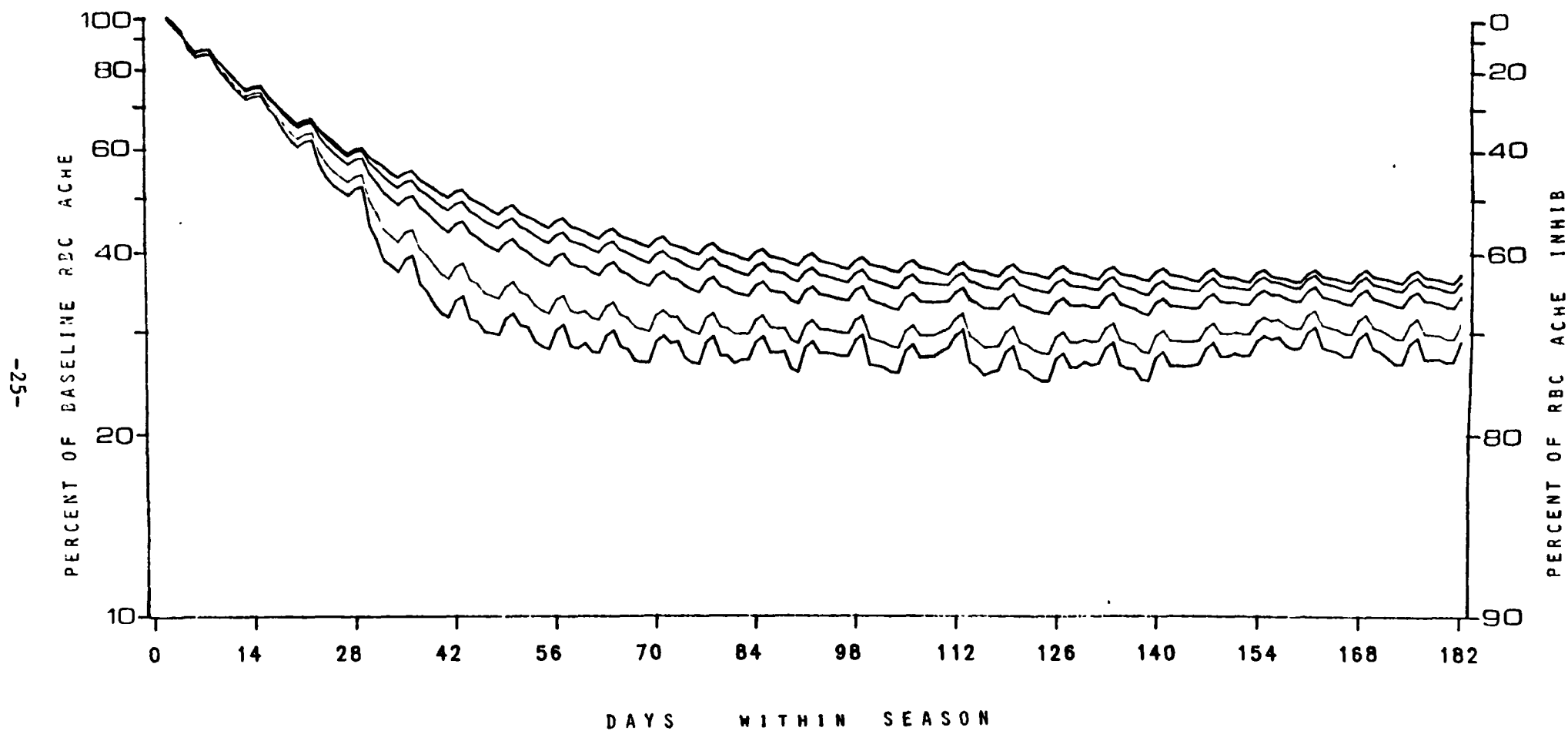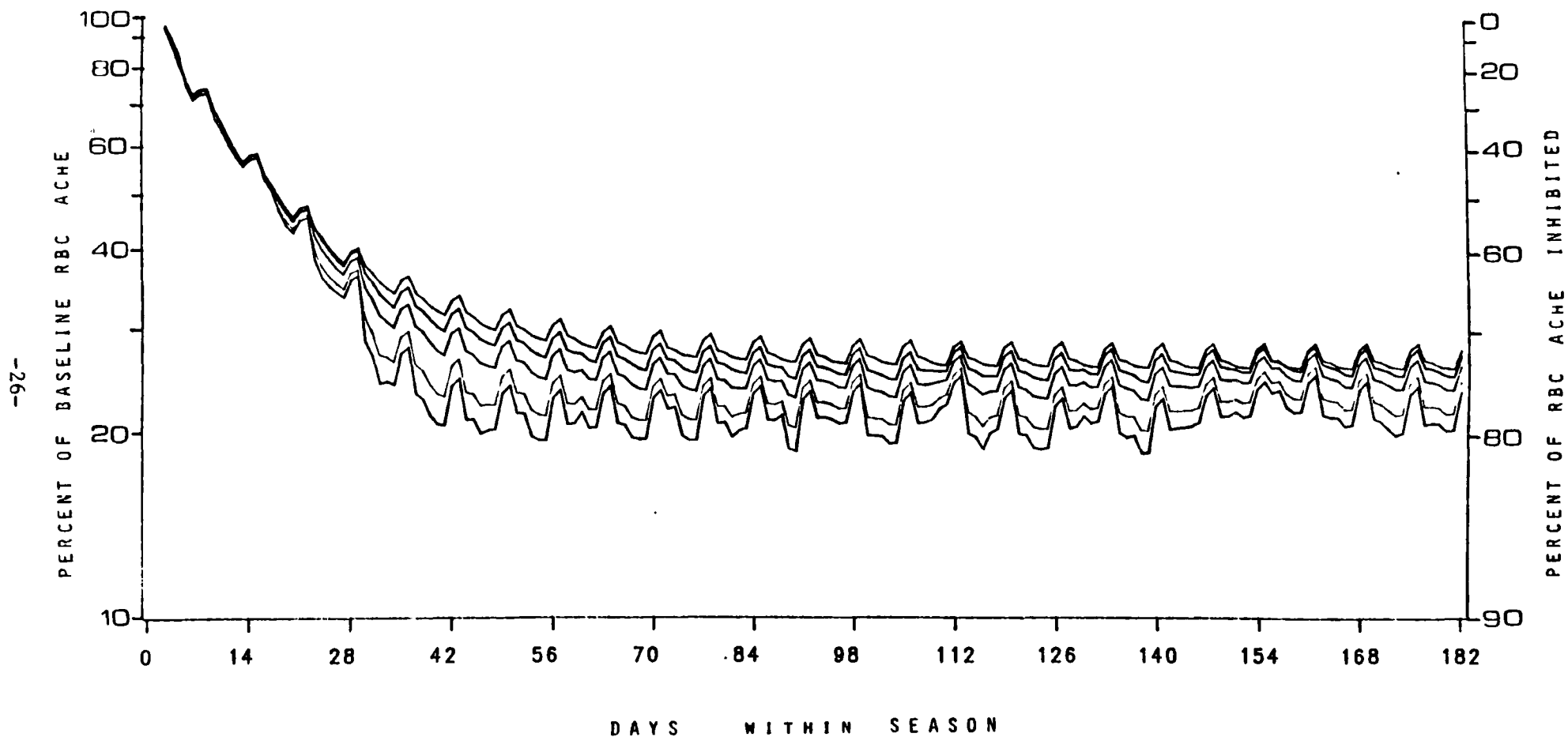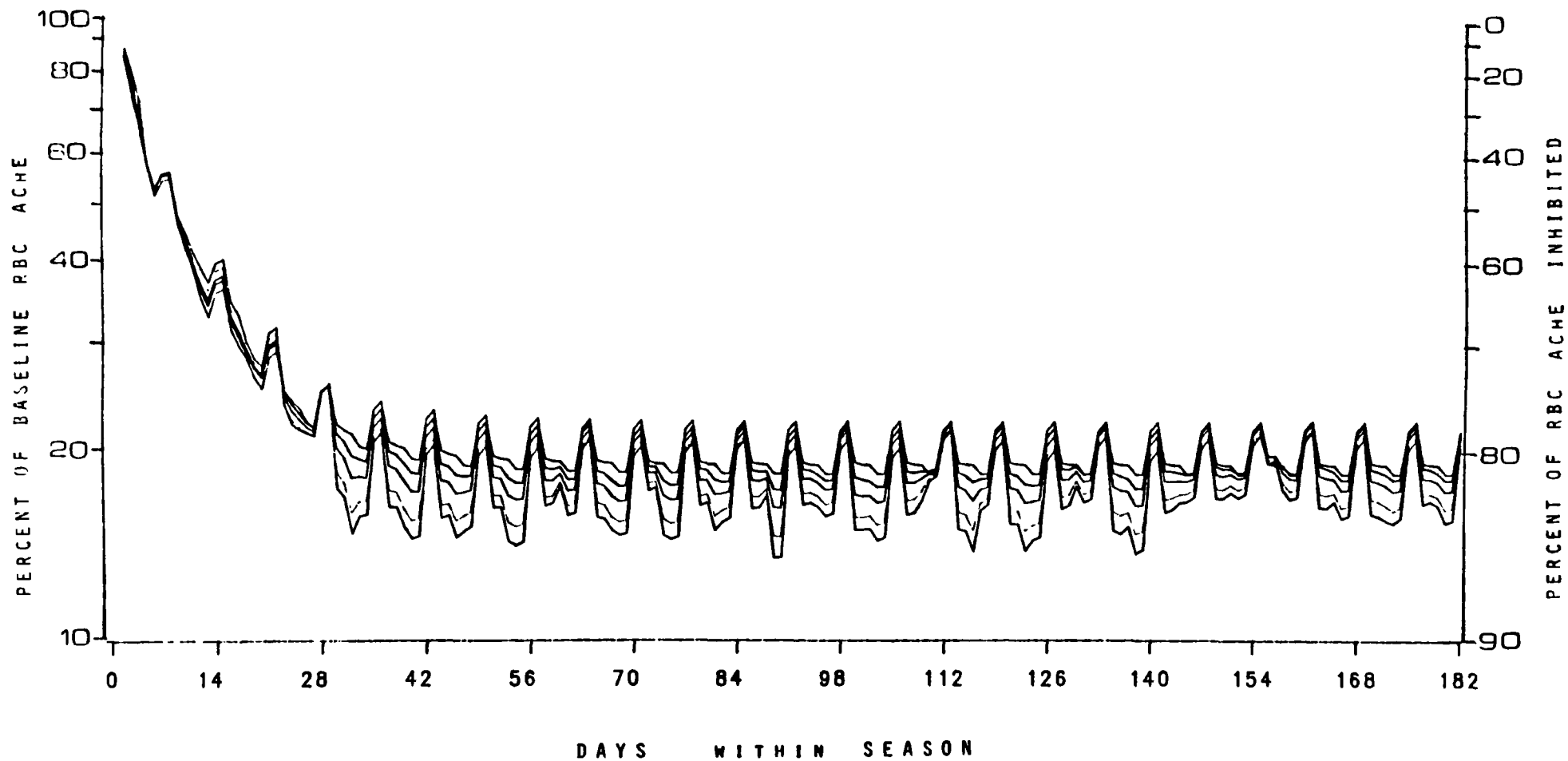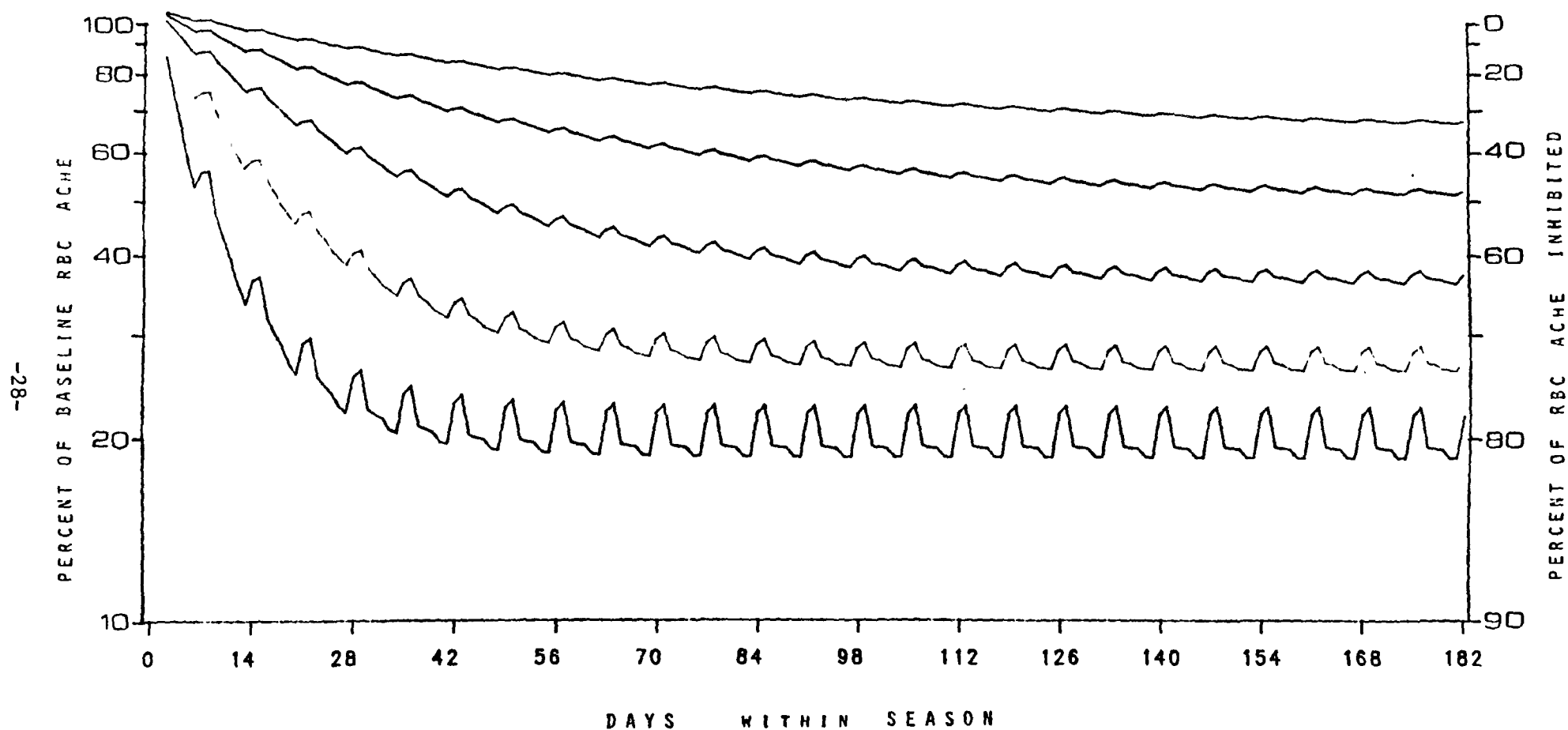
Figure 6. Plot of AChE activity on the Y axis versus seasonal time in days
on the X axis for 0 residue variability, with daily delAChE
increasing progressively from the top to bottom line from 1% to 2%,
4%, 8%, and 16%, respectively.

Appendix A: listing of Fortran simulation program (with comments) to be run
on an IBM 370 with VS operating system. Lines following
//GO.FT01F001 DD * are input data for batch mode operation.

```
// JOB (,25),'F1 FREY',TIME=(002),MSGLEVEL=(1,1)
/*PASSWORD PPSU8
/*ROUTE PRINT WYLBUR
// EXEC FORTVCLG,FVREGN=1200K,GOREGN=1024K
//FORT.SYSIN DD *
c
c Reentry Simulation Program , IBM 360 Version 1
c
c input used for this simulation problem:
c
c  i.    means and sd (geometric means and sd for kd,p,pl,res.eq.coeff.)
c        1. rmp, regeneration of rbc and their enzymes [usually 1-2%]
c           rmpl, reversion of rbc   [usually 0-15]:
c           rmp,sdp,rmpl,sdpl                          (4F10.5)
c
c        2. kd dose coefficient, ke enzyme coefficient:
c           rmkd,sdkd, rmke,sdke                       (4F10.5)
c
c        3. mass (body weight) of workers:
c           rmwt,sdwt                                  (2F10.5)
c
c
c  ii.   parameters determing pattern of field exposure
c        1. nf = number of fields worked per crew:     (i3)
c        2. nc = number of crews to be placed in fields: (i3)
c        3. nm = number of members per crew:           (20i3)
c        4. te = time (days) of initial re-entry into each field
c              after spraying:                         (f10.5)
c        5. tw = time (hours) worked per day :         (f10.5)
c        6. 1d50 = LD50 for parent and each oxon:      (4f10.5)
c        7. nd = number of days to complete each field: (i3)
c
c  iii.  input residues of parent [and oxon]:
c        1. read mean and geometric deviation of parent and ditto for oxons
c                                                      (4F10.5).
c
c  iv.   other input variables
c        1. dseed = an integer value (1-2147483647) typed in double
c                 precision, to be used to generate random number:
c                                                      (f10.0)
c
      CHARACTER*4  NMC(20)
      CHARACTER*40 INPUT,OUTPUT,RESDUE
      DOUBLE PRECISION DSEED
      REAL  P(18,12),P1(18,12),KK(18,12,100),LD50(10),
     +      KD(18,12),KE(18,12),WT(18,12),DEL(18,12,100),
     +      RP(301),RKE(301),RKD(301),RWT(301),RAA(301),RP1(301),
     +      R(18,18),H(18,12,100),H1(18,12,101),HE(12),
     +      HM(18,100),HSD(18,100)

c     lun is a vestigal parameter from a F77 version directing output:
      LUN = 4
      READ  (1,10) RMP,SDP,RMP1,SDP1
      READ  (1,10) RMKD,SDKD,RMKE,SDKE
```

```
      READ (1,10) RMWT,SDWT
c
c     print means and sd
c
      WRITE (LUN,20) RMKE,SDKE,RMWT,SDWT,RMP,SDP,RMP1,SDP1,RMKD,SDKD
   20 FORMAT(1X,/,
     +  1X,'MEANS AND DEVIATIONS GIVEN ON INPUT'   /
     +  7X,'FOR NORMALLY DISTRIBUTED VARIABLES'     /
     +  10X,'ENZYME COEFFICIENT KE',     T45,2F10.5 /
     +  10X,'WORKERS WEIGHT',            T45,2F10.5 /
     +  7X,'FOR LOGNORMALLY DISTRIBUTED VARIABLES '/
     +  10X,'REGENERATION, P',           T45,2F10.5 /
     +  10X,'REVERSION,P1',              T45,2F10.5 /
     +  10X,'DOSING COEFFICIENT KD',     T45,2F10.5 / )
c
c     input other parameters describing field
      READ (1,25) NF
      READ (1,25) NC
      READ (1,30) NM
      READ (1,10) TE
      READ (1,10) TW
      READ (1,10) LD50(1)
      READ (1,30) ND
      READ (1,10) RESSS,REGED
      READ (1,40) DSEED
c     input formats
   10 FORMAT(4F10.5)
   15 FORMAT(8F10.5)
   25 FORMAT(I3)
   30 FORMAT(20I3)
   40 FORMAT(F10.0)
c
c     output parameters describing field
      WRITE (LUN,35) NC,NF,ND,TW,TE,DSEED,LD50(1),RESSS,REGED
   35 FORMAT( 1X,'OTHER PARAMETERS GIVEN ON INPUT',                  /
     +      10X,'NO. OF CREWS',                      T41,I3     /
     +      10X,'NO. OF FIELDS PER CREW',            T41,I3     /
     +      10X,'NO. OF DAYS TO COMPLETE FIELD',     T41,I3     /
     +      10X,'NO. OF HOURS WORKED PER DAY',       T40,F10.5 /
     +      10X,'TIME OF RE-ENTRY INTO FIELDS',      T40,F10.5 /
     +      10X,'INPUT VALUE FOR DSEED',             T60,E13.7 /
     +      10X,'LD50 FOR PARENT',                   T40,F10.5 /
     +      10X,'MEAN RESIDUAL VALUE',               T60,F10.5 /
     +      10X,'GEOMETRIC DEVIATION FOR RESIDUAL VALUE',T60,F10.5)
c
c     notation and documentation of arrays
c     i.  for crew i, member j
c            p  (i,j)  per cent regeneration
c            p1 (i,j)  per cent reversion
c            rkd(i,j)
c            rke(i,j)
c            wt (i,j)
c
c     ii.  for crew i, member j, day 1 (field k)
c            del(i,j,1)  represents the percent of enzyme activity inhibited
```

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```
c                          after one dose
c           kk (i,j,1)   ratio of active enzyme after 1 dose = 1- del(i,j,k)
c           h  (i,j,1)   health (ratio to initial of enzyme remeaining after
c                          the kth dose)
c           hl (i,j,1)   ratio of enzyme after recovery of 1-1 doses
c                          and therefore also the ratio before the lth dose
c                          and health at beginning of the kth day
c
c    iii. for coefficients of residue equation
c           cf(n,k)  n coefficients for the k fields worked per crew
c           r (i,1)  is residue to parent (i=1) or oxon (i=no. oxon+1)
c                    for day 1
c
c      get characteristics for each individual from using either a
c      lognormal or normal random no generator (imsl routine)
c
c      get random values for wt, and ke using the normal dist., imsl ggmnl
c
c
        DO 500 I=1,NC
            CALL LGNM (DSEED,NM,RMP, SDP, RP)
            CALL LGNM (DSEED,NM,RMP1,SDP1,RP1)
            CALL LGNM (DSEED,NM,RMKD,SDKD,RKD)
            CALL GGNML(DSEED,NM,RWT)
            CALL GGNML(DSEED,NM,RKE)
c
c      now assign each member of field a random no. chosen above
c
            DO 400 J = 1,NM
                KD(I,J) = RKD(J)
                KE(I,J) = RKE(J)*SDKE+RMKE
                WT(I,J) = RWT(J)*SDWT+RMWT
                P (I,J) = RP (J)
                P1(I,J) = RP1(J)
400            CONTINUE
500        CONTINUE
c
c      for each crew member get the ratio of the percent of active
c      enzyme to the initial amount of active enzyme after nf fields
c      have been harvested.
c
c      parameters used here
c
c      h(i,j,1) fraction of depleted enzyme after 1 days (in kth field)
c         for crew i,member j, field 1 (health after 1 days in kth field)
c      hl(i,j,1) fraction of active enzyme 24 hours after the lth dose
c         or the fraction of active to start the (1+1)th day (kth field)
c         for crew i, member j, 1 days in field k
c
c      set health for initial to 1  (i.e. hli,j,1)=1 for all i,j)
        DO 700 I = 1,NC
            DO 710 J = 1,NM
                H1(I,J,1) = 1
710            CONTINUE
700        CONTINUE
```

```
c
c      print table discribing events
c
       DO 1000 I = 1,NC
           WRITE (LUN,1001) I
           WRITE (LUN,1010) (WT(I,J),J=1,NM)
           WRITE (LUN,1020) (KE(I,J),J=1,NM)
           WRITE (LUN,1030) (KD(I,J),J=1,NM)
           WRITE (LUN,1040) (P(I,J),J=1,NM)
           WRITE (LUN,1050) (P1(I,J),J=1,NM)
 1001 FORMAT(1X ,////,' RESULTS OF ANALYSIS FOR CREW ',I3,
      +                ' WHERE H=FRACTION OF ENZYME INHIBITED',//
      + 5X,            ' FIELD CONDITIONS',T28,'CREW MEMBERS'/
      + T33, '1',T42, '2',T52, '3',T62 ,'4',T72, '5',T82, '6',T92, '7',
      + T102,'8',T112,'9',T122,'10' // )
 1010 FORMAT(T28,'WT=', F6.2,T41,F6.2,  8(4X,F6.2))
 1020 FORMAT(T28,'KE=', F7.3,T41,F7.3,  8(3X,F7.3))
 1030 FORMAT(T28,'KD=', F7.3,T41,F7.3,  8(3X,F7.3))
 1040 FORMAT(T28,' P=', F9.5,T41,F9.5,  8(1X,F9.5))
 1050 FORMAT(T28,'P1=', F9.5,T41,F9.5,  8(1X,F9.5))


           DO 850 K = 1,NF
               NIII = 50
               CALL LGNM (DSEED,NIII,RESSS,REGED,RAA)
               IF (RAA(1).GE.RESSS) FPER=3
               IF (RAA(1).LT.RESSS) FPER=2


               DO 777 L = 1,ND
c      calculate dose for each residue (from parent and oxon)
c      note r(mm,1) is residue for 1th day for parent(mm=1) or
c                            oxon number mm-1
c
c      determine residue for each of parent and oxons
                   DO 803 MM = 1,1
                       IDDD    = L*5+MM
                       R(MM,L) = RAA(IDDD)
                       IF (L.EQ.3) R(MM,L)=R(MM,2)*EXP(-0.074)
                       IF (L.EQ.4.AND.FPER.EQ.3) R(MM,L)=R(MM,2)*EXP(-0.148)
                       IF (L.EQ.5.AND.FPER.EQ.2) R(MM,L)=R(MM,4)*EXP(-0.074)
                       IF (L.EQ.6.AND.FPER.EQ.2) R(MM,L)=R(MM,4)*EXP(-0.148)
                       IF (L.EQ.6.AND.FPER.EQ.3) R(MM,L)=R(MM,5)*EXP(-0.074)
                       IF (L.EQ.1) R(MM,L) = 0.
                       IF (L.EQ.7) R(MM,L) = 0.
 803               CONTINUE

                   DO 800 J = 1,NM
                   SUM = 0
                   DO 801 MM = 1,1
                       D   = (KD(I,J)*R(MM,L)*TW)/(WT(I,J)*1000.)
                       SUM = (D/LD50(MM))+SUM
 801               CONTINUE
                   DEL(I,J,L) = 1-EXP(-KE(I,J)*SUM)
                   KK(I,J,L)  = 1-DEL(I,J,L)
                   H(I,J,L)   = KK(I,J,L)*H1(I,J,L)
                   P2         = 1.-P(I,J)/2.
```

```
            P3          = 1.+P(I,J)/2.
            R1          = H(I,J,L)*P2
            R2          = P1(I,J)*DEL(I,J,L)
            TOP         = R1+R2+P(I,J)
            H1(I,J,L+1)= TOP/P3
            H(I,J,L)    = 1.-H(I,J,L)
            HE(J)       = H1(I,J,L+1)
800         CONTINUE

            SUMH    = 0.
            SUMH2   = 0.
            DO 802 J = 1,NM
                SUMH    = SUMH+H(I,J,L)
                SUMH2 = SUMH2+H(I,J,L)*H(I,J,L)
802         CONTINUE
            HM(I,L)  = SUMH/NM
            HSD(I,L) = ((SUMH2-HM(I,L)*SUMH)/(NM-1))**0.5
            WRITE (LUN,1060)K,L,R(1,L),(H(I,J,L),J=1,NM),
     +                      HM(I,L),HSD(I,L)

1060        FORMAT(1X,'W',I3,'D',I3,T11,'RESIDUE=',F8.3,T28,'H=',
     +             F6.4,T37,F6.4,12(1X,F6.4))
777         CONTINUE
          DO 888 J = 1,NM
            H1(I,J,1) = HE(J)
888         CONTINUE
850       CONTINUE
1000    CONTINUE
      END

      SUBROUTINE LGNM(DSEED,NF,A,B,X)
      DOUBLE PRECISION DSEED
      DIMENSION X(301)
      S  = ALOG(B)
      XM = ALOG(A)
      CALL GGNLG(DSEED,NF,XM,S,X)
      RETURN
      END

//GO.FT04F001 DD DSN=WYL.CMD.SIM.AAA,UNIT=DISK,VOL=SER=WYLB02,
// DCB=(RECFM=FB,LRECL=133,BLKSIZE=6118),
// SPACE=(TRK,(27,2)),DISP=(NEW,CATLG)
//GO.FT01F001 DD *
 0.0089286    1.0457    0.15000    1.01000
    5.10000    1.41000    6.00000    1.30000
   70.00000    7.00000
026
018
012
    7.00000
    8.00000
   10.00000
007
 119.00000    2.00000
3857100000
```

Appendix B: Listing of the simulation program run on the IBM-PC with   454
         MicroSoft Fortran compiler. Lines following the last "end" are
         a separate input file called "simlib" .

```
        program sim5
c       unified field model simulation program , "version 5.2" [23 Jul 86]
c       comprising submodels 2-3 with variability in the H measurement added
c           submodel 1: R   = Ro exp(-Kr T)
c           submodel 2: D   = R Kd t / m
c           submodel 3: del = 1 - exp(Ke sum(D / LD50))
c       therefore        R  = -LD50 ln(1 - del) m / Kd Ke t
c       This version groups and prints (with no option) all crews by day to
c           facilitate operation of summary program pp5, and staggers the working
c           pattern experienced by each crew.

c   batch file input for this simulation program in a file to-be-named:
c
c   i.  input the field residue conditions: mean daily inhibition,
c       geometric deviation of that residue, and short-term decay rate:
c           1. percent daily inhibition "delbar"                    (f10.2)
c           2. geometric deviation of the residue "gdres"           (f10.2)
c           3. half-life [days] of residue during harvest "half"    (f10.2)
c           4. AChE measurement (interday intraperson) variability  (f10.2)
c   ii. means and sd of worker parameters:
c           5. gmp, regeneration of rbc and their enzymes, usually 1-2%
c               gmpp, reversion of rbc, usually 0-15%:
c               "gmp","gdp","gmpp","gdpp"                            (4f10.5)
c           6. kd dose coefficient, ke enzyme coefficient:
c               "gmkd","gdkd","gmke","gdke"                          (4f10.5)
c           7. arithmatic mean and standard deviation of mass of worker:
c               "rmwt","sdwt"                                        (2f10.5)
c   iii. parameters determing field exposure
c           8. nw    = number of weeks worked per crew:              (i3)
c           9. nc    = number of crews to be placed in fields:       (i3)
c           10. nm   = number of members per crew:                   (20i3)
c           11. dpa  = time (days) of initial re-entry into
c                       each field after (post) spraying:            (i3)
c           12. hwpd = time (hours) worked per day :                 (i3)
c           13. nd   = number of days to complete each field
c                       (a repeatable pattern of from 1-10 values
c                         ending in 0; any negative values are accepted
c                         as specifying days with no additional exposure): (10i3)
c           14. ld50 = LD50 for parent (and each of up to 3 oxons):  (4f10.5)
c   iv.  other input variables
c           14. iseed = three integer values (1-2147483647)
c                       to be used to generate random numbers:       (3i10)

c   to input and output data to and from this program:
c       1) the program will ask the user the name of the file which has
c           data for input (assigned as file 1);
c       2) the program asks the user if output is to be written on the
c           termianal or to be saved as an output file;
c       3) the file number and name are then given by the user.
c           If user enters 0 then the terminal receives the output;
c           If  "       "    1 and a file name, health only output is saved f6.4
```

```
c          If  "      "  2 and a file name, more complete output is saved f5.3

         character*14 input,output
         integer    . iseed(3),nd(10),dpa,hwpd,file1,file2,
       +              ipat(18),ires(18),m(18),noff(18)
          real       res(2000),    r(4),ld50(4),
       +              p(18,12),pp(18,12),wt(18,12),kd(18,12),ke(18,12),
       +              rp(216), rpp(216), rwt(216), rkd(216), rke(216),
   .   +              kk(18,12), h(18,12),hl(18,12)

         file1  = 1
         file2  = 2
c        indicate the name of the file to find input data
         write  (*,101)
   101 format (' Enter name of input file :  ' )
         read   (*,102) input
   102 format (a)
c        indicate the name of the file to receive the worker health output.
*        write  (*,103)
* 103 format(' Enter either 0 for the output to return to the terminal',
*     + /,8x,' or 1 if health status  only  is to be saved as a file',
*     + /,8x,' or 2 if more complete output is to be saved as a file:')
*        read   (*,104) lun
         lun    = 1
   104 format (i1)
         if     (lun .eq. 0) go to 106
         write  (*,105)
   105 format (' Enter the name of the health status output file : ' )
         read   (*,102) output
         open   (file2,file=output,status='new')
         rewind  file2
   106 open   (file1,file=input)
         rewind  file1


c        read average daily inhibition, its variability, and
c        the within field residue decay rate (half life);
c        followed by other means and deviations
c        (geometric for lognormal distributions p, pp, kd, ke, and (arith) wt);
c        and finally other input parameters describing field.
         nr     = 1
         mnp    = 10
         read  (1,10) delbar,gdres,half, gdlab
         read  (1,10) gmp,   gdp,  gmpp, gdpp
         read  (1,10) gmkd, gdkd,  gmke, gdke
         read  (1,10) rmwt, sdwt
         read  (1,25) nw
         read  (1,25) nc
         read  (1,30) nm
         read  (1,25) dpa
         read  (1,25) hwpd
         read  (1,30) nd
         read  (1,10) (ld50(nres),nres=1,nr)
         read  (1,45) iseed
    10 format(4f10.5)
    25 format(i3)
```

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```
   30 format(20i3)
   40 format(f10.0)
   45 format(4i10)

      npp   = 0  ·
      ndinp = 0
      do 50 i = 1,mnp
         ndinp = ndinp + abs(nd(i))
         if    (nd(i) .gt. 0) npp = npp + 1
         if    (nd(i) .eq. 0) go to 51
   50    continue
   51 np    = i-1
      nf    = nc * (npp * (nw * 5) / ndinp)
      npop  = nm * nc
*     nlab  = npop * (nw * 7)
      gmres = -ld50(1)*alog(1.-(delbar/100.))*rmwt / (gmke*gmkd*hwpd)
      if    (gdlab .le. 1.0) gdlab = 1.0
      do 53 i = 1,nc
         ipat(i) = mod(i,np) + 1
         ires(i) = i
         m(i)    = 1
         noff(i) = 0
   53    continue
c     internal variables defined above:
c     mnp   = maximum number of "within field harvest" patterns.
c     nd    = (array) repeatable pattern of the number of days to complete
c             each field.  Note nd<0 means to work in field with no anti-AChE
c             residues; weekends (iday = 6 and 7) are also no-exposure days.
c     np    = number of patterns specified by user.
c     npp   = number of positive pattterns (fields with residues) per cycle.
c     ndinp = total number of working days within all patterns.
c     nf    = total number of fields required to be simulated.
c     npop  = total size of population (cohort) required to be simulated.
c     ires  = (array) residue (or field) counter stepping res() up to nf.
c     nlab  = number of simulated laboratory measurements (assumed to be each
c             day of season) and associated measurement variations.
c     noff  = (array) number of weekend days (off) during which residue decays
c     gmres = geom. mean residue corresponding to the mean delta AChE specified

c     get characteristics for each individual in population and
c     field in the entire season by using
c     either a lognormal or normal random number generator (subroutine) :
  500 write (*,*) 'Creating body weights'
      call   nml   (iseed,npop,rwt,rmwt,sdwt)
      write (*,*) 'Creating dosing coefficients'
      call   lgnml (iseed,npop,rkd,gmkd,gdkd)
      write (*,*) 'Creating enzyme coefficients'
      call   lgnml (iseed,npop,rke,gmke,gdke)
      write (*,*) 'Creating RBC regeneration rates'
      call   lgnml (iseed,npop,rp ,gmp ,gdp )
      write (*,*) 'Creating RBC reversion rates'
      call   lgnml (iseed,npop,rpp,gmpp,gdpp)
      write (*,*) 'Creating residues'
      call   lgnml (iseed,nf,res, gmres,gdres)
```

```
              if    (lun .eq. 0) go to 600
              write (*,*) 'Beginning simulation:'
              write (*,*) 'Day    of    Crew    Residue    of'
c
c   notation and documentation of subsequent arrays
c     for crew i, member j (day k in season, day m(i) in field)
c       p  (i,j) = per cent regeneration / 100.
c       pp (i,j) = per cent reversion  / 100.
c       rkd(i,j) = dosing coefficient
c       rke(i,j) = enzyme response coefficient
c       wt (i,j) = body weight (mass)
c
c       kk (i,j) = enzyme activity after any one dose = 1- del(j),
c                  relative to pre-dose activity
c       h  (i,j) = health (enzyme activity remaining after the kth dose
c                  relative to initial activity)
c       hl (i,j) = relative enzyme activity after 24-hr recovery of kth dose
c                  and therefore also the pre-dose activity before the k+1th
c                  dose
  600 CONTINUE
      k    = 0
      do 1000 iwk = 1,nw                                        WEEKS

c         A "pattern" do loop could not be constrained either internal to
c         or external from the week loop (used to define weekends off).
c         Thus, each new ipat is set prior to line 870 to another field
c         (ires) whose initial reentry residue (day m-1 in the field) is
c         selected from the random array of nf residues created earlier
c         but which also undergoes decay after each (m) harvest-working
c         day in that field plus any intervening (noff) days off at the
c         half-life specified until the harvest has been completed
c         (m = number of days in nd(ipat(i))).

          do 880 iday = 1,7                                     DAYS
              k  = k + 1
              do 870 i = 1,nc                                   CREWS
                  if ((iday .eq. 6).or.(iday .eq. 7)) noff(i) = noff(i) + 1
*                 if (lun .eq. 0) go to 630
                  write (*,1065) k,nw*7,i,ires(i),nf
  630             do 800 j = 1,nm                               MEMBERS
                      if ((iwk  .ne. 1) .or. (iday .ne. 1)) go to 700
                      wt(i,j) = rwt(((i-1)*nm)+j)
                      kd(i,j) = rkd(((i-1)*nm)+j)
                      ke(i,j) = rke(((i-1)*nm)+j)
                      p (i,j) =  rp(((i-1)*nm)+j)
                      pp(i,j) = rpp(((i-1)*nm)+j)
c                     set initial health to 1  (i.e. hl(i,j) = 1 for each j)
                      hl(i,j) = 1.
  700                 sum     = 0.0
                      if      ((iday .eq. 6) .or. (iday .eq. 7)) go to 702
                      if      (nd(ipat(i)) .lt. 0) go to 702
                      r(1)    = res(ires(i)) / (2.**((m(i)+noff(i)-1)/half))
                      do 701 mm = 1,nr                          CHEMRES
                          d       = (kd(i,j)*r(mm)*hwpd) / wt(i,j)
                          sum     = (d/ld50(mm)) + sum
```

```
701                     continue
702                     kk(i,j) = exp(-ke(i,j)*sum)
                        h(i,j)  = kk(i,j) * hl(i,j)
                        p2      = 1. - p(i,j)/2.
                        p3      = 1. + p(i,j)/2.
                        hl(i,j) = ((h(i,j)*p2)+(pp(i,j)*(1.-kk(i,j)))+p(i,j))
      +                               / p3
c                       process validation print test
*                       write (*,739) k,i,j,m(i),nd(ipat(i))
*     6                 ,ipat(i),noff(i),ires(i),res(ires(i))
*     6                 ,r(1),d,sum,kk(i,j),h(i,j),hl(i,j)
*     6                 ,p2,p3,p(i,j),pp(i,j),wt(i,j)
*     6                 ,kd(i,j),ke(i,j)
*739                    format(/1x
*     6                 ,'day,cr#,mem#,m,nd(i),i,,noff,ires =',/1x,8i3,/1x
*     6                 ,'res,r(1),d,sum,kk,h,hl ='          ,/1x,7f11.7,/1x
*     6                 ,'p2,p3,p,pp,wt,kd,ke ='             ,/1x,7f11.7)
c                       end print test

c                       an expected level of laboratory AChE measurement variability
c                       has been integrated into version 4 and later updates, which
c                       affects output via "h" but not the actual health via "hl".
                        vlab    = gauinv(random(iseed),ifault)
                        if     (ifault .eq. 1) stop 'ifault error in lab var.'
                        h(i,j)  = 1. - (h(i,j)*(gdlab**vlab))
800                     continue
* 820           if     (lun .eq. 1) go to 821
*               write (lun,   1060) i,iwk,iday,r(1),(h(j),j=1,nm)
*               go to 830
  821           write (file2,1061) i,iwk,iday,r(1),(h(i,j),j=1,nm)
  830           if     ((iday .eq. 6) .or. (iday .eq. 7)) go to 870
                m(i)     = m(i) + 1
                if     (m(i) .le. abs(nd(ipat(i))))       go to 870
                ipat(i) = ipat(i) + 1
                if     (nd(ipat(i)) .lt. 0)               go to 870
                if     ((ires(i)+nc) .le. nf) ires(i) = ires(i) + nc
                m(i)     = 1
                noff(i) = 0
                if     (ipat(i) .gt. np) ipat(i) = 1
  870           continue
  880        continue
 1000     continue
c     print residue and toxicologic means and deviations
c     followed by other parameters describing field
      write (file2,1054) rmwt,sdwt,gmkd,gdkd,gmke,gdke,
     +                   gmp,gdp,gmpp,gdpp,delbar,gdlab,gmres,gdres
      write (file2,1055) nm,nc,npop,nw,nf,nd,hwpd,half,(ld50(i),i=1,3),
     +                   iseed
c     print individual crew descriptors unless the condensed
c     output file (lun=1) was requested.
      if (lun .eq. 1)  go to 2000
      do 1100 i = 1,nc
          write (file2,1001) i, (j, j=1,nm)
          write (file2,1010) (wt(i,j),j=1,nm)
          write (file2,1020) (ke(i,j),j=1,nm)
```

```
      write (file2,1030) (kd(i,j),j=1,nm)
      write (file2,1040) ( p(i,j),j=1,nm)
      write (file2,1050) (pp(i,j),j=1,nm)
1100 continue
2000 stop ' Normal termination of Sim5'

c --- THE LAST PORTION OF THIS PROGRAM SPACE IS RESERVED FOR FORMAT STATEMENTS
1054 format(1x,/,1x,' Means and deviations given on input'/
    +   7x,'for normally distributed variables:'/
    +  10x,'workers weight',                    t45,2f10.5/
    +   7x,'for lognormally distributed variables: '   /
    +  10x,'dosing coefficient kd',             t45,2f10.5/
    +  10x,'enzyme coefficient ke',             t45,2f10.5/
    +  10x,'regeneration, p',                   t45,2f10.5/
    +  10x,'reversion, pp',                     t45,2f10.5/
    +  10x,'mean daily inhibition, Z',          t45,1f10.5/
    +  10x,'variability in AChE measurement',t55,1f10.5/
    +  10x,'reentry residue, ug/cm2',           t45,2f10.5)
1055 format(1x,' Other parameters given on input:',    /
    +  10x,'number of members per crew ',   t46,i3    /
    +  10x,'number of crews',               t46,i3    /
    +  10x,'total size of population    ',  t46,i3    /
    +  10x,'no. of weeks worked per crew',  t46,i3    /
    +  10x,'total no. of fields sprayed',   t39,i10   /
    +  10x,'no. of days to complete field', t46,10i3  /
    +  10x,'no. of hours worked per day',   t46,i3    /
    +  10x,'subsequent half-life, days',    t45, f10.5/
    +  10x,'LD50 for OP pesticide(s)',      t45,3f10.5/
    +  10x,'input values for iseed',        t39,3i10  )
1001 format(1x ,//1x,
    +'Fraction Acetyl Cholinesterase inhibition for crew ',i3,
    +/1x,'Field conditions:',t22,'Crew members:',
    +/,t22,36(i2,3x) )
1010 format( t18,'wt=',   36(f5.1,0x))
1020 format( t18,'ke=',   36(f5.2,0x))
1030 format( t18,'kd=',   36(f5.2,0x))
1040 format( t18,'p =',   36(f5.4,0x))
1050 format( t18,'pp=',   36(f5.4,0x))
1060 format('C',i2,'W',i2,'D',i1,t10,'R=', f6.4,t19,'H=',14(f5.3,0x))
1061 format('C',i2,'W',i2,'D',i1,t10,'R=', f6.4,t19,'H=',14(f6.4,1x))
1065 format('+Day',i4,' of',i4,' Crew',i3,'  Residue',i5,' of',i5)
     end
C-------------------------------------------------------------------------
     subroutine nml (iseed,nx,x,a,b)
     dimension  iseed(3),x(2000)
     s    = b
     xm   = a
     call mcarlo(iseed,nx,x,xm,s)
     return
     end
C-------------------------------------------------------------------------
     subroutine lgnml (iseed,nx,x,a,b)
     dimension  iseed(3),x(2000)
     s    = alog(b)
     xm   = alog(a)
```

```
      call mcarlo(iseed,nx,x,xm,s)
      do 1 i = 1,nx
         x(i) = exp(x(i))
   1     continue
      return
      end
C--------------------------------------------------------------------------
      subroutine mcarlo (iseed,nx,x,a,b)
c     creates a random sequence of 'nx' values of 'x' which taken as a whole
c     are EXACTLY normally distributed between 0 and 1 in steps of 1/nx
c     (see line 001 taken from U.S. HEW (NIOSH) Publ. #77-173)
      real      x(2000),  y(2000)
      integer   iseed(3),iy(2000)

      do 10 i = 1,nx
         y(i) = random(iseed)
  10     continue
      call    rankc (nx,y,iy)
      do 20 i = 1,nx
 001     p    = (float(i) - 0.5) / nx
         y(i) = gauinv(p,ifault)
         if    (ifault .eq. 0) go to 20
         write (*,1001) i,a,b
         stop 'Due to fault error in INVGAU from MCARLO'
  20     continue
      do 30 i = 1,nx
         x(i) = a + (b*y(iy(i)))
  30     continue
      return
 1001 format  (' A fault error resulted when processing the ',i5,
     +      'th value with mean of ',g12.4,' and deviation of ',g12.4)
 1002 format  (' A no-match error resulted when searching for "min"'
     +          ,/,' of ',i5,' values with mean of ',g12.4,
     +              ' and deviation of ',g12.4)
      end
C--------------------------------------------------------------------------
      FUNCTION RANDOM(iseed)
*      FUNCTION RANDOM(IX,IY,IZ)

C     ALGORITHM AS 183 modified FROM B.A. WICHMANN and I.D. HILL
C     An Efficient and Portable Pseudo-random Number Generator.
C     APPL. STATIST. 31:188-190, 1982.
C     incorporating the amendment proposed by A.I. McLeod
C     APPL. STATIST. 34:198-200, 1985.

C     On input IX,IY,IZ are seed integers between 1 and 30,000
C     RETURNS A PSEUDO-RANDOM NUMBER RECTANGULARLY DISTRIBUTED
C     BETWEEN 0 AND 1.

C     INTEGER ARITHMATIC UP TO 30323 IS REQUIRED.

      INTEGER*4  iseed(3),IX,IY,IZ

      ix = iseed(1)
      iy = iseed(2)
```

```
          iz = iseed(3)

          IX = 171 * MOD(IX,177) -  2*(IX/177)
          IY = 172 * MOD(IY,176) - 35*(IY/176)
          IZ = 170 * MOD(IZ,178) - 63*(IZ/178)

          IF (IX .LT. 0) IX = IX + 30269
          IF (IY .LT. 0) IY = IY + 30307
          IF (IZ .LT. 0) IZ = IZ + 30323

C     IF INTEGER ARITHMATIC UP OT 5212632 IS AVAILABLE,
C     THE PRECEDING 6 STATEMENTS MAY BE REPLACED BY

*         IX = MOD(171 * IX, 30269)
*         IY = MOD(172 * IY, 30307)
*         IZ = MOD(170 * IZ, 30323)

C     ON SOME MACHINES THIS MAY SLIGHTLY INCREASE THE SPEED,
C     THE RESULTS WILL BE IDENTICAL.

          iseed(1)=ix
          iseed(2)=iy
          iseed(3)=iz
          RANDOM = AMOD(FLOAT(IX)/30269.+FLOAT(IY)/30307.+FLOAT(IZ)/30323.,
         +             1.0)
C     McLeod amendment follows:
          IF (RANDOM.GT.0.0) RETURN
          RANDOM = DMOD(DBLE(FLOAT(IX))/30269.D0 + DBLE(FLOAT(IY))/30307.D0
         +              + DBLE(FLOAT(IZ))/30323.0D0,1.0D0)
          IF (RANDOM.GE.1.0) RANDOM = 0.999999
          RETURN
          END
C-------------------------------------------------------------------
          FUNCTION GAUINV (P, IFAULT)

C     ALGORITHM modified FROM R.E. ODEH and J.O. EVANS
C     The Percentage Points of the Normal Distribution. AS 70
C     APPL. STATIST. 23:96-97, 1974.

C     Note the additional following reference provides a polynomial
C          for (0.8 .le. p .lt. infinity) if needed:
C     M.E. Tarter:
C     Inverse Cumulative Approximation and Applications.
C     Biometrika 55:29-41, 1968.
C     See also AS 111, APPL. STATIST. 26:118-121, 1977 for an alternative form.

C     AS 70 was originally called GAUINV:
C     GAUINV FINDS PERCENTAGE POINTS OF THE NORMAL DISTRIBUTION
C        P on input is the lower tail area p
C        IFAULT is a fault indicator :
C          " = 1 and gauinv = 0 if (E-20 .le. p .le. 1.- E-20)
C               (ERROR: the requrested x exceeds the outer limits of p
C                        for which the inverse is accurate to within E-7)
C          " = 0 and gauinv = 0 if (p .eq. 0.5)
C               (the true value but not calculable from the polynomial)
```

```
C          " = 0 in all other cases.

      DATA         P0,    P1,            P2,              P3
     + /-.322232431088, -1.0, -.342242088547, -.204231210245E-1/
      DATA         P4,            Q0,          Q1
     + /-.453642210148E-4, .993484626060E-1, .588581570495/
      DATA         Q2,            Q3,          Q4
     + / .531103462366, .103537752850, .38560700634E-2/


      IFAULT = 1
      GAUINV = 0.0
      PS     = P
      IF     (P .GT. 0.5)      PS = 1. - PS
      IF     (PS .LT. 1.0E-20) RETURN
      IFAULT = 0
      IF     (PS .EQ. 0.5)     RETURN
      YI     = SQRT(ALOG(1./(PS*PS)))
      GAUINV = YI + ((((YI*P4+P3) *YI+P2) *YI+P1) *YI+P0)
     +            / ((((YI*Q4+Q3) *YI+Q2) *YI+Q1) *YI+Q0)
      IF     (P .LT. 0.5)      GAUINV = -GAUINV
      RETURN
      END
C----------------------------------------------------------------------
      subroutine rankc (nx,x,ix)
      dimension x(2000),ix(2000)


      do 1 i = 1,nx
         ix(i) = 0
 1    continue
      do 3 j = 1,nx
         ilast = 2000
         xmin  = 10.**30
         do 2 i = 1,nx
            if ((x(i) .lt. xmin) .and. (ix(i) .eq. 0)) then
            ix(ilast) = 0
            xmin      = x(i)
            ix(i)     = j
            ilast     = i
            end if
 2       continue
 3    continue
      return
      end
```

```
Input file, typically called simlib:
     4.00      3.00      7.00      1.0 >delbar,gdres,half,gdlab
   .0089286   1.0457      .15      1.01>gmp (regen.),gdp,gmpp (revers.),gdpp
     5.10      1.41      6.00      1.30>kd,gdkd,ke,gdke
     70.       7.                     >wt,sdwt
  26>nw eeks
  18>nc rews
  12                          >nm embers per crew
  14>dpa (days post-application)
```

```
8>hwpd (hours worked per day)
2 -3  3 -2                      >nd (pattern of number of days in each field)
   10.00                        >LD50
      25784       985    12919  >iseed
```

Appendix C: Listing of the daily health status analysis and summary program
written to be run on an IBM-PC with Microsoft Fortran compiler.
Lines following last "end" are an external input file typically
called "pplib" .

    Program PP2
C   PhaseII Program 2, Version 5
C   to read simulation (SIM5) output option #1 files;
C   (1) scan daily through all crews for "illness" using four
C   threshold criteria as specified in a separate "pplib" file,
C   (2) tabulate and calculate daily summary health statististics, and
C   (3) conduct analysis of variance among crews for health status
C   in both arithmatic and geometric modes, optional to do
C   every day or only on each clinic day of each week (see inclin)

C   Defined variable list follows:
*   CPOI   counter for poisoning cases within day (see also fpoi and inpoi)
*   DEL   delta AChE
*   F   F test statistic for arithmatic distribution
*   FILE0   assigned file: keyboard and screen
*   FILE1   "   "   : input data
*   FILE2   "   "   : output of analysis of variance
*   FILE3   "   "   : input library of run parameters (pplib)
*   FILE4   unused
*   FPOI   counter for fields in which poisoning cases occurred
*   G   F test statistic for geometric distribution
*   GD   geometric deviation for group
*   GM   geometric mean for group
*   GX   log-transformed values of x
*   H   health (enzyme activity) = 1-x
*   I   index for days
*   IDAY   day of week within input sequence
*   II   "del" counter
*   IWK   week within input sequence
*   INCLIN (from pplib) day of the week crews are in clinic for "h" samples
*   INPOI   counter for incidents of poisoning (defined as .gt. 1/2 of crew)
*   INPUT   character name of input file
*   J   index for crew
*   K   index for person within crew
*   LINE   line of narrative text; a maximum of 79 characters
*   M   index for running cumulative days, equivalent to nthres
*   N1   degrees of freedom for numerator   of arithmatic F
*   N2   degrees of freedom for denominator of arithmatic F
*   N3   degrees of freedom for numerator   of geometric F
*   N4   degrees of freedom for denominator of geometric F
*   NCREW   crew number as listed within data
*   NCREWS (from pplib) number of crews included within the study design
*   NDAY0   (from pplib) day of the programmed "week" exposure starts
*   NDAYS   total number of days in study = nwks*7
*   NG   overall number of geometric data points
*   NLINE1 (from pplib) number of narrative lines to be copied at end
*   of input file
*   NLINE2 (from pplib) number of narrative lines to be skipped at end
*   of input file
*   NN   overall number of arithmatic data points

```
*      NPERC  (from pplib) number of people per crew
*      NTHRES (from pplib)
*      NWKS   (from pplib) number of weeks in study
*      NX
*      OAM    overall arithmatic mean
*      OGM    overall geometric  mean
*      OUTP2  character name of anova output file = file2
*      PDAY   integer number of previous days within study (max=nthres)
*      PGD    pooled geometric deviation
*      PINC   counter for poisoning cases within a crew-day (see also cpoi)
*      PSD    pooled arithmatic deviation
*      RES    residue for each exposure day (not manipulated)
*      S2SG   (see anov)
*      S2SX   (see anov)
*      SD     standard deviation for group (array)         )
*      SIMAN  external library of program run parameters
*      SSG    (see anov)
*      SSG2   (see anov)
*      SSX    (see anov)
*      SSX2   (see anov)
*      TCPOI  counter for seasonal total cases of poisoning within each category
*      THRES  (from pplib) quantitative poisoning criteria for 1-AChE (see
*             "Parameters from pplib" description below)
*      X      level of inhibition (read from input)
*      XM     arithmatic mean for group (array)


       character*14 input,outp2
       character*79 line
       dimension    h(4,18,12),x(12),gx(12),thres(4)
       dimension    xm(18), sd(18),gm(18), gd(18)
       integer      file0,file1,file2,file3,day,pday
       integer      cpoi(4),fpoi(4),inpoi(4),tcpoi(4),pinc(4)
       logical      negx

C>>>>>   INPUT FORMAT FROM SIM5 option 1
 1000 format (a79)
 1001 format (4x,i2,1x,i1, 3x,f6.4,3x,14(f6.4,1x))
*     +      ,(/,20x,14(f6.4,1x)),(/,20x,14(f6.4,1x)))
C 1W-1D1 R= .1986 H= .0817  .0781 -.0195  .0429  .2360  .1964  .1505  .0969  .304

C>>>>>

       file0 = 0                                                    user
       file1 = 1                                                    input
       file2 = 2                                                    output
       file3 = 3                                                    pplib
       file4 = 4                                                    unused

C.... ask for and read the name of input and output files.
  100 continue
       write (file0,1005)
       read  (file0,1004) input
       if    ((input .eq. 'quit').or.(input .eq. 'exit').or.
      +      (input .eq. 'stop').or.(input .eq. 'end')) go to 999
       write (file0,1007)
       read  (file0,1004) outp2
```

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```
      open    (file1, file=input)
      rewind  file1
      open    (file2, file=outp2, status='new')
      rewind  file2
      open    (file3, file='pplib')
      rewind  file3
      write   (file0,1009) input,outp2

C....  READ the operating PARAMETERS FROM PPLIB (file3)
C      ncrews = number of crews included within the study design;
C      nperc  = number of people per crew;
C      nwks   = total number of weeks expected to be read from "input";
C      nday0  = day of the week exposure starts, assuming 1 equals Monday;
C      inclin = day of the week blood samples are taken in the clinic (0=all);
C      thres  = criteria for 1-AChE ( or x(k) within this program) at
C               which person i considered "overexposed".  Criteria are
C               initially set based on    Daily Inhibition
C                        Simple      day 1 .5      .4      .35
C                        Cumulative  day 2 .75     .64     .58
C                        Effect      day 3 .875    .78     .725
C               therefore, respective values of thres in array
C               (1) a single daily inhibition, x .ge. 0.5
C               (2) a 2-day cumulative   "    , x .ge. 0.65
C               (3) a 3-day       "      "    , x .ge. 0.75
C               (4) a cumulative reduction in h below 0.5
C                m subscript used
C                to store h        and    to calculate del h
C                1: today's h               single daily inhibition (h2-h1/h2),
C                2: yesterday's h           2-day cumulative   "    (h3-h1/h3),
C                3: two day's ago h         3-day       "      "    (h4-h1/h4),
C                4: three day's ago h       cumulative reduction in h
C      nline1 = number of narrative lines to be copied at end of file (input)
C      nline2 = number of crew narrative lines to be skipped

      read    (file3,3001) ncrews,nperc,nwks,nday0,inclin,nthres,thres
     +                     ,nline1,nline2,nline3

C      type input parameters, output table, and screen headers
      write   (file2,3001) ncrews,nperc,nwks,nday0,inclin,nthres,thres
     +                     ,nline1,nline2,nline3
      write (file2,2002) 'Wk','Day','OAM','PSD','F','n1','n2','OGM',
     +                   'PGD','G','n3','n4','po1','po2','po3','po4'
      write (file2,2002) '--','---','---','---','-','--','--','---',
     +                   '---','-','--','--','---','---','---','---'
      write (*,*) 'now on crew#    and day    of'

C....  set health array (m,j,k) equal to 1.0 (each individual's "normal")
C      subscript i = day within study (season)        limit : ndays = nwks*7
C                j = crew                                      ncrews
C                k = person within crew                        nperc
C                m = running day (1 = today, 2 = yesterday, etc) nthres
      do 152 j = 1,ncrews
         do 151 k = 1,nperc
            do 150 i = 1,nthres
               h(i,j,k) = 1.0
```

```
150        continue
151      continue
152    continue
       do 153 m = 1,nthres
         fpoi(m)  = 0
         tcpoi(m) = 0
         inpoi(m) = 0
153    continue


C - - Begin daily analysis of all crews: - - - - - - - - - - - - - - - - -
       iday    = 7
       ndays   = nwks * iday
       do 450 i = 1,ndays                                          DAY >
         negx  = .false.
         iday  = iday + 1
         if   (iday .gt. 7) iday = 1
C        zero the poisoning cases for that day counter
210      do 215 m = 1,nthres
           cpoi(m)  = 0
215        continue
C        initialize anova arrays if anova is to be run for the day
         if   ((iday .ne. inclin)  .and. (inclin .ne. 0)) goto 220
         call  anov0 (ssx,ssx2,s2sx,nn,ngpn)
         call  anov0 (ssg,ssg2,s2sg,ng,ngpg)
C        day i for crew "j" read "k=1,nperc" daily health values
220      do 300 j = 1,ncrews                                       CREW >
           write (*,1111) j,i,ndays
222        read  (file1,1001,end=501) iwk,iday,res,(x(k),k=1,nperc)
*          write (*,    1001         ) iwk,iday,res,(x(k),k=1,nperc)
           do 223 m = 1,nthres
             pinc(m) = 0
223        continue
C          talley cases in 'Poisonings IN Crew' counter.
           do 6 k = 1,nperc                                        MEMB.>
             if (negx)      goto 1
             if (x(k) .le. 0.0) then
               negx = .true.
               goto 1
               endif
             gx(k)  = alog(x(k))
1            do 2 m = 1,nthres-1
               h(nthres-m+1,j,k) = h(nthres-m,j,k)
2            continue
3            h(1,j,k) = 1. - x(k)
             do 4 m = 1,nthres-1
               del = (h(m+1,j,k)-h(1,j,k))/h(m+1,j,k)
               if (del .gt. thres(m)) pinc(m) = pinc(m)+1
4            continue
5            del = (1. -      h(1,j,k))/1.
             if (del .ge. thres(nthres)) pinc(nthres) = pinc(nthres)+1
6            continue                                              <MEMB.
c          the next counters are used to talley daily cases within all crews,
c          fields(days) in which cases occured, and potentially reportable
c          "incidents" as defined by at least one-half of one crew exceeding
c          one of the poisoning criteria thresholds.
```

```
            do 7 m = 1,nthres
                cpoi(m) = cpoi(m) + pinc(m)
                if (pinc(m) .gt. 0) fpoi(m) = fpoi(m) + 1
                if (float(pinc(m))/nperc .ge. .5) inpoi(m) = inpoi(m) + 1
      7         continue
C           if desired (inclin .ne. 0) anova may be run only on clinic days
            if ((iday .ne. inclin) .and. (inclin .ne. 0)) goto 300
            call  anovl (x, nperc,xm,sd,ssx,ssx2,s2sx,nn,ngpn)
            if    (negx) goto 300
            call  anovl (gx,nperc,gm,gd,ssg,ssg2,s2sg,ng,ngpg)
  300       continue                                              <CREW
C....   line 300 ends the j do-loop for crews:
C       now tabulate anova and the number of poisoning incidents,
            if    ((iday .ne. inclin) .and. (inclin .ne. 0)) goto 350
            call  anov2 (ssx,ssx2,s2sx,nn,ngpn,oam,psd,f,n1,n2)
            if    (negx)  goto 325
            call  anov2 (ssg,ssg2,s2sg,ng,ngpg,ogm,pgd,g,n3,n4)
            ogm  = exp(ogm)
            pgd  = exp(pgd)
            write (file2,2003) iwk,iday,oam,psd,f,n1,n2,
     +                                  ogm,pgd,g,n3,n4,cpoi
            goto  400
  325       write (file2,2004) iwk,iday,oam,psd,f,n1,n2,cpoi
            goto  400
  350       write (file2,2005) iwk,iday,cpoi
  400       continue
            do 420 m = 1,nthres-1
                tcpoi(m) = tcpoi(m) + cpoi(m)
  420           continue
  450       continue                                              <DAY
C     line 450 ends the day do-loop

         write (file2,2006) (tcpoi(m),m=1,nthres-1),(fpoi(m),m=1,nthres-1),
     +                    (inpoi(m),m=1,nthres-1)
C     copy  nlinel narrative lines at end of input file
         do 500 nl = 1,nlinel
            read  (file1,1000,end=501) line
*           write (*,    1000         ) line
            write (file2,1000         ) line
  500       continue
*         GO TO 100
         go to 999

  501 stop 'Unexpected end of file encountered.'
  502 stop 'Apparent error in crew or line sequence.'
  503 stop 'Health .le. 0 error.'
  999 stop 'Normal termination of PP5'

 1004 format (a14)
 1005 format (' Type INPUT filename, up to 14 characters:')
 1007 format (/,' Type anova OUTPUT filename, up to 14 characters:')
 1009 format (/,' Now reading ',a14,' and writing file ',a14,'.....')
 1111 format ('+now on crew#',i3,' and day',i4,' of',i4)
 2002 format (1x,a2,1x,a3,4x,a3,6x,a3,5x,a1,3x,a2,2x,a2,5x,a3,5x,a3,
     +           6x,a1,4x,a2,2x,a2,1x,4(1x,a3))
```

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```
 2003 format (i3,i2,1x, 2(2x,2f8.5,2x,f5.2,i3,i4), 2x,4i4)
 2004 format (i3,i2,1x, 1(2x,2f8.5,2x,f5.2,i3,i4),34x,4i4)
 2005 format (i3,i2,1x, 2(32x                     ), 2x,4i4)
 2006 format (1x,//,39x,'Total number of poisoning cases: ', 3i4,/,
     +              36x,'Days on which a poisoning occurred: ',3i4,/,
     +              38x,'Potentially reportable incidents: ',3i4)
 3001 format (6i4,4f4.2,3i4)
      end
c.....................................................................
      subroutine anov0 ( ssx,ssx2,s2sx,nn,ngp)
c     sx   = sum of x within group
c     sx2  = sum of x**2 within group
c     ssx  = sum of sums of x within group
c     ssx2 = sum of sums of x**2 within group
c     s2sx =
c     nn   = cumulative number of observations in groups 1,ngp
c     ngp  = cumulative number of groups
      ssx  = 0.
      ssx2 = 0.
      s2sx = 0.
      nn   = 0
      ngp  = 0
      return
      end
C.....................................................................
      subroutine anov1 (x,nx,xm,sd,ssx,ssx2,s2sx,nn,ngp)
      dimension  x(nx),xm(ngp),sd(ngp)
c     x (i)= array of x values within group ngp
c     nx   = number of observations within group j
c     xm(j)= mean within group j
c     sd(j)= std. dev. within group j
c     sx   = sum of x within group
c     sx2  = sum of x**2 within group
c     ssx  = sum of sums of x within group
c     ssx2 = sum of sums of x**2 within group
c     s2sx =
c     nn   = cumulative number of observations in groups 1,ngp
c     ngp  = cumulative number of groups
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c                                                           c
c  Note :  it is possible for nx (no. of prsons) to equal   c
c          zero, which in turn would cause division by      c
c          zero in mean and s2sx variables.  If there is    c
c          such a possibility, if could be fixed with an    c
c          "IF...THEN"  statement.                          c
c                                                           c
ccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c
      sx   = 0.
      sx2  = 0.
      do 1  i = 1, nx
          sx   = sx+x(i)
          sx2  = sx2+(x(i)**2)
    1     continue
      nn   = nn+nx
```

```
          ngp  = ngp + 1
          fn   = float(nx)
          ssx  = ssx+sx
          ssx2 = ssx2+sx2
          s2sx = s2sx+((sx**2)/fn)
          xm(ngp)= sx/fn
          sd(ngp)= sqrt((sx2-((sx**2)/fn))/(fn-1.))
        2 return
          end
C..............................................................................
          subroutine anov2 (ssx,ssx2,s2sx,nn,k,oam,psd,f,n1,n2)
c         k    = total number of groups [ngp in anov1]
c         ssx  = sum of sums of x within group
c         ssx2 = sum of sums of x**2 within group
c         s2sx =
c         oam  = over-all-mean
c         psd  = pooled standard deviation
c         f    = F statistic
c         n1   = numerator degrees of freedom, k - 1 = ngp - 1
c         n2   = denominator degrees of freedom, nn - k
          oam   = ssx/float(nn)
          totss = ssx2-((ssx**2)/float(nn))
          betss = s2sx-((ssx**2)/float(nn))
          witss = totss-betss
          betms = betss/float(k-1)
          witms = witss/float(nn-k)
          psd   = sqrt(witms)
          f     = 9999.99
          if (witms .ne. 0)  f = betms/witms
          n1    = k-1
          n2    = nn-k
          return
          end


Listing of input file pplib:
   18  12  26   1   0   4 .50 .65 .75 .50  23 114
ncrwnpernwksday0inclnthrthrs   2   3   41in11in2
```

Appendix D: listing of a typical output from the health analysis summary
program (Appendix C); this particular run was for a daily mean
response of 4% with a residue variation of 3.0 (plotted as the
second line from the bottom in Figure 3).

Wk Day	OAM	PSD	F	n1	n2	OGM	PGD	G	n3	n4	po1	po2	po3	po4
1 1	.03603	.01988	19.65	17	198	.02608	1.57011	28.68	17	198	0	0	0	0
1 2	.06132	.03254	20.37	17	198	.04489	1.55964	28.68	17	198	0	0	0	0
1 3	.11174	.05850	15.86	17	198	.08421	1.53532	31.22	17	198	0	0	0	1
1 4	.17631	.08352	16.32	17	198	.13742	1.50343	31.56	17	198	0	1	0	5
1 5	.24283	.09752	19.88	17	198	.19112	1.47487	38.00	17	198	3	0	0	17
1 6	.22551	.08994	18.86	17	198	.17892	1.47140	36.97	17	198	0	0	0	10
1 7	.22351	.08917	18.85	17	198	.17733	1.47139	36.97	17	198	0	0	0	10
2 1	.26962	.10039	24.60	17	198	.21348	1.45621	40.27	17	198	1	0	0	22
2 2	.29544	.10221	28.26	17	198	.24231	1.44281	29.99	17	198	0	1	0	25
2 3	.32077	.10551	23.56	17	198	.27309	1.42929	23.58	17	198	0	0	1	33
2 4	.34635	.11053	18.18	17	198	.30271	1.41401	20.31	17	198	0	0	0	38
2 5	.36641	.11393	16.26	17	198	.32424	1.40100	19.20	17	198	0	0	0	44
2 6	.35558	.10940	17.06	17	198	.31452	1.39808	19.64	17	198	0	0	0	42
2 7	.35241	.10843	17.06	17	198	.31172	1.39808	19.64	17	198	0	0	0	40
3 1	.36939	.11314	15.42	17	198	.32915	1.39214	18.57	17	198	0	0	0	44
3 2	.37835	.11392	15.14	17	198	.33864	1.38479	18.37	17	198	0	0	0	48
3 3	.39645	.11553	16.38	17	198	.35519	1.37696	19.31	17	198	0	0	0	54
3 4	.45244	.12241	13.06	17	198	.41731	1.35599	12.68	17	198	9	2	1	80
3 5	.47523	.12176	15.79	17	198	.43807	1.34167	14.83	17	198	0	11	5	92
3 6	.45783	.11608	14.34	17	198	.42399	1.33822	13.91	17	198	0	0	0	85
3 7	.45376	.11506	14.34	17	198	.42022	1.33822	13.91	17	198	0	0	0	84
4 1	.48126	.11940	15.06	17	198	.44724	1.33211	13.07	17	198	1	0	0	92
4 2	.49771	.11983	14.55	17	198	.46482	1.32171	12.72	17	198	1	0	0	102
4 3	.52123	.12135	14.76	17	198	.48866	1.30919	12.96	17	198	0	0	0	114
4 4	.54419	.12285	9.83	17	198	.51783	1.29359	9.11	17	198	0	0	0	126
4 5	.55989	.12216	9.14	17	198	.53540	1.28051	8.55	17	198	0	0	0	133
4 6	.54372	.11613	9.61	17	198	.52029	1.27598	8.87	17	198	0	0	0	126
4 7	.53889	.11511	9.61	17	198	.51567	1.27597	8.87	17	198	0	0	0	125
5 1	.56026	.11840	9.11	17	198	.53713	1.27244	8.48	17	198	0	0	0	138
5 2	.56846	.11741	8.94	17	198	.54613	1.26592	8.36	17	198	0	0	0	144
5 3	.57354	.11612	8.80	17	198	.55204	1.26034	8.16	17	198	0	0	0	147
5 4	.58424	.11670	8.20	17	198	.56371	1.25225	7.82	17	198	1	0	0	151
5 5	.59814	.11592	8.29	17	198	.57812	1.24382	8.10	17	198	0	0	0	162
5 6	.58172	.11036	8.23	17	198	.56301	1.23949	7.96	17	198	0	0	0	156
5 7	.57654	.10938	8.23	17	198	.55800	1.23946	7.96	17	198	0	0	0	151
6 1	.59733	.11272	9.78	17	198	.57701	1.23727	9.41	17	198	1	0	0	158
6 2	.60104	.11036	9.98	17	198	.58135	1.23152	9.60	17	198	0	0	0	161
6 3	.61392	.11063	8.90	17	198	.59574	1.22561	8.31	17	198	0	0	0	170
6 4	.62627	.10989	7.70	17	198	.60978	1.21847	7.06	17	198	0	0	0	174
6 5	.63371	.10823	7.14	17	198	.61842	1.21168	6.44	17	198	0	0	0	179
6 6	.61678	.10310	6.97	17	198	.60248	1.20741	6.46	17	198	0	0	0	176
6 7	.61130	.10220	6.97	17	198	.59712	1.20741	6.46	17	198	0	0	0	174
7 1	.63185	.10590	5.26	17	198	.61861	1.20606	4.81	17	198	1	1	0	183
7 2	.63794	.10426	5.11	17	198	.62536	1.20067	4.57	17	198	0	1	0	186
7 3	.64973	.10203	7.78	17	198	.63620	1.19554	6.24	17	198	11	5	2	188
7 4	.65380	.10062	8.59	17	198	.64034	1.19174	6.60	17	198	0	11	5	187
7 5	.65166	.09948	6.67	17	198	.63942	1.18870	5.63	17	198	0	0	0	187
7 6	.63887	.09625	6.31	17	198	.62734	1.18619	5.39	17	198	0	0	0	186

7	7	.63318	.09541	6.31	17	198	.62175	1.18620	5.39	17	198	0	0	0	184
8	1	.63905	.09654	6.57	17	198	.62737	1.18639	5.54	17	198	0	0	0	186
8	2	.63861	.09585	6.52	17	198	.62712	1.18477	5.53	17	198	0	0	0	186
8	3	.65286	.09750	7.25	17	198	.64104	1.18097	6.15	17	198	5	3	1	191
8	4	.66828	.09723·	7.31	17	198	.65686	1.17597	5.95	17	198	0	5	2	195
8	5	.67431	.09480	8.05	17	198	.66317	1.17004	6.41	17	198	0	0	3	199
8	6	.65403	.08864	6.62	17	198	.64448	1.16466	5.44	17	198	0	0	0	196
8	7	.64821	.08785	6.62	17	198	.63875	1.16465	5.44	17	198	0	0	0	193
9	1	.65964	.09082	6.78	17	198	.64974	1.16609	5.57	17	198	1	0	0	198
9	2	.66059	.08973	6.84	17	198	.65091	1.16346	5.65	17	198	0	0	0	199
9	3	.67096	.08978	6.90	17	198	.66130	1.16089	5.93	17	198	0	0	0	202
9	4	.67860	.08880	5.96	17	198	.66964	1.15713	5.25	17	198	0	0	0	203
9	5	.68954	.08815	7.65	17	198	.68012	1.15319	6.61	17	198	0	0	0	204
9	6	.66900	.08267	6.51	17	198	.66085	1.14835	5.72	17	198	0	0	0	204
9	7	.66305	.08194	6.51	17	198	.65497	1.14835	5.72	17	198	0	0	0	200
10	1	.67675	.08462	8.59	17	198	.66752	1.14998	7.25	17	198	0	0	0	204
10	2	.68077	.08394	8.73	17	198	.67167	1.14807	7.38	17	198	0	0	0	204
10	3	.68229	.08271	7.50	17	198	.67386	1.14577	6.57	17	198	0	0	0	203
10	4	.68312	.08195	7.49	17	198	.67486	1.14411	6.53	17	198	0	0	0	204
10	5	.68311	.08110	7.63	17	198	.67498	1.14249	6.62	17	198	0	0	0	205
10	6	.66969	.07786	7.28	17	198	.66214	1.13967	6.36	17	198	0	0	0	202
10	7	.66373	.07718	7.27	17	198	.65625	1.13968	6.35	17	198	0	0	0	199
11	1	.67367	.08035	6.60	17	198	.66600	1.14198	5.94	17	198	0	0	0	202
11	2	.67417	.07974	6.55	17	198	.66666	1.14017	5.95	17	198	0	0	0	202
11	3	.68439	.08111	7.45	17	198	.67647	1.13925	6.74	17	198	2	1	1	206
11	4	.68765	.07995	8.13	17	198	.67974	1.13649	7.31	17	198	0	1	0	206
11	5	.68540	.07791	7.21	17	198	.67810	1.13373	6.72	17	198	0	0	0	205
11	6	.67174	.07409	7.32	17	198	.66494	1.13020	6.72	17	198	0	0	0	204
11	7	.66576	.07344	7.31	17	198	.65902	1.13021	6.72	17	198	0	0	0	201
.12	1	.67827	.07681	4.66	17	198	.67209	1.13209	4.37	17	198	0	0	0	205
12	2	.68072	.07605	4.29	17	198	.67481	1.12985	4.10	17	198	0	0	0	208
12	3	.68977	.07696	3.52	17	198	.68413	1.12901	3.31	17	198	0	0	0	210
12	4	.69414	.07597	3.10	17	198	.68883	1.12653	2.89	17	198	0	0	0	212
12	5	.69613	.07496	3.53	17	198	.69084	1.12442	3.24	17	198	0	0	0	212
12	6	.68074	.07109	2.99	17	198	.67601	1.12094	2.80	17	198	0	0	0	212
12	7	.67469	.07047	2.99	17	198	.66999	1.12094	2.80	17	198	0	0	0	212
13	1	.68659	.07308	3.57	17	198	.68149	1.12278	3.24	17	198	2	0	0	212
13	2	.68713	.07204	4.59	17	198	.68190	1.12105	3.99	17	198	0	0	0	212
13	3	.68651	.07193	2.87	17	198	.68177	1.12061	2.69	17	198	0	0	0	213
13	4	.68931	.07235	3.05	17	198	.68451	1.12061	2.81	17	198	0	0	0	213
13	5	.69022	.07170	3.38	17	198	.68540	1.11946	3.09	17	198	0	0	0	213
13	6	.67655	.06818	3.10	17	198	.67216	1.11609	2.86	17	198	0	0	0	213
13	7	.67054	.06760	3.10	17	198	.66618	1.11611	2.86	17	198	0	0	0	212
14	1	.67358	.06914	3.27	17	198	.66901	1.11798	3.01	17	198	0	0	0	213
14	2	.67428	.06914	3.43	17	198	.66966	1.11794	3.18	17	198	0	0	0	213
14	3	.67816	.07026	3.71	17	198	.67334	1.11904	3.47	17	198	0	0	0	213
14	4	.68484	.07160	4.14	17	198	.67979	1.11945	3.89	17	198	1	0	0	213
14	5	.68636	.07072	5.05	17	198	.68117	1.11789	4.66	17	198	0	0	0	213
14	6	.67134	.06626	4.23	17	198	.66684	1.11374	3.96	17	198	0	0	0	213
14	7	.66537	.06569	4.23	17	198	.66090	1.11376	3.96	17	198	0	0	0	213
15	1	.68046	.07031	2.68	17	198	.67599	1.11789	2.57	17	198	0	0	0	214
15	2	.68286	.07002	3.29	17	198	.67829	1.11652	3.09	17	198	0	0	0	214
15	3	.68617	.07002	3.75	17	198	.68151	1.11576	3.51	17	198	0	0	0	214
15	4	.69337	.07022	4.10	17	198	.68858	1.11543	3.86	17	198	0	0	0	215
15	5	.69376	.06930	4.82	17	198	.68891	1.11394	4.43	17	198	0	0	0	215

15	6	.67845	.06527	4.00	17	198	.67421	1.11009	3.76	17	198	0	0	0 215
15	7	.67241	.06471	3.99	17	198	.66821	1.11011	3.76	17	198	0	0	0 214
16	1	.68278	.06787	5.39	17	198	.67791	1.11328	4.89	17	198	0	0	0 215
16	2	.68449	.06936	3.80	17	198	.67996	1.11369	3.43	17	198	1	0	0 215
16	3	.68407	.06854	3.77	17	198	.67968	1.11178	3.40	17	198	0	0	0 215
16	4	.69443	.06943	4.58	17	198	.68979	1.11167	4.02	17	198	0	0	0 215
16	5	.69671	.06856	5.57	17	198	.69194	1.10990	4.84	17	198	0	0	0 215
16	6	.68013	.06403	4.25	17	198	.67613	1.10551	3.77	17	198	0	0	0 215
16	7	.67408	.06348	4.24	17	198	.67012	1.10553	3.76	17	198	0	0	0 215
17	1	.68483	.06724	3.95	17	198	.68057	1.10941	3.51	17	198	1	0	0 215
17	2	.68521	.06670	4.50	17	198	.68089	1.10842	3.98	17	198	0	0	0 215
17	3	.68693	.06683	4.82	17	198	.68252	1.10826	4.32	17	198	0	0	0 215
17	4	.70322	.06859	9.25	17	198	.69760	1.10828	8.00	17	198	7	3	0 214
17	5	.70202	.06584	11.00	17	198	.69642	1.10476	9.18	17	198	0	6	0 214
17	6	.68422	.06142	7.55	17	198	.67984	1.10061	6.68	17	198	0	0	0 213
17	7	.67813	.06090	7.53	17	198	.67379	1.10064	6.67	17	198	0	0	0 213
18	1	.68657	.06375	8.52	17	198	.68168	1.10376	7.50	17	198	0	0	0 213
18	2	.69120	.06398	8.56	17	198	.68628	1.10324	7.71	17	198	2	0	0 213
18	3	.70149	.06570	10.18	17	198	.69601	1.10453	9.05	17	198	2	1	0 213
18	4	.72029	.06879	11.54	17	198	.71410	1.10567	10.60	17	198	9	5	2 213
18	5	.72489	.06679	14.46	17	198	.71840	1.10218	12.98	17	198	0	8	2 213
18	6	.70069	.05924	11.04	17	198	.69595	1.09475	10.19	17	198	0	0	0 213
18	7	.69446	.05873	11.03	17	198	.68975	1.09476	10.19	17	198	0	0	0 212
19	1	.70179	.06218	9.23	17	198	.69699	1.09836	8.91	17	198	0	0	0 212
19	2	.70063	.06170	9.23	17	198	.69589	1.09742	9.05	17	198	0	0	0 211
19	3	.70645	.06173	10.12	17	198	.70152	1.09700	9.92	17	198	3	0	0 211
19	4	.71128	.06138	10.18	17	198	.70646	1.09658	9.38	17	198	0	1	0 213
19	5	.70775	.06067	7.36	17	198	.70359	1.09590	6.93	17	198	0	0	0 214
19	6	.69465	.05781	7.81	17	198	.69070	1.09309	7.39	17	198	0	0	0 213
19	7	.68847	.05731	7.80	17	198	.68455	1.09311	7.38	17	198	0	0	0 213
20	1	.69491	.05966	6.92	17	198	.69091	1.09606	6.50	17	198	0	0	0 212
20	2	.69206	.05937	7.08	17	198	.68804	1.09584	6.74	17	198	0	0	0 212
20	3	.69234	.05991	7.14	17	198	.68825	1.09655	6.75	17	198	0	0	0 213
20	4	.70141	.06174	6.39	17	198	.69732	1.09836	5.78	17	198	0	0	0 215
20	5	.70308	.06162	6.62	17	198	.69899	1.09787	5.90	17	198	0	0	0 215
20	6	.68726	.05775	5.82	17	198	.68370	1.09401	5.28	17	198	0	0	0 215
20	7	.68114	.05726	5.81	17	198	.67762	1.09403	5.27	17	198	0	0	0 214
21	1	.69383	.06174	6.24	17	198	.68979	1.09865	5.60	17	198	1	0	0 214
21	2	.69452	.06124	7.06	17	198	.69039	1.09772	6.25	17	198	0	0	0 214
21	3	.69413	.06080	7.06	17	198	.69005	1.09712	6.20	17	198	0	0	0 214
21	4	.69746	.06135	7.47	17	198	.69324	1.09767	6.53	17	198	0	0	0 214
21	5	.69898	.06122	7.79	17	198	.69473	1.09731	6.79	17	198	0	0	0 214
21	6	.68374	.05717	6.78	17	198	.68009	1.09323	5.99	17	198	0	0	0 214
21	7	.67766	.05668	6.78	17	198	.67405	1.09326	5.98	17	198	0	0	0 214
22	1	.68031	.05841	6.69	17	198	.67651	1.09559	5.96	17	198	0	0	0 214
22	2	.68411	.05969	5.64	17	198	.68039	1.09656	5.10	17	198	0	0	0 214
22	3	.69277	.06182	5.64	17	198	.68886	1.09831	5.09	17	198	0	0	0 214
22	4	.69705	.06260	6.13	17	198	.69299	1.09855	5.56	17	198	0	0	0 214
22	5	.69849	.06214	6.86	17	198	.69434	1.09743	6.24	17	198	0	0	0 214
22	6	.68251	.05724	6.03	17	198	.67902	1.09242	5.49	17	198	0	0	0 214
22	7	.67644	.05675	6.02	17	198	.67298	1.09245	5.48	17	198	0	0	0 213
23	1	.68934	.06171	7.40	17	198	.68510	1.09788	6.63	17	198	0	0	0 213
23	2	.69012	.06146	8.10	17	198	.68578	1.09730	7.24	17	198	0	0	0 213
23	3	.69190	.06128	7.93	17	198	.68762	1.09700	7.05	17	198	0	0	0 213
23	4	.68984	.06018	6.52	17	198	.68594	1.09596	5.93	17	198	0	0	0 213

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23	5	.68964	.06030	6.05	17	198	.68582	1.09628	5.49	17	198	0	0	0	213
23	6	.67730	.05726	6.14	17	198	.67376	1.09321	5.55	17	198	0	0	0	213
23	7	.67127	.05677	6.13	17	198	.66776	1.09324	5.54	17	198	0	0	0	213
24	1	.68276	.06086	6.87	17	198	.67868	1.09772	6.25	17	198	0	0	0	213
24	2	.68871	.06165	7.56	17	198	.68440	1.09803	7.01	17	198	0	0	0	213
24	3	.69289	.06136	6.56	17	198	.68883	1.09737	6.14	17	198	0	0	0	213
24	4	.69272	.06087	5.68	17	198	.68889	1.09684	5.32	17	198	0	0	0	213
24	5	.69295	.06060	5.55	17	198	.68918	1.09650	5.18	17	198	0	0	0	213
24	6	.67956	.05722	5.58	17	198	.67611	1.09308	5.23	17	198	0	0	0	213
24	7	.67351	.05674	5.58	17	198	.67009	1.09311	5.23	17	198	0	0	0	212
25	1	.69006	.06149	7.84	17	198	.68567	1.09814	7.36	17	198	2	0	0	212
25	2	.69211	.06110	9.64	17	198	.68742	1.09742	8.87	17	198	0	0	0	211
25	3	.70083	.06125	17.02	17	198	.69494	1.09724	13.18	17	198	12	10	8	213
25	4	.71212	.06283	16.44	17	198	.70613	1.09839	12.69	17	198	0	12	8	214
25	5	.71644	.06190	17.01	17	198	.71050	1.09694	13.08	17	198	0	0	7	214
25	6	.69305	.05702	9.78	17	198	.68894	1.09200	8.35	17	198	0	0	0	214
25	7	.68688	.05654	9.77	17	198	.68280	1.09203	8.34	17	198	0	0	0	214
26	1	.70544	.06109	11.04	17	198	.70053	1.09655	.9.75	17	198	3	0	0	214
26	2	.70569	.06002	11.61	17	198	.70081	1.09523	10.24	17	198	0	1	0	213
26	3	.70812	.05999	11.77	17	198	.70323	1.09504	10.30	17	198	0	0	0	213
26	4	.70679	.05997	10.10	17	198	.70219	1.09489	9.15	17	198	0	0	0	213
26	5	.70585	.05959	10.39	17	198	.70125	1.09422	9.48	17	198	0	0	0	213
26	6	.69219	.05609	10.20	17	198	.68805	1.09072	9.22	17	198	0	0	0	213
26	7	.68603	.05561	10.18	17	198	.68193	1.09075	9.21	17	198	0	0	0	213

```
                        Total number of poisoning cases:  83  90  48
                   Days on which a poisoning occurred:  27  25  15
                   Potentially reportable incidents:   5   6   3
```

Means and deviations given on input
    for normally distributed variables:
        workers weight   70.00000   7.00000
    for lognormally distributed variables:
        dosing coefficient kd   5.10000   1.41000
        enzyme coefficient ke   6.00000   1.30000
        regeneration, p   .00893   1.04570
        reversion, pp   .15000   1.01000
        mean daily inhibition, %   4.00000
        variability in AChE measurement   1.00000
        reentry residue, ug/cm2   .11673   3.00000
Other parameters given on input:
        number of members per crew   12
        number of crews   18
        total size of population   216
        no. of weeks worked per crew   26
        total no. of fields sprayed   936
        no. of days to complete field   2 3 3 2 0 0 0 0 0 0
        no. of hours worked per day   8

Pesticide Exposure of Harvesters of Blueberries,
Blackberries, and Raspberries

Research performed by

University of California
Richmond, CA   94804

October 15, 1985

Abstract

During the 1983 growing season in California three field studies were conducted on the exposure of harvesters of berry crops to pesticide residues. These studies were designed to compare dermal exposure to children (10-12 years old) and adults harvesting these crops. In all three studies, methiocarb on blueberries, benlate on blackberries and benlate on raspberries, a consistent relationship between age and exposure was observed. When exposure is measured as total weight of pesticide deposited per hour worked, there is an increase of exposure with age. When the exposure measure is normalized by body weight there is no difference in exposure as a function of age. One study where work rate was available, provided evidence that differences in total exposure with age are attributable to differences in work rate.

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3. PROJECT DESCRIPTION AND ADMINISTRATIVE SUMMARY

During the 1983 growing season the California PHAP Project conducted three field studies on the exposure of the harvesters of berry crops to pesticide residues. These studies were designed to compare the dermal exposure of children (10-12 years old) and adults harvesting these crops. Secondly an attempt was to be made to compare dermal exposures as measured by the patch technique and glove monitors with exposures quantified by the urinary excretion of the pesticides and their metabolites.

The scope of these studies was limited, where possible, to the analyses of exposures to the pesticides applied to the crops most recently before harvesting commenced. These pesticides turned out to be methiocarb on blueberries and benomyl on blackberries and raspberries. Approximately twenty workers were involved in each of these studies. In addition to the collection of data on dermal exposures, foliar residue data were also collected.

The principal failure in achieving the goals of these studies is that no urinary metabolite data can be reported. The background behind this failure is detailed in the correspondence included here as Appendix B. At this time these samples remain in storage awaiting analysis by EPA or its designee. As a result, the individual study reports, Sections 4, 5, and 6, deal with the patch, glove and foliar residue data only. Included as Appendix

C is the information needed for subsequent analysis of the metabolite results when they become available.

A consistent relationship between exposure and age was observed in all three studies. When exposure is measured as total weight of pesticide deposited per hour worked, e.g. mg/hr, there is an increase of exposure with age. When the exposure measure is normalized by the body weight of the worker, i.e. mg/kg/hr, then there is no difference in exposure as a function of age. The blueberry study, where information related to workrate was available, provided some evidence that the differences in total exposure with age are attributable to differences in workrate between children and adults.

The staff of the California PHAP was assisted in all phases of the field studies by Dr. James M. Witt of the Department of Agricultural Chemistry, Oregon State University, Corvallis, Oregon, and Ken Brown, Extension Agent, Oregon State University, Salem, Oregon. Through their knowledge of the agriculture in the region and their liason with many growers, they and their staffs were able to locate suitable field sites and enlist the cooperation of the owners. John Reinhold, working under Dr. Witt's aegis, took foliar samples prior to our arrival in Oregon and assisted the PHAP staff in conducting the monitoring studies. We are grateful for their assistance.

4. HARVESTER EXPOSURES TO METHIOCARB IN BLUEBERRIES

4.1 Introduction

In a continuing effort to develop experimental data on the exposure to pesticides of fruit harvesters of different ages, a study was conducted involving the exposure of blueberry harvesters to residues of the pesticide methiocarb (Mesurol). The volunteers for this study were divided into two groups, one provided with cotton gloves and dermal patches to measure dermal exposures and the other not so provided so that there would be no unnatural barrier to their exposure. Urine samples were collected from all subjects to be analyzed for metabolites of the pesticide.

The purpose of the study was two-fold. The primary intent was to measure the worker's dermal exposures and determine whether a significant difference exists between the exposures experienced by children and adults. Second, an attempt was to be made to correlate dermal exposure to methiocarb as determined by patch and glove monitors with that determined by the concentration of the metabolite of the pesticide excreted in the urine of the exposed workers. An additional, but secondary goal, was to contrast the absorbtion of the pesticide, as measured by the urinary metabolite concentration, between the group wearing gloves with that not so protected with the object of determining the degree of protection afforded.

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4.2 Study site and experimental design

A fifteen acre plot of the Bluecrop variety of blueberries, located about two miles north of Salem, Oregon, was chosen as the site of the study. Twenty five harvesters, including men, women and children, participated in the study on a voluntary basis. They were paid $20 for completing the five day course of monitoring and urine collection. Detailed consent forms and instructions were handed to each participant before the study began. The participation of all minors required the signed consent of the parents.

On Friday, 22 July 1983, methiocarb had been applied to the blueberries between 0800 and 0900 hours by fixed wing aircraft. A 75% wettable powder formulation was applied at a rate of 1.5 lb/A. This plot had been previously treated with methiocarb at the same rate on 5 July 1983. The harvesters were permitted to enter the field on Monday, 25 July, the day that the study commenced. Weather conditions were recorded and are given in Table 4.1.

The study was designed to last five days. None of the subjects, as far as could be ascertained, picked blueberries on the preceding Saturday or Sunday. All subjects were instructed to collect a urine specimen before they entered the field on Monday to serve as a pre-exposure control. On Monday the workers were divided into two groups, A and B. Group A was provided light-weight cotton gloves, similar to those used in photographic

Table 4.1

Meterological Data

Blueberry Site, 2 miles N of Salem, Oregon

Date	DPA[*]	Time	Temp. C	RH[*]	Weather
7/22/83	0	0925	21.0	70%	partly cloudy
7/25/83	3	0730	18.0	80	heavy overcast
		0918	18.5	70	heavy overcast
		1105	19.0	80	partly sunny
		1325	21.2	60	partly sunny
		1508	22.0	60	sunny
7/26/83	4	06ΰ0	18.3	80	partly sunny
		1128	21.0	58	partly sunny
7/27/83	5	not recorded			heavy rain
7/28/83	6	0800	18.0	90	sunny
		1115	21.0	50	sunny

darkroom work, to be worn throughout the workday while picking berries. During the lunch break the gloves were removed and new gloves issued after the break. Also, new gloves were provided if a pair became too soiled or wet.

On Tuesday Group A was outfitted with cotton gauze-patch monitors, in addition to the cotton gloves, to measure total dermal exposure. Details of the placement and handling of the patches and gloves are contained in Appendix A. Group B wore neither gloves nor patches at any time during the study.

The collection of urine specimens was scheduled to begin on Wednesday when it was assumed excretion would have reached something near steady state. Starting Tuesday after work all subjects were provided with 1-liter plastic specimen bottles and intructed to collect their urine for the reminder of the 72 hours of the study in the following regimen: night samples to go from the termination of work to through the next morning's void; day samples from that point through the termination of work. On Wednesday, 26 July, about half the subjects did not pick berries due to a heavy rainfall that commenced about 8 AM and lasted for about one hour. The subjects from group A who did harvest berries despite the rain were provided with gloves ano patches.

On Thursday, 27 July, all participants worked in the field. Group A was provided with gloves only, but not patches. None of the subjects picked on Friday, 28 July but they did deliver their

final overnight urine sample that morning.

Throughout the study foliar residue samples were collected according to the procedures detailed in Appendix A. On three occasions participants were also outfitted with personal air samplers to measure pesticide residues existing as aerosols. These procedures are also detailed in Appendix A.

4.3 Sample storage handling and preparation

Urine samples were stored on ice for no more than 4-6 hours and transported to the laboratory the same day as they were received from the subjects. Individual urine sample volumes were measured and duplicate 20 mL aliquots were pipetted into glass ampules to which 1.5 mL of concentrated hydrochloric acid was added as a preservative resulting in a final pH of less than 0.5). The ampules were sealed and stored at room temperature.

Gloves and patches were collected from participants by project personnel and stored in zip-loc plastic bags. (See section 6.7 of the QA Plan for sample preservation procedures.)

4.4 Analytical procedures

Extraction of samples was as detailed in section 9 of the Quality Assurance Plan.

Methiocarb residues were analyzed by reverse-phase HPLC using a Waters 6000A dual pump Solvent Delivery System, a WISP Model 710A Automatic Sample Processor, a Waters Model 720 System

Controller with a Mode 730 Data Module and a Model 4530 Variable
Wave-length Detector. A Supelco C_{18} reverse-phase column (25 cm
x 4.2 mm ID) was capable of seperating each of the three com-
pounds reported to be associated with methiocarb residues
{methiocarb: 3,5 dimethyl-4-(methylthio)phenyl-N-methyl carbam-
ate; methiocarb sulfoxide: 3,5 dimethyl-4-(methylsulfonyl)phenyl-
N-methyl carbamate; methiocarb sulphone: 3,5 dimethyl-4-(methyl-
sulfonyl)phenyl-N-methyl carbamate} without appreciable interfer-
ence from extraneous materials originating in the field. The
mobile phase was a mixture of acetonitrile and water and the
optimum chromatographic conditions for each compound are listed
in Table 4.2.

TABLE 4.2

Chromatographic Parameters
for the
Analysis of Mesurol
and
Related Compounds

Column	25 cm X 4.6 mm C_{18} Supelco LC-18-DB with a C_{18} Guard-PAK precolunm
Mobile Phase	65% Acetonitrile, 35% Water
Flow Rate	0.9 ml/min
Detecrtor Parameters	Wavelength: 265 nm Sensitivity: 0.02 AUFS
Integration Parameters	Peak Width: 20 Noise Rejection: 7.5 Chart Speed: 0.5 cm/min Run Time: 10 min

4.5 Crew characteristics

The crew characteristics, including sex, height, weight, age and computed body surface area are given in Table 4.3. In additon, the crew included six Asian workers in Group A and two in Group B.

The owner of the blueberry farm selected his harvesters individually, and allowed only approved personnel to work in his plots; because of this procedure, he maintained a relatively stable work crew, year-to-year. The owner adhered to this practice because the blueberry bush is a perenial that is not cut back heavily each year like the other types of berries included in this series of studies; and damage caused by careless workers could cause long-term losses in productivity for the plants.

Upon arrival at the study site it was discovered that the grower had preselected the crew for the exposure study. These individuals came from the growers regular crew, and included relatives and friends of his family. The entire crew was comprised of 24 individuals, ranging in age from 10 to 47 years old. Four (17%) were at the age of ten, while ten of the subjects (42%) were between 11 and 15 years, and the remaining ten were 16 years or older. In Group A (the 13 individuals wearing gloves and patches), three (23%) were ten years old; five (39%) were between 11 and 15 years; and the remaining five were over 15.

Table 4.3

Blueberry Study

Physical Characteristics of Crew

ID#	Group	Sex	Age	weight (kg)	Height (cm)	Area (m^2)
2	A	F	15	52.2	160	1.50
3	A	F	10	31.8	114	1.00
4	A	M	14	48.5	152	1.45
5	A	F	10	36.3	147	1.20
6	A	M	14	54.4	170	1.60
7	A	M	20	63.5	165	1.65
8	A	F	18	45.4	152	1.40
9	A	F	14	45.4	152	1.40
10	A	M	16	53.5	163	1.55
11	A	M	10	34.0	140	1.15
12	A	F	47	45.4	152	1.40
17	A	M	11	35.8	137	1.15
26	A	F	28	60.0	162	1.60
1	B	F	40	61.2	168	1.65
14	B	F	14	54.4	168	1.65
15	B	F	16	61.7	168	1.65
16	B	M	14	47.6	168	1.50
18	B	M	15	59.4	146	1.55
19	B	M	11	27.2	137	1.05
20	B	F	30	61.2	165	1.65
21	B	M	17	49.9	160	1.50
22	B	F	37	72.6	175	1.85
23	B	M	14	79.4	187	2.00
25	B	M	10	37.6	127	1.15

4.6 Results

As noted above, only on Tuesday was there a complete set of both patch data and glove data. On all four days, however, glove data was collected. An important issue then, is the degree of correlation between the glove exposure and total exposure. Figure 4.1 shows the scatterplot of patch exposure vs. glove exposure. The two variables are positively correlated and the regression is significant, but the r^2 value of 0.40 is not particularly impressive. However, as will be discussed below, about 50% of the total exposure is to the hands. Hence, glove exposure will be a much better predictor of total exposure than of patch exposure alone.

It is clear that the degree of exposure to foliar residues is a function of the residue level and the activity of the worker. Because of the method of payment of the workers in blueberries, it was possible to obtain data on the mean daily harvesting rate in lbs/hr for each worker. Because all workers were engaged in harvesting it seems reasonable to hypothesize that the mean daily yield should provide a good index of the activity related effect on exposure. It seems highly likely, however, that yield is a strong function of age. Indeed, it seems likely that the principal effect of age on exposure among workers carrying out the same task will be through the workrate variable.

Figure 4.2 and 4.3 show the mean yield rate for the entire period of the experiment vs. age for males and females respectively. In both cases there is an increase of yield with age.

Figure 4.1

ABSTAT 3.00   BLUEBERRY STUDY, PATCH EXPOS. VS GLOVE EXPOS. (MG/HR), DAY 2   FILE: B:8303-2P   REV# 7

COMMAND: PLOT

MISSING VALUE TREATMENT: LISTWISE

Figure 4.2

ABSTAT 3.00   BLUEBERRY STUDY, MEAN YIELD (KG/HR) VS AGE, MALES   FILE: 8303-PM

COMMAND: PLOT

2 AGE

Figure 4.3

ABSTAT 3.00   BLUEBERRY STUDY, MEAN YIELD (KG/HR) VS AGE, FEMALES   FILE: 8303-PF

COMMAND: PLOT

2 AGE
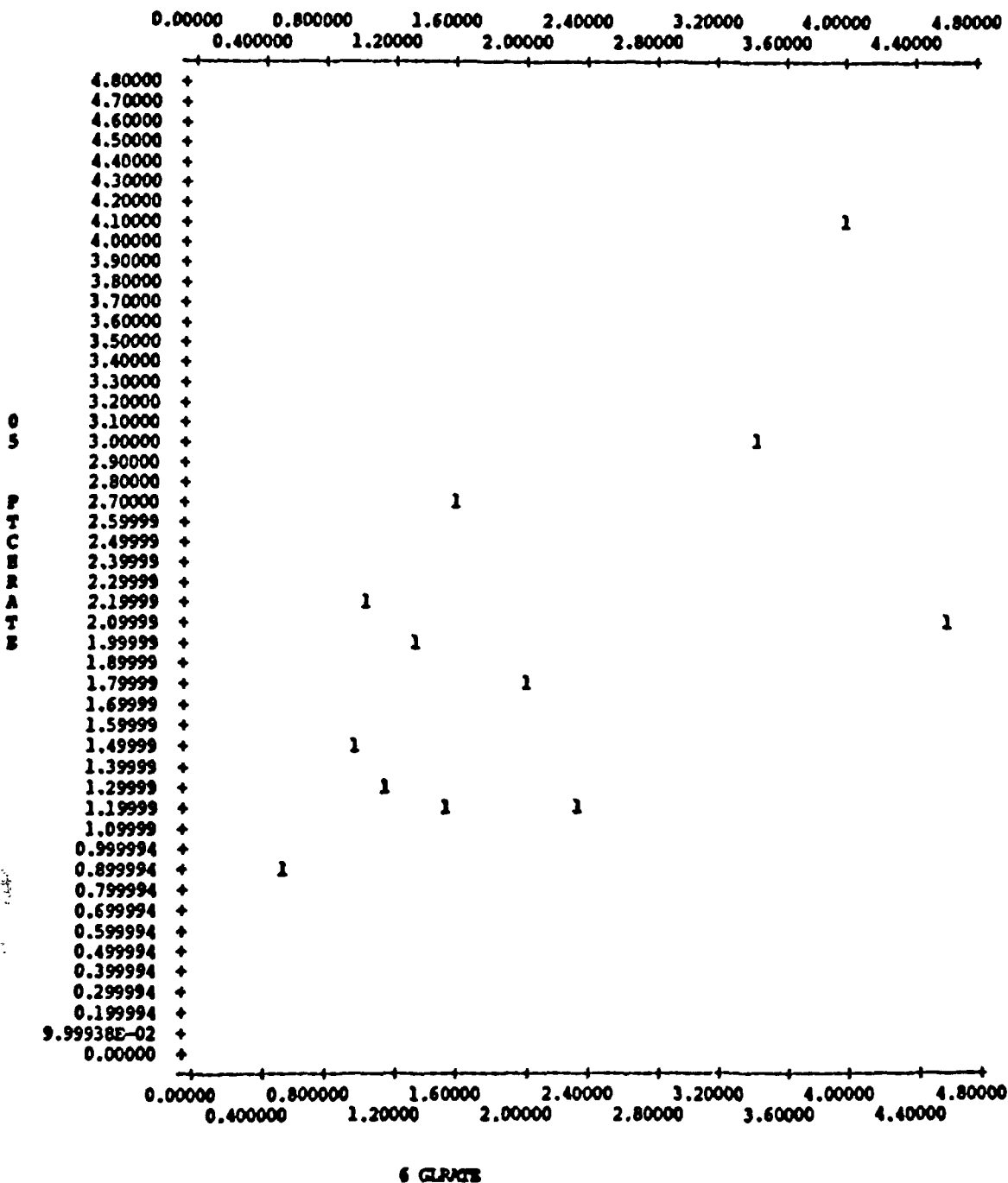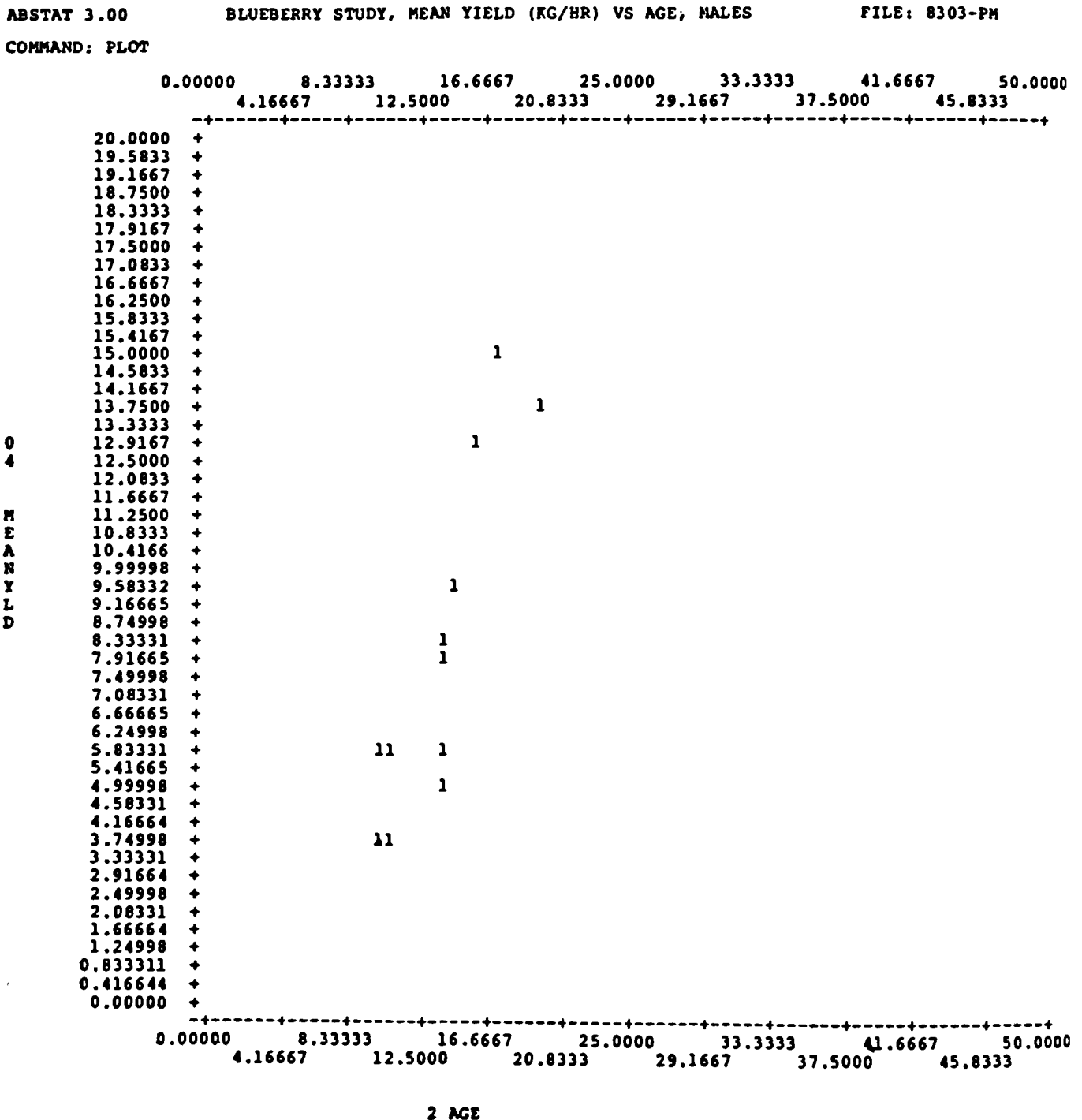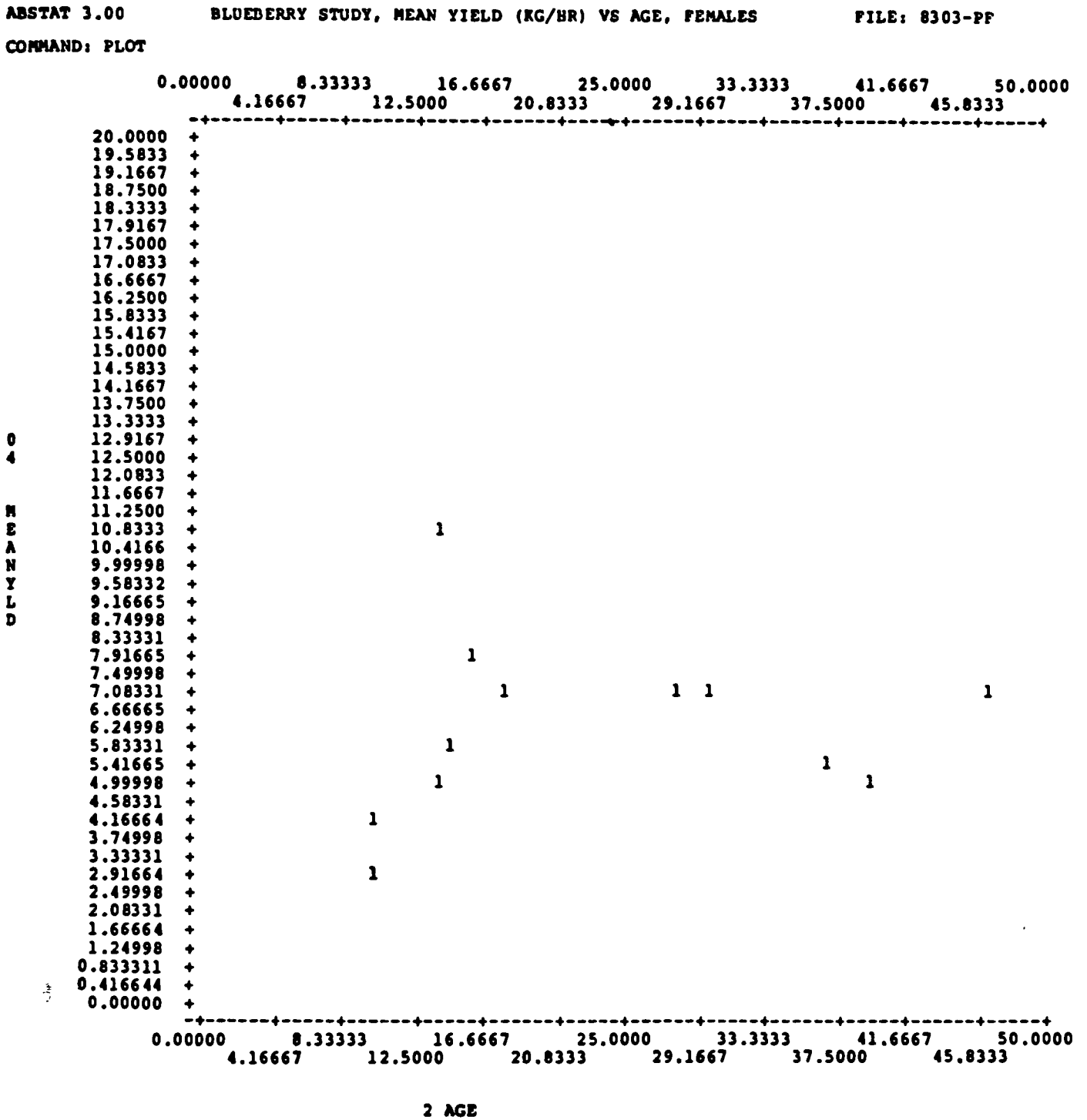
The age range for females is sufficient to suggest a plateau in the neighborhood of 8 kg/hr, but no such plateau is seen for males because of the limited age range of the workers. In any case there is clear evidence that yield rate is a function of age and sex.

If, then, we consider exposure a function of residue level and yield rate, age and sex are taken into account through their non-linear effect on yield rate. Table 4.4 contains the results of a multiple linear regression of the log of residue and the log of the yield rate against the log of the glove exposure rate which we use here as a surrogate of the total exposure rate. The logarithmic relationship is suggested by the fact that without residue there can be no exposure as is the case with work rate. Hence a multiplicative relation is plausible and the logarithmic transform appropriate.

As can be seen in Table 4.4 the F value indicates that both regression coefficients are non-zero and that these two variables account for about 60% of the variability in the data. The foliar residue is the more important predictor of exposure as indicated by the standardized coefficients. These numbers indicated the change in the dependent variable resulting from a change in the independent variable of one standard deviation. Hence, a one standard deviation change in the log of the yield rate changes the log of the glove exposure by 0.376 as contrasted with a change of 0.745 with a one standard deviation change in the log

Table 4.4

ABSTAT 3.00   BLUEBERRY STUDY, MULTIPLE REGRESSION, GLOVE VS RESIDUE & YIELD

COMMAND: REGR

MISSING VALUE TREATMENT: LISTWISE

*** MULTIPLE LINEAR REGRESSION ***

DEPENDENT VARIABLE: 10 LNGLRATE   34 VALID CASES

COEFF OF DETERMINATION: 0.578869   ESTIMATED CONSTANT TERM: -1.61601
MULTIPLE CORR COEFF: 0.760835   STANDARD ERROR OF ESTIMATE: 0.717036

ANALYSIS OF VARIANCE FOR THE REGRESSION:

SOURCE OF VARIANCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN OF SQUARES	F TEST
REGRESSION	2	21.9082	10.9541	21.3057
RESIDUALS	31	15.9383	0.514140	
TOTAL	33	37.8465		

VARIABLE	REGRESSION COEFFICIENT	STANDARDIZED COEFFICIENT	CORRELATION WITH DEPENDENT
12 LNYLDRAT	0.853255	0.376589	0.218159
13 LNRES	0.759902	0.745907	0.665919

DURBIN-WATSON =   2.26362

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of the residue level.

A second regression was carried out with the log of age included as a third predictor variable to see if there was evidence of any independent influence of age other than through work rate. As shown in Table 4.5 the result is essentially unaffected as measured by the coefficient of determination (r^2). The appropriate F test applied to the residuals in the two variable vs. the three variable case indicates that the small increase in r^2 is only what one would expect from random variation. Here age and yield rate have a similar influence on the outcome as might be expected because of the high correlation between the two as evidenced by Figure 4.2. Hence, we conclude that there is no evidence that age is an important variable except thru its influence on work rate.

This conclusion is supported by a different analysis in which each individual's average glove exposure, normalized for the weight of the individual (mg/kg/hr), is calculated over the course of the experiment and regressed against age. Figure 4.4 shows the scatter plot. The F-value is 0.009 and r^2 about 10^{-3} indicating an almost totally random relationship between these variables. That is, exposure rate on a per unit weight basis is virtually unrelated to the age of the worker. This finding supports the interpretation that workrate is the important variable and that younger workers, who tend to be smaller, work at lower rates and thus receive less total exposure than adults.

Figure 4.4

ABSTAT 3.00   BLUEBERRY STUDY, WEIGHT NORMALIZED GLOVE EXPOSURE VS AGE   FILE: B:8303-GL   REV: 7

COMMAND: PLOT

MISSING VALUE TREATMENT: LISTWISE

```
              0.00000      8.33333      16.6667      25.0000      33.3333      41.6667      50.0000
                    4.16667      12.5000      20.8333      29.1667      37.5000      45.8333
            -+------+------+------+------+------+------+------+------+------+------+------+-----+
   8.00000E-02 +
   7.87500E-02 +
   7.75000E-02 +
   7.62499E-02 +
   7.49999E-02 +
   7.37499E-02 +                          1
   7.24999E-02 +
   7.12499E-02 +
   6.99999E-02 +
   6.87499E-02 +
   6.74999E-02 +
   6.62499E-02 +
   6.49999E-02 +
   6.37499E-02 +
   6.24999E-02 +
   6.12499E-02 +
   5.99999E-02 +
 1 5.87499E-02 +
 3 5.74999E-02 +                1
   5.62499E-02 +         1          1
   5.49999E-02 +
 W 5.37499E-02 +
 A 5.24999E-02 +         1
 V 5.12499E-02 +
 G 4.99999E-02 +              1           1
 L 4.87499E-02 +
 E 4.74999E-02 +       1
 A 4.62499E-02 +
 T 4.49999E-02 +
   4.37499E-02 +                                      1
   4.24999E-02 +       1
   4.12499E-02 +
   3.99999E-02 +          1
   3.87499E-02 +       1
   3.74998E-02 +
   3.62498E-02 +
   3.49998E-02 +
   3.37498E-02 +
   3.24998E-02 +
   3.12498E-02 +
   2.99998E-02 +
   2.87498E-02 +
   2.74998E-02 +
   2.62498E-02 +
   2.49998E-02 +
   2.37498E-02 +
   2.24998E-02 +
   2.12498E-02 +       1
   2.00000E-02 +
            -+------+------+------+------+------+------+------+------+------+------+------+-----+
              0.00000      8.33333      16.6667      25.0000      33.3333      41.6667      50.0000
                    4.16667      12.5000      20.8333      29.1667      37.5000      45.8333
```

3 AGE

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Table 4.5

ABSTAT 3.00   BLUEBERRY STUDY, MULT. REGR., GLOVE VS RESIDUE, YIELD & AGE

COMMAND: REGR

MISSING VALUE TREATMENT: LISTWISE

*** MULTIPLE LINEAR REGRESSION ***

DEPENDENT VARIABLE: 10 LNGLRATE   34 VALID CASES

COEFF OF DETERMINATION: 0.595609   ESTIMATED CONSTANT TERM: -2.24593
MULTIPLE CORR COEFF: 0.771757   STANDARD ERROR OF ESTIMATE: 0.714256

ANALYSIS OF VARIANCE FOR THE REGRESSION:

SOURCE OF VARIANCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN OF SQUARES	F TEST
REGRESSION	3	22.5417	7.51390	14.7285
RESIDUALS	30	15.3048	0.510161	
TOTAL	33	37.8465		

VARIABLE	REGRESSION COEFFICIENT	STANDARDIZED COEFFICIENT	CORRELATION WITH DEPENDENT
11 LNAGE	0.348166	0.149566	0.267307
12 LNYLDRAT	0.679906	0.300080	0.218159
13 LNRES	0.749882	0.736071	0.665919

DURBIN-WATSON =   2.37323

Table 4.6 shows the anatomical distribution of methiocarb exposure. Here less of the exposure was to the hands than was the case in the strawberry studies reported previously. Since the blueberry variety involved in these studies grew on bushes as tall as 1.7 meters, there was a substantially greater potential for body contact than is the case with strawberries. There is a considerable difference in the data for the two different days, presumably because of the substantial rainfall on the third day of the study. The data on day 4 post-application should be regarded as more representative of the normal exposure situation.

Table 4.6
Anatomical Distribution of Dermal Exposure to
Methiocarb on Blueberry Harvesters

Body Part	Days Post-Application	
	4	5
Head+Neck	0.28 (7.4)*	0.13 (6.2)
Back+Shoulders	0.13 (3.4)	0.19 (8.8)
Chest+Stomach	0.23 (6.0)	0.23 (10.6)
Lower Legs	0.23 (6.0)	0.34 (15.9)
Upper Arms	0.22 (5.8)	0.20 (9.7)
Lower Arms	0.64 (16.8)	0.74 (34.6)
Hands	2.05 (53.9)	0.31 (14.3)
Total	3.80	2.14

*Tabled numbers are exposure rates in mg/hr followed by the percent of the total in parentheses.

5. HARVESTER EXPOSURES TO BENLATE IN BLACKBERRIES

5.1 Introduction

In a continuing effort to develop experimental data on the exposure to pesticides of fruit harvesters of different ages, a study was conducted involving the exposure of blackberry harvesters to residues of the pesticide Benlate (benomyl). The volunteers for this study were divided into two groups, one provided with cotton gloves and dermal patches to measure dermal exposures and the other not so provided so that there would be no unnatural barrier to their exposure. Urine samples were collected from all subjects to be analyzed for metabolites of the pesticide.

The purpose of the study was two-fold. The primary intent was to measure the worker's dermal exposures and determine whether a significant difference exists between the exposures experienced by children and adults. Second, an attempt was to be made to correlate dermal exposure to benlate as determined by patch and glove monitors with that determined by the concentration of the metabolite of the pesticide excreted in the urine of the exposed workers; An additional, but secondary goal, was to contrast the absorption of the pesticide, as measured by the urinary metabolite concentration, between the group wearing gloves with that not so protected with the object of determining the degree of protection afforded.

5.2 Study Site and Experimental Design

The site chosen for an exposure study among blackberry harvesters was located within a plot of about 30 acres of the Marion variety near Independence, Oregon. Over the growing season this field had been treated with a variety of insecticides, herbicides and fungicides; and the spray history is delineated in Table 5.1. The most recent treatment had been with Lannate and Thylate applied to various portions of the plot on 6 and 9 July. However, for several practical reasons, the 1 July treatment was chosen as the pesticide application to follow with our measurements. First, the entire plot was treated in one day, offering the possibility of more homogeneous foliar residues. Second, in addition to Lannate and Thylate, benomyl had been applied on 1 July, and this happened to be the same compound followed in the raspberry study conducted the previous week, meaning that the same residue and metabolite analytical methodology could be utilized for both studies. Third, no readily detectable urinary metabolites could be expected from Lannate, and we did not know what dermal adsorption and urinary excretion patterns might be expected from Thylate; whereas, we did know some of the pertinent toxicological and metabolic information regarding benomyl.

The study lasted for five days, running from Monday, 18 July 1983 through Friday, 22 July 1983. On-site weather observations for the study site covering 19 through 22 July are found in Table 5.2. There was one heavy rainfall early in the study, having come during Monday night. Although the field was wet on

TABLE 5.1

1983 Spray Schedule*

Marion Blackberry Field

Date	Product	Application Rate and Mode
3 March	Lime Sulfur	7.5 gal/A in 100 gal
	Spray-Aid	0.25 gal/A
17-18 March	Parathion	1 lb/A
28 March	Karmex (diuron)	2.4 lb in 4" band
	Paraquat	1.1 pt
	X77 (sic)	3.2 oz
13 April	Dinitro	2.0 qt/100 gal
		50 gal/A
	WDX77 (sic)	1 pt
		General Burn-back
15 April	Roundup	0.5 qt on centers
6-9 May	Guthion	0.5 lb/A
13-16 May	Dinitro	Burn-back
	WDX77 (sic)	1 pt
14 May	Ronilan	1.75 lb/100 gal
		1.3125 lb
		on West 1/2
	??	8 oz
5 June	Thiram	3· lb/100 gal
	Benlate	1 lb
1 July	Lannate	0.5 gal/100 gal
	Benlate	1 lb
	Thiram	3 lb
6, 9 July	Lannate	0.5 gal
	Thylate (thiram)	3.0 lb

* This table does not contain all of the 1983 spray history, but terminates at the time of the study.

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TABLE 5.2

Weather Observations

Marion Blackberry Field

Date	Time	Dry Bulb (°C.)	Wet Bulb (°C.)	% RH	Description
19 July	1430	22.8	19.4	73	Cloudy and partly sunny; had rained the night before.
20 July	1300	21.1	15.8	57	Sunny with spotty clouds.
	1408	23.3	20.0	74	*
21 July	0730	14.2	13.1	89	*
	1008	21.1	17.2	67	*
22 July	0925	21.1	17.8	72	*

* Although no information was recorded for these days, the weather was generally clear and sunny for the duration of the study.

Tuesday morning, relatively warm weather that day dried the foliage within a reasonable time, allowing the crew to work without dealing with very wet gloves.

Consent forms approved by the Committee for the Protection of Human Subjects at the University of California at Berkeley (see Appendix D) were distributed to each participant along with detailed instructions for their particular subgroup (Appendix D). In order for anyone to be allowed to join the Study, they were required to return their consent form signed; and if they were minors, their form had to be signed by their parents, as

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well. Each participant was paid a bonus of $20.00 for the com-
pletion of the study if all urine samples were collected as
instructed. This was done, not as an inducement to participate,
but to offset the inconvenience and potential aggravation of
providing total urine collection for up to 72 hours.

As with the blueberry study (See Section 4.2), the volun-
teers were divided into two subgroups. The first, Group A, was
assigned to wear patch monitors and gloves, while the second were
to have no unusual impediments to exposure, which the gloves
might constitute. Thus, Group B wore neither gloves nor patches
at any time during the study. All subjects were instructed to
collect a urine specimen before they entered the field on Monday
to serve as a pre-exposure control. On Monday Group A was pro-
vided light-weight cotton gloves to be worn throughout the work-
day while picking berries. During the lunch break the gloves
were removed and new gloves issued after the break. Also, new
gloves were provided if a pair became too soiled or wet.

On Tuesday Group A was outfitted with cotton gauze-patch
monitors, in addition to the cotton gloves, to measure total
dermal exposure. Details of the placement and handling of the
patches and gloves are contained in Appendix A.

The collection of urine specimens was scheduled to begin on
Wednesday when it was assumed excretion would have reached some-
thing near steady state. Starting Tuesday after work all sub-
jects were provided with 1-liter plastic specimen bottles and
instructed to collect their urine for the remainder of the 72

hours of the study in the following regimen: Night samples to go from the termination of work to through the next morning's void; day samples from that point through the termination of work.

The owner of this plot did not select individuals for his crew, but allowed anyone who wished to do so to come and pick; he merely decided which portions of the field would be harvested each day. In spite of the fluid nature of the work force, there were a number of family groups that either came from the surrounding area or followed the hand harvest crops through Oregon and Washington as migrants, and these groups made up a relatively stable population at the study site for the duration of the experiment. This characteristic of the work force also meant that there were children available for inclusion in the study who were younger than the 12-year old legal age limit for children who can be hired directly by a grower. Also, the task of recruiting the participation of youngsters with parental approval was greatly simplified when the parents were also participating.

5.3 Sample Storage Handling and Preparation

Urine samples were stored on ice for no more than 4-6 hours and transported to the laboratory the same day as they were received from the subjects. Individual urine sample volumes were measured and duplicate 20 mL aliquots were pipetted into glass ampules to which 1.5 mL of concentrated hydrochloric acid was added as a preservative (resulting in a final pH of less than 0.5). The ampules were sealed and stored at room temperature.

Gloves and patches were collected from participants by project personnel and stored in zip-loc plastic bags. (See section 6.7 of the QA Plan for sample preservation procedures.)

5.4 analytical Procedures

Extraction of samples was as detailed in Section 9 of the Quality Assurance Plan.

Benomyl residues were analyzed by reverse-phase HPLC using a Waters 6000A dual pump Solvent Delivery System, a WISP Model 710 A automatic sample processor, a Waters Model 720 System Controller with a Model 730 Data Module and a Model 4530 Variable Wavelength Detector. A μBondapak C_{18} reverse-phase column (25 cm X 2 mm ID) was capable of separating benomyl from interference by substances originating in the field. The mobile phase found to be most effective was 65% acetonitrile and 35% water. Chromatographic conditions for benomyl analysis are in Table 5.3.

Since benomyl spontaneously converts to Carbendazim in the environment, it is the latter compound that is found in all personal and environmental samples, if present at all. Benomyl has a substantially longer retention time than does Carbendazim under the chromatographic conditions describe above, and it is desirable to convert the Carbendazim back to benomyl in order to better separate the analyte of interest from interferences. This was accomplished by the addition of 20 microliters of butyl isocyanate to each sample as it was prepared in its autosampler vial. This treatment assured a large, stable benomyl peak, in

standards, spiked blanks and samples, alike.

TABLE 5.3

Chromatographic Parameters
for the
Analysis of Benomyl

Column	25 cm X 2.0 mm C_{18} μBondapak with a C_{18} Guard-PAK precolumn
Mobile Phase	65% Acetonitrile, 35% Water
Flow Rate	2.0 ml/min.
Detector Parameters	Wavelength: 292 nm Sensitivity: 0.02 AUFS
Integration Parameters	Peak Width: 30 Noise Rejection: 3.0 Chart Speed 0.5 cm/min Run Time: 10 min

5.5 Crew Characteristics

Nearly thirty volunteers were recruited from among the work force of more than 80 which was found already working at the site. Twenty-two subjects completed enough of the study to be included in the data set; although, only sixteen lasted through the entire study. The physical characteristics of the participants in the blackberry study are contained in Table 5.4. As can be seen, five (22.7%) of the volunteers were ten years old or below, and another five were between ten and fifteen. Of the twelve people in Group A (wearing gloves and patches), there were three (25%) who were ten or less, while two (16.7%) were between ten and fifteen.

Table 5.4

ABSTAT 3.00   BLACKBERRY STUDY, PERSONAL CHARACTERISTICS OF THE CREW   FILE: 8302-1   REV# 4

COMMAND: PRINT DATA

VARIABLES:

CASE	1 SUBJECT	2 GROUP	3 SEX	4 AGE	5 WGHTKG	6 HEIGHTCM	7 AREAM2
1	1.00000	1.00000	1.00000	37.0000	113.400	180.000	2.35000
2	2.00000	1.00000	1.00000	31.0000	68.0000	190.000	1.85000
3	3.00000	1.00000	2.00000	49.0000	93.4000	170.000	2.05000
4	4.00000	1.00000	2.00000	25.0000	56.2000	168.000	1.60000
5	5.00000	1.00000	2.00000	10.0000	22.7000	128.000	0.900000
6	6.00000	1.00000	2.00000	7.00000	20.4000	118.000	0.800000
7	7.00000	1.00000	1.00000	11.0000	31.8000	140.000	1.20000
8	8.00000	1.00000	1.00000	9.00000	34.0000	143.000	1.20000
9	9.00000	1.00000	1.00000	21.0000	68.9000	170.000	1.80000
10	10.0000	1.00000	2.00000	39.0000	57.2000	153.000	1.55000
11	11.0000	1.00000	2.00000	19.0000	117.900	162.000	2.30000
12	12.0000	1.00000	2.00000	15.0000	94.8000	154.000	2.00000
13	13.0000	2.00000	2.00000	11.0000	36.3000	141.000	1.20000
14	14.0000	2.00000	1.00000	8.00000	31.3000	129.000	1.05000
15	15.0000	2.00000	1.00000	33.0000	99.8000	175.000	2.20000
16	16.0000	2.00000	2.00000	30.0000	73.0000	173.000	1.85000
17	21.0000	2.00000	2.00000	45.0000	68.0000	170.000	1.75000
18	22.0000	2.00000	2.00000	11.0000	49.0000	157.000	1.45000
19	23.0000	2.00000	1.00000	42.0000	56.7000	187.000	1.70000
20	24.0000	2.00000	2.00000	28.0000	59.0000	162.000	1.60000
21	28.0000	2.00000	1.00000	12.0000	68.0000	154.000	1.70000
22	29.0000	2.00000	2.00000	10.0000	58.1000	159.000	1.60000

5.6 Results

All of the dermal patch data was below the limit of detection for benomyl. Foliar residues and amounts of benomyl in the gloves of the workers were, however, sufficient to quantitate. Foliar residues were collected on days 17, 19 and 20 post application. Figure 5.1 is a scatter-plot of these residue values versus day post-application. The corresponding regression analysis, Table 5.5, results in an F value of 4.21 which indicates that the regression is significant at the 90% level.

Using the regression equation to estimate the decay curve for all five days allows an investigation of the relation between hand exposure, as measured by the glove residues, and the residue on the foliage. Figure 5.2 shows a scatter-plot of the daily exposure rate, averaged across the entire crew, and the estimated residue level for that day. Table 5.6 shows the result of the corresponding regression which is significant at above the 95% level.

Table 5.7 contains the glove exposure rate, in mg/hr, by day and individual worker. The average exposure rate was calculated for each worker. These values are also given in Table 5.7. Figure 5.3 is a scatter-plot of the average individual glove exposure rate vs. age which suggests that the hand exposure rate is less for young workers than for adults. Taking age twelve as the dividing line between children and adults, for present purposes, a Mann-Whitney U test was performed to test the hypothesis that the distribution of hand exposures was the same for children

and adults against the alternate hypothesis that the exposure of the children was less. The U value was calculated to be 5 which, for 4 children and 8 adults, would be observed with probability 0.036 under H_o. Hence, we conclude that the children do have a lower average hand exposure than the adults. In contrast to the blueberry study, the absence of yield data makes it impossible to verify that differences in workrate account for this difference in exposure, but it seems highly likely that this is the case.

As was done in the case of blueberries, the average glove exposure for each individual was normalized by body weight, resulting in a exposure rate expressed in mg/kg/hr. This value was regressed against age with the corresponding scatter-plot shown as Figure 5.4. The value of the F statistic was 0.355 with the corresponding r^2 equal to 0.0034, indicating an essentially random relation between these variables. Hence, as in the blueberry study, adults have a higher total exposure than children; but, on a mg/kg/hr basis, there is no evidence of differences in exposure as a function of age.

Figure 5.1

ABSTAT 3.00   BLACKBERRY STUDY, RESIDUE DECAY (NG/CM2) VS DPA   FILE: PUNCH2   REV#12

COMMAND: PLOT

MISSING VALUE TREATMENT: LISTWISE

```
           15.0000        16.6667        18.3333        20.0000        21.6667        23.3333        25.0000
                 15.8333        17.5000        19.1667        20.8333        22.5000        24.1667
           -+-------+------+------+------+------+------+------+------+------+------+------+------+------+------+-----+
  500.000  +
  497.917  +
  495.833  +
  493.750  +
  491.667  +
  489.583  +
  487.500  +
  485.417  +              1
  483.333  +
  481.250  +
  479.167  +
  477.083  +
  475.000  +              1
  472.917  +
  470.833  +
  468.750  +                                   1
  466.666  +
0 464.583  +
4 462.500  +
  460.416  +
  458.333  +
N 456.250  +
G 454.166  +
C 452.083  +
M 450.000  +
2 447.916  +
  445.833  +
  443.750  +                           2
  441.666  +
  439.583  +
  437.500  +
  435.416  +
  433.333  +
  431.250  +
  429.166  +
  427.083  +
  425.000  +
  422.916  +
  420.833  +
  418.750  +
  416.666  +
  414.583  +
  412.500  +
  410.416  +
  408.333  +
  406.250  +
  404.166  +                                 1
  402.083  +
  400.000  +
           -+-------+------+------+------+------+------+------+------+------+------+------+------+------+------+-----+
           15.0000        16.6667        18.3333        20.0000        21.6667        23.3333        25.0000
                 15.8333        17.5000        19.1667        20.8333        22.5000        24.1667
```

1 DPA

Table 5.5

ABSTAT 3.00   BLACKBERRY STUDY, RESIDUE DECAY (NG/CM2) VS DPA   FILE: PUNCH2

COMMAND: REGR

MISSING VALUE TREATMENT: LISTWISE

*** MULTIPLE LINEAR REGRESSION ***

DEPENDENT VARIABLE: 4 NGCM2   6 VALID CASES

COEFF OF DETERMINATION: 0.513016   ESTIMATED CONSTANT TERM: 741.793
MULTIPLE CORR COEFF: 0.716252   STANDARD ERROR OF ESTIMATE: 22.8753

ANALYSIS OF VARIANCE FOR THE REGRESSION:

SOURCE OF VARIANCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN OF SQUARES	F TEST
REGRESSION	1	2205.00	2205.00	4.21383
RESIDUALS	4	2093.11	523.277	
TOTAL	5	4298.11		

VARIABLE	REGRESSION COEFFICIENT	STANDARDIZED COEFFICIENT	CORRELATION WITH DEPENDENT
1 DPA	-15.3704	-0.716251	-0.716251

DURBIN-WATSON =   2.71818

Figure 5.2

ABSTAT 3.00   BLACKBERRY STUDY, AVERAGE EXPOSURE RATE VS ESTIMATED RESIDUES   FILE: PUNCH3   REV#16

COMMAND: PLOT

MISSING VALUE TREATMENT: LISTWISE

```
            400.000       416.667       433.333       450.000       466.667       483.333       500.000
                 408.333       425.000       441.667       458.333       475.000       491.667
             -+------+------+------+------+------+------+------+------+------+------+------+------+------+
     0.300000 +
     0.295833 +
     0.291667 +
     0.287500 +
     0.283333 +
     0.279167 +
     0.275000 +
     0.270833 +
     0.266666 +
     0.262500 +                                                         1
     0.258333 +
     0.254166 +
     0.250000 +                                                                    1
     0.245833 +
     0.241666 +
     0.237500 +
     0.233333 +
  0  0.229166 +
  7  0.225000 +
     0.220833 +
     0.216666 +
  A  0.212500 +
  V  0.208333 +
  E  0.204166 +
  X  0.200000 +
  P  0.195833 +
  O  0.191666 +
  S  0.187500 +
     0.183333 +
     0.179166 +
     0.174999 +
     0.170833 +
     0.166666 +
     0.162499 +
     0.158333 +
     0.154166 +
     0.149999 +                                     1
     0.145833 +
     0.141666 +
     0.137499 +                             1
     0.133333 +              1
     0.129166 +
     0.124999 +
     0.120833 +
     0.116666 +
     0.112499 +
     0.108333 +
     0.104166 +
  1.00000E-01 +
             -+------+------+------+------+------+------+------+------+------+------+------+------+------+
            400.000       416.667       433.333       450.000       466.667       483.333       500.000
                 408.333       425.000       441.667       458.333       475.000       491.667
```

6 EST

Table 5.6

ABSTAT 3.00   BLACKBERRY STUDY, AVERAGE EXPOSURE RATE VS ESTIMATED RESIDUES   FILE: PUNCH3

COMMAND: REGR

MISSING VALUE TREATMENT: LISTWISE

*** MULTIPLE LINEAR REGRESSION ***

DEPENDENT VARIABLE: 7 AVEXPOS   5 VALID CASES

COEFF OF DETERMINATION: 0.776790   ESTIMATED CONSTANT TERM: -0.839192
MULTIPLE CORR COEFF: 0.881357   STANDARD ERROR OF ESTIMATE: 3.423E-02

ANALYSIS OF VARIANCE FOR THE REGRESSION:

SOURCE OF VARIANCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN OF SQUARES	F TEST
REGRESSION	1	1.223E-02	1.223E-02	10.4403
RESIDUALS	3	3.515E-03	1.171E-03	
TOTAL	4	1.574E-02		

VARIABLE	REGRESSION COEFFICIENT	STANDARDIZED COEFFICIENT	CORRELATION WITH DEPENDENT
6 EST	2.285E-03	0.881357	0.881357

DURBIN-WATSON =   1.33459

Table 5.7

ABSTAT 3.00   BLACKBERRY STUDY, GLOVE EXPOSURE DATA, ALL DAYS   FILE: C:8302-P   REV#12

COMMAND: PRINT DATA

MISSING VALUE TREATMENT: INCLUDE

VARIABLES:

CASE	1 SUBJECT	7 GL1	8 GL2	9 GL3	10 GL4	11 GL5	12 AVGLRATE	13 WGLRATE
1	1.00000	0.549846	0.469895	0.342956	0.139692	0.113778	0.323233	2.85038E-03
2	2.00000	0.342769	0.230706	0.261391	0.203692	0.231556	0.254023	3.73563E-03
3	3.00000	0.223716	0.382164	0.244348	0.162000	0.179755	0.238396	2.55242E-03
4	4.00000	0.198595	0.214153	0.130957	0.143077	0.120444	0.161445	2.87269E-03
5	5.00000	0.161276	0.232982	6.92174E-02	0.129231	0.109778	0.140497	6.18929E-03
6	6.00000	0.245500	0.258432	0.128522	0.167692	0.183778	0.196785	9.64631E-03
7	7.00000	0.120154	0.161390	9.79131E-02	9.92308E-02	7.93334E-02	0.111604	3.50957E-03
8	8.00000	8.45896E-02	0.210842	6.50435E-02	7.75385E-02	7.95556E-02	0.103514	3.04452E-03
9	9.00000	9.24053E-02	0.163817	9.65000E-02	MISSING	MISSING	0.117574	1.70644E-03
10	10.0000	0.604182	0.432267	0.207500	MISSING	MISSING	0.414649	7.24912E-03
11	11.0000	0.251091	0.255733	8.45000E-02	MISSING	MISSING	0.197108	1.67182E-03
12	12.0000	0.139273	0.139733	8.85000E-02	MISSING	MISSING	0.122502	1.29221E-03

40

Figure 5.3

ABSTAT 3.00   BLACKBERRY STUDY, AVERAGE EXPOSURE RATE (MG/HR) VS AGE   FILE: C:8302-P   REV#12

COMMAND: PLOT

MISSING VALUE TREATMENT: LISTWISE

3 AGE

41
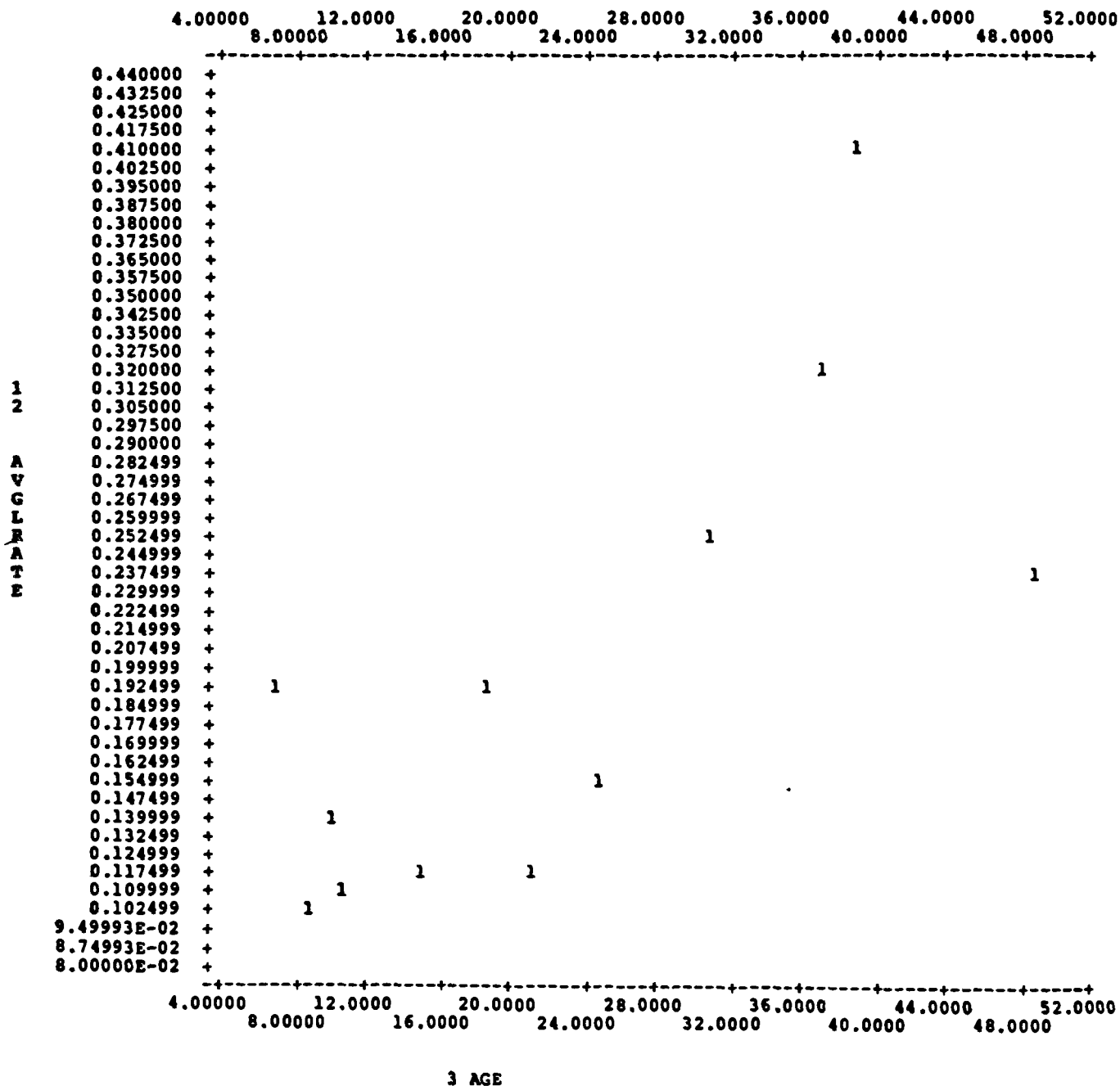
Figure 5.4

ABSTAT 3.00   BLACKBERRY STUDY, AVERAGE EXPOS. NORMALIZED FOR WIEGHT VS AGE   FILE: C:8302-P   REV#12

COMMAND: PLOT

MISSING VALUE TREATMENT: LISTWISE

3 AGE

42
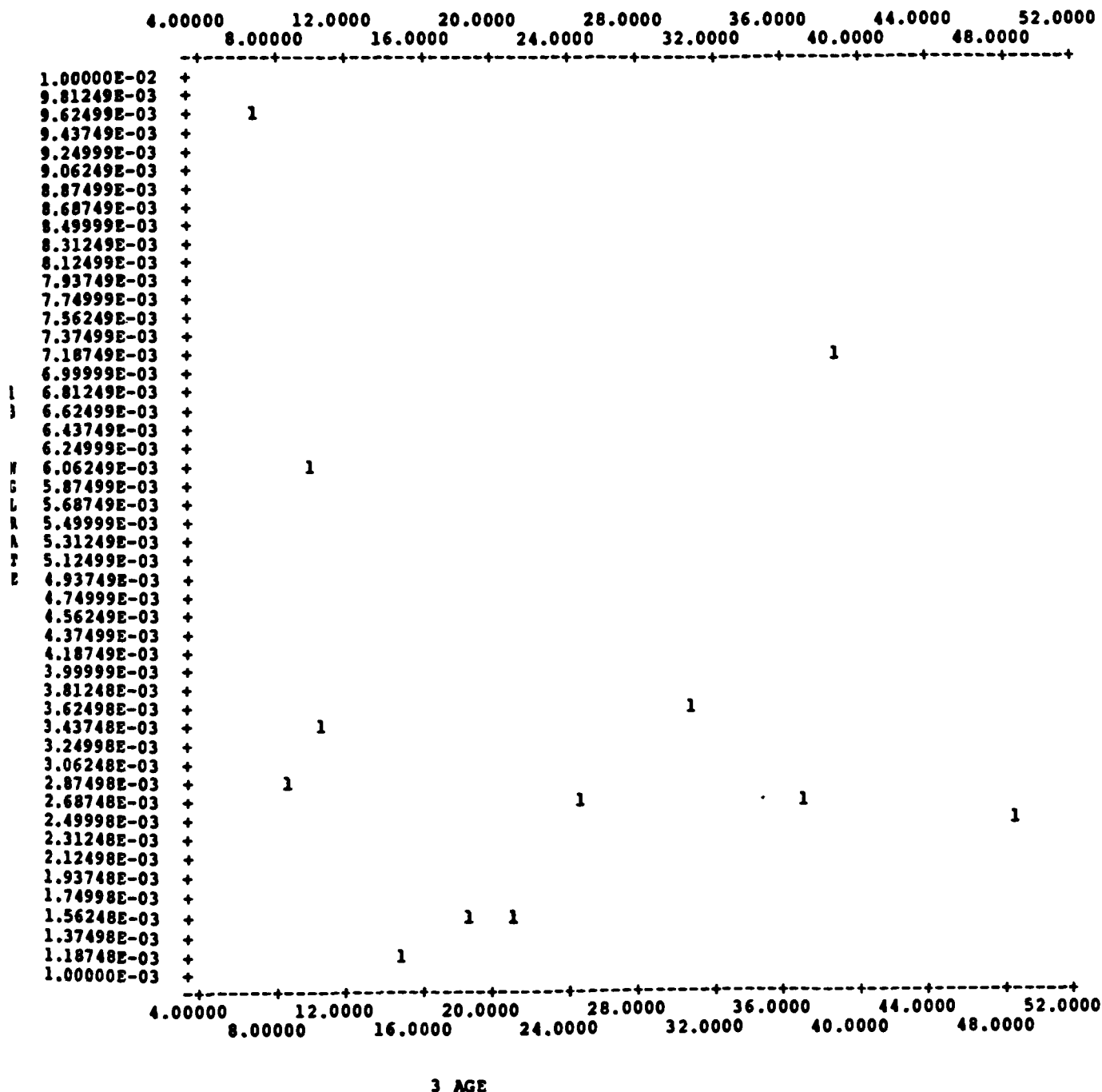
6. HARVESTER EXPOSURES TO BENLATE IN RASPBERRIES

6.1 Introduction

In a continuing effort to develop experimental data on the exposure to pesticides of fruit harvesters of different ages, a study was conducted involving the exposure of raspberry harvesters to residues of the pesticide Benlate (benomyl). The volunteers for this study were divided into two groups, one provided with cotton gloves and dermal patches to measure dermal exposures and the other not so provided so that there would be no unnatural barrier to their exposure. Urine samples were collected from all subjects to be analyzed for metabolites of the pesticide.

The purpose of the study was two-fold. The primary intent was to measure the worker's dermal exposures and determine whether a significant difference exists between the exposures experienced by children and adults. Second, an attempt was to be made to correlate dermal exposure to benlate as determined by patch and glove monitors with that determined by the concentration of the metabolite of the pesticide excreted in the urine of the exposed workers; An additional, but secondary goal, was to contrast the absorption of the pesticide, as measured by the urinary metabolite concentration, between the group wearing gloves with that not so protected with the object of determining the degree of protection afforded.

6.2 Site and Experimental Design

The site chosen for an exposure study among raspberry harvesters was a 50 acre plot of the Canby variety located on a berry farm in Troutdale, Oregon. It was late in the season for this variety, and the plot had been picked over at least one time prior to the commencement of the study. This field had been treated with very few insecticides, herbicides or fungicides; but the spray history up to the study date, such as it was, is delineated in Table 6.1. The most recent treatment had been with Lannate on the first and second of June, some 40 days prior to our crew's entry. Even though it was 60 days post application, the benomyl treatment was chosen as the one to use in the monitoring study, since no readily detectable urinary metabolites could be expected from Lannate. However, we did know some of the pertinent metabolic information regarding benomyl.

TABLE 6.1

1983 Spray Schedule*

Canby Raspberry Plot

Date	Product	Application Rate
25 February	Orthrex (sic)	3 gal/A
5-7 April	Karmex (diuron)	1.6 lb/A
	Paraquat	1 qt/A
15-18 May	Benlate	2 lb/A
1-2 June	Lannate	25 gal/A (sic)

* This table does not contain all of the 1983 spray history, but terminates at the time of the study.

The study lasted for four days, running from Monday, 11 July 1983 through Thursday, 14 July 1983. On-site weather observations for the study site covering 11 through 14 July are found in Table 6.2. This particular study was plagued with frequent rains, cutting the workdays short and keeping the foliage, the subjects, and the glove and patch monitors wet much of the time. Table 6.2 also includes information about the crew in addition to weather data. For a number of reasons, individual times for entry to and exit from the field were not recorded, obviating the assignment of individual exposure times. This arose, in large part, due to the fact that as part of a school bus operation this group arrived at the field all at one time, and the PHAP staff was obliged to conduct its business (collection of forms, taking down personal information, applying patch monitors and gloves, etc.) to all the subjects at once and in as small a time span as possible; therefore, movement into and out of the field was taken for the group, altogether.

On Thursday, July 14th, the Canby plot had been completely harvested out soon after the crew began working in it; so the entire operation was moved to a plot adjacent to the Canbies that happened to be the Meriam variety. This plot was made up of considerably older plants than the Canbies and had considerably less foliage. Less foliage resulted in lowering the potential for the workers to contact and pick up residues. In addition, it was impossible to determine whether this particular plot had received the same pesticide regimen as the Canby plot.

TABLE 6.2

Weather and General Observations
of Conditions in the
Canby Raspberry Plot

Date	Time	Dry Bulb (°C.)	Wet Bulb (°C.)	% RH	Description of Weather and Other Observations
11 July	0630				Rain the night before, heavy dew on leaves. School bus arrived, collected evening (pre-exposure) urines.
	0730				Completed patching Group A.
	0735	15.3	14.2	91	Sunny and clear, light wind.
	0855				Dew beginning to dry. Workers' shirts are wet from dew.
	1200				Crew left field.
12 July	0640				Crew arrived. Sunny with spotty clouds. Heavy dew.
	0655				Group A completely patched.
	0915	18.9			
	0945				Heavy Clouds have moved in. Worker 11 arrived.
	1000				Drizzle begun.
	1010-1015				Crew leaves field for 1/2 hour lunch. Gloves are very wet; Lower legs dry; Lower arms wet.
	1250				Crew leaves field.

TABLE 6.2

Weather and General Observations of Conditions in the Canby Raspberry Plot cont.

Date	Time	Dry Bulb (°C.)	Wet Bulb (°C.)	% RH	Description of Weather and Other Observations
13 July	0640				Crew into field. Drizzle.
	0947	18.6			
	1020				Drizzle turns to heavy rain; crew leaves field for the day.
14 July	0630				Crew into field.
	0700				Worker 21 arrived.
	0800				Canby plot picked out; Crew moved to an adjacent plot, Meriam variety.
	0845	15.0	10.0	53	Good weather, no clouds.
	1000				Crew leaves field for 1/2 hour lunch.
	1115	18.1	14.7	72	No clouds.
	1130				Meriams picked out; crew leaves and will not return Friday.

Consent forms approved by the Committee for the Protection

of Human Subjects at the University of California at Berkeley

(see Appendix D) were distributed to each participant along with

detailed instructions for their particular subgroup (Appendix D).

In order for anyone to be allowed to join the Study, they were

required to return their consent form signed; and if they were

minors, as was this entire crew, their form had to be signed by

their parents, as well. Each participant was paid a bonus of

$20.00 for the completion of the study if all urine samples were

collected as instructed. This was done, not as an inducement to participate, but to offset the inconvenience and potential aggravation of providing total urine collection for up to 72 hours.

As with the blueberry study (See Section 4.2), the volunteers were divided into two subgroups. The first, Group A, was assigned to wear patch monitors and gloves, while the second were to have no unusual impediments to exposure, which the gloves might constitute. Thus, Group B wore neither gloves nor patches at any time during the study. All subjects were instructed to collect a urine specimen before they entered the field on Monday to serve as a pre-exposure control. On Monday Group A was provided light-weight cotton gloves to be worn throughout the workday while picking berries. During the lunch break the gloves were removed and new gloves issued after the break. Also, new gloves were provided if a pair became too soiled or wet. However, adhering to this policy was difficult in this particular study, because of the heavy moisture on the foliage due to the great deal of dew, drizzle and rain experienced during the week of 11 to 14 July.

On Tuesday Group A was outfitted with cotton gauze-patch monitors, in addition to the cotton gloves, to measure total dermal exposure. Details of the placement and handling of the patches and gloves are contained in Appendix A. The initial distribution of subjects between the two groups was sufficiently imbalanced (14 to 10) that one person (Subject 13) was moved from Group A to Group B on Tuesday. Table 6.3 does not reflect this

shift of one subject from one group to another, but simply shows Subject 13 as part of Group 2 or B.

The collection of urine specimens was scheduled to begin on Wednesday when it was assumed excretion would have reached something near steady state. Starting Tuesday after work all subjects were provided with 1-liter plastic specimen bottles and instructed to collect their urine for the remainder of the 72 hours of the study in the following regimen: Night samples to go from the termination of work to through the next morning's void; day samples from that point through the termination of work.

The owners of the raspberry farm had both a drive-up work force and a school bus operation. The former is much the same as was described for the Marion blackberry field, where just about anyone who wished to do so could come and pick. These people were kept segregated from the monitoring study and did not work in the same plot with our crew at any time.

The school bus crew was designated to work with the monitoring study and was constituted the same as the crews that had worked with this organization in strawberries in Corvallis, Oregon, during 1981 and 1982. The grower contracts with a Crew Boss for a crew. The Crew Boss recruits a school bus driver who contracts with the school district to rent one of the district's busses for the summer. A crew of thirty to forty children is recruited from the local school(s) (with parental consent, and/or urging). On work days the Crew Boss and Driver go to each child's house and picks them up before work and returns them home

after work.   In the field, the harvesters are paid piece rate, and the Crew Boss is credited for the produce harvested.

6.3 Sample Storage Handling and Preparation

Urine samples were stored on ice for no more than 4-6 hours and transported to the laboratory the same day as they were received from the subjects.   Individual urine sample volumes were measured and duplicate 20 mL aliquots were pipetted into glass ampules to which 1.5 mL of concentrated hydrochloric acid was added as a preservative (resulting in a final pH of less than 0.5).   The ampules were sealed and stored at room temperature.

Gloves and patches were collected from participants by project personnel and stored in zip-loc plastic bags.   (See section 6.7 of the QA Plan for sample preservation procedures.)

6.4 Analytical Procedures

Extraction of samples was as detailed in Section 9 of the Quality Assurance Plan.   A description of the chromatographic analysis of benomyl is contained in Section 5.4, including a listing of the chromatographic conditions in Table 5.3.

6.5 Crew Characteristics

This group, because of the fact that it was a school bus operation, was made up almost exclusively of youngsters; only two individuals were older than 16 years, and they were friends or related to the Crew Boss.   Table 6.3 shows the physical characteristics of the entire crew of volunteers for the monitoring

study which consisted of 24 individuals, of which 13 were assigned to Group A (wearing glove and patch monitors) while 11 made up Group B.

Taking the crew as a whole, the ages distributed as follows: Ten years or less, 1 (4%); 11 and 12 years, 6 (25%); 13 - 15 years, 12 (50%); and 16 years and older, 5 (21%). They were divided evenly between the sexes, and ranged in weight from 31 to 86 kg with the bulk (54%) falling into the 40 - 60 kg range.

The group wearing patches (Group A), numbering 13, ranged in age from 9 to 16 and were distributed thus: Ten years or less, 1 (8%); 11 and 12 years, 4 (31%); 13 - 15 years, 5 (38%); and 16 years, 3 (23%). This subgroup was made up of seven males and six females. Weights ranged from 32 to 77 kg, again with the greatest number of subjects (69%) falling into the 40 to 60 kg range.

6.6 Results

Because this field had been treated with benomyl 60 days prior to entry, the foliar residues were much lower than was the case in the blackberry study. As in that case, all of the dermal patch data was below the limit of detection for benomyl. The foliar residue data is shown in Table 6.4. No clear time trend would be expected in this case since the sampling interval was over only two days and sampling variability is high when residue levels are very low. Hence, the residue environment is best characterized by the mean of all sample values which was 175 ng cm^{-2}.

COMMAND: PRINT DATA

VARIABLES:

CASE	1 SUBJECT	2 GROUP	3 SEX	4 AGE	5 WGHTKG	6 HEIGHTCM	7 AREAM2
1	1.00000	1.00000	1.00000	12.0000	43.1000	142.000	1.30000
2	2.00000	1.00000	2.00000	9.00000	31.8000	135.000	1.10000
3	3.00000	1.00000	1.00000	15.0000	77.1000	176.000	1.90000
4	4.00000	1.00000	1.00000	15.0000	61.2000	175.000	1.70000
5	6.00000	1.00000	1.00000	16.0000	77.1000	175.000	1.90000
6	7.00000	1.00000	2.00000	13.0000	58.1000	162.000	1.60000
7	12.0000	1.00000	1.00000	13.0000	44.0000	157.000	1.40000
8	15.0000	1.00000	2.00000	16.0000	52.2000	157.000	1.50000
9	16.0000	1.00000	1.00000	16.0000	56.7000	170.000	1.60000
10	17.0000	1.00000	1.00000	15.0000	59.0000	173.000	1.65000
11	18.0000	1.00000	2.00000	12.0000	48.5000	160.000	1.50000
12	19.0000	1.00000	2.00000	12.0000	51.3000	170.000	1.55000
13	20.0000	1.00000	2.00000	12.0000	54.0000	165.000	1.55000
14	5.00000	2.00000	1.00000	15.0000	45.4000	168.000	1.50000
15	8.00000	2.00000	2.00000	15.0000	61.7000	150.000	1.60000
16	9.00000	2.00000	2.00000	13.0000	63.5000	160.000	1.65000
17	10.0000	2.00000	1.00000	14.0000	43.1000	152.000	1.35000
18	11.0000	2.00000	1.00000	14.0000	81.6000	183.000	2.00000
19	13.0000	2.00000	2.00000	11.0000	35.4000	141.000	1.20000
20	14.0000	2.00000	2.00000	14.0000	49.0000	156.000	1.45000
21	21.0000	2.00000	2.00000	12.0000	36.3000	152.000	1.25000
22	22.0000	2.00000	2.00000	28.0000	86.2000	162.000	1.95000
23	23.0000	2.00000	1.00000	19.0000	77.1000	180.000	1.90000
24	24.0000	2.00000	1.00000	13.0000	52.6000	164.000	1.55000

TABLE 6.4

Foliar Residue Data

Raspberry Study

Sample Number	Total Micrograms	Number of Leaf Disks*	Residue ng/cm^{2}**
8301-P-61.1	66.6	43	219
8301-P-61.2	45.1	43	148
8301-P-62.1	43.0	47	129
8301-P-62.2	68.8	48	203
		Average	175
		s	43
		% RSD	25

* 3.0 cm diameter.
** Single side basis.

As in the blackberry study, the measure of exposure is the residue found in the gloves. Table 6.5 contains the glove exposure rate, in μg/hr, by day and individual worker. The average glove exposure rate was calculated for each worker for the entire course of the study. These values are also shown in Table 6.5. Figure 6.1 is a scatterplot of this average exposure rate vs age, which is mildly suggestive of the same positive correlation between exposure and age which was seen in both the blackberry and blueberry studies. The regression results are given in Table 6.6 and indicate an F value on the verge of significance, but a very low r^2 value of 0.27.

As in the blueberry and blackberry studies, even this weak correlation between exposure and age disappears if the exposure measure is normalized by the body weight of the individual

worker.   Figure 6.2 shows the scatterplot of exposure in
μg/kg/hr, versus age.   As expected, the F value declines to 0.40
with an r^2 of 0.17 as shown in Table 6.7.   Note that these
exposure values are given in micrograms rather than in milligrams
as in the previous studies.   Therefore, despite the very low
foliar residues and the adverse weather conditions encountered in
this study, the conclusion is the same: Older workers tend to be
exposed to a greater total residue than younger workers, but when
exposure is measured on a mg/kg basis, there is no evidence of an
age-related difference in exposure.

Table 6.5

RASPBERRY STUDY, GLOVE EXPOSURE DATA, ALL DAYS   FILE: 8301-P   REV#22

COMMAND: PRINT DATA

MISSING VALUE TREATMENT: INCLUDE

VARIABLES:

CASE	1 SUBJECT	7 GL1	8 GL2	9 GL3	10 GL4	11 AVGLRATE	12 WGLRATE
1	1.00000	51.2000	19.4445	37.0270	32.0000	34.9179	0.810160
2	2.00000	27.2000	7.11111	20.3514	35.5556	22.5545	0.709262
3	3.00000	22.0000	21.8519	25.4324	82.0000	37.8211	0.490546
4	4.00000	112.200	30.7408	33.5135	22.8889	49.8358	0.814310
5	6.00000	83.0000	MISSING	35.1351	54.0000	57.3784	0.744207
6	7.00000	145.000	22.0370	14.0541	28.4444	52.3839	0.901616
7	12.0000	34.0000	23.3333	17.6487	28.8889	25.9677	0.590175
8	13.0000	53.8000	MISSING	MISSING	MISSING	53.8000	1.51977
9	15.0000	92.0000	0.00000	73.2433	40.6667	51.4775	0.986159
10	16.0000	72.4000	0.00000	79.1892	32.8889	46.1195	0.813395
11	17.0000	23.2000	22.7778	22.3243	71.5556	34.9644	0.592617
12	18.0000	37.8000	14.0000	25.3514	26.4444	25.8990	0.533999
13	19.0000	67.8000	21.1111	22.2703	49.5556	40.1842	0.783319
14	20.0000	38.6000	MISSING	47.2973	36.6667	40.8547	0.756568

Figure 6.1

STAT 3.00   RASPBERRY STUDY, MEAN EXPOSURE RATE (UG/HR) VS AGE   FILE: 0301-P   REV#22

MMAND: PLOT

SSING VALUE TREATMENT: LISTWISE

```
              8.00000      9.50000     11.0000      12.5000     14.0000     15.5000     17.0000
                  8.75000      10.2500      11.7500      13.2500     14.7500     16.2500
             -+------+-----+------+-----+------+------+------+------+------+------+------+-----+
   58.0000  +
   57.2500  +                                                                    1
   56.5000  +
   55.7500  +
   55.0000  +
   54.2500  +
   53.5000  +                            1
   52.7500  +
   52.0000  +                                       1
   51.2500  +                                                           1
   50.5000  +
   49.7500  +                                                  1
   49.0000  +
   48.2500  +
   47.5000  +
   46.7500  +
   46.0000  +                                                           1
   45.2500  +
   44.5000  +
   43.7500  +
   43.0000  +
   42.2500  +
   41.5000  +
   40.7500  +                     1
   40.0000  +                     1
   39.2500  +
   38.5000  +
   37.7500  +                                                  1
   37.0000  +
   36.2500  +
   35.5000  +
   34.7500  +                     1                            1
   34.0000  +
   33.2500  +
   32.5000  +
   31.7500  +
   31.0000  +
   30.2500  +
   29.5000  +
   28.7500  +
   28.0000  +
   27.2500  +
   26.5000  +
   25.7500  +                   1          1
   25.0000  +
   24.2500  +
   23.5000  +
   22.7500  +
   22.0000  +         1
             -+------+-----+------+-----+------+------+------+------+------+------+------+-----+
              8.00000      9.50000     11.0000      12.5000     14.0000     15.5000     17.0000
                  8.75000      10.2500      11.7500      13.2500     14.7500     16.2500
```

                                    3 AGE

Table 6.6

RASPBERRY STUDY, MEAN EXPOSURE RATE VS AGE   `FILE: 8301-P

COMMAND: REGR

MISSING VALUE TREATMENT: LISTWISE

*** MULTIPLE LINEAR REGRESSION ***

DEPENDENT VARIABLE: 11 AVGLRATE   14 VALID CASES

COEFF OF DETERMINATION: 0.270291   ESTIMATED CONSTANT TERM: 4.91215
MULTIPLE CORR COEFF: 0.519896   STANDARD ERROR OF ESTIMATE: 10.0295

ANALYSIS OF VARIANCE FOR THE REGRESSION:

SOURCE OF VARIANCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN OF SQUARES	F TEST
REGRESSION	1	447.116	447.116	4.44492
RESIDUALS	12	1207.08	100.590	
TOTAL	13	1654.20		

VARIABLE	REGRESSION COEFFICIENT	STANDARDIZED COEFFICIENT	CORRELATION WITH DEPENDENT
3 AGE	2.70261	0.519895	0.519895

Figure 6.2

ABSTAT 3.00   RASPBERRY STUDY, EXPOS. RATE NORM. FOR WGHT. (UG/KG/HR) VS AGE   FILE: 8301-P   REV#22

COMMAND: PLOT

MISSING VALUE TREATMENT: LISTWISE

3 AGE

Table 6.7

COMMAND: REGR

MISSING VALUE TREATMENT: LISTWISE

*** MULTIPLE LINEAR REGRESSION ***

DEPENDENT VARIABLE: 12 WGLRATE   14 VALID CASES

COEFF OF DETERMINATION: 3.226E-02   ESTIMATED CONSTANT TERM: 1.06819
MULTIPLE CORR COEFF: 0.179615   STANDARD ERROR OF ESTIMATE: 0.258549

ANALYSIS OF VARIANCE FOR THE REGRESSION:

SOURCE OF VARIANCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN OF SQUARES	F TEST
REGRESSION	1	2.674E-02	2.674E-02	0.400043
RESIDUALS	12	0.802173	6.684E-02	
TOTAL	13	0.828915		

VARIABLE	REGRESSION COEFFICIENT	STANDARDIZED COEFFICIENT	CORRELATION WITH DEPENDENT
3 AGE	-2.090E-02	-0.179615	-0.179615

APPENDIX A

QUALITY ASSURANCE PROJECT PLAN

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PESTICIDE EXPOSURE BY HARVESTERS

OF BUSHBERRIES, TRAILING- AND

CANEBERRIES

by

John T. Leffingwell
Hugh R. McLean
Gunther Zweig

Quality Assurance Project Plan
Pesticide Hazard Assessment Project
University of California
Berkeley, California

Approval:

Principal Investigator:_____Date_____

Project QA Officer:_____Date_____

EPA Project Officer:_____Date_____

EPA QA Officer:_____Date_____

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3. PROJECT DESCRIPTION

The purposes of the proposed field studies to be conducted by the California PHAP during the summer of 1983 are several fold: 1) The harvesting activities of children in the cane-, bush- and trailing berry crops in all likelihood presents a different pesticide exposure pattern to pesticides than does strawberries because of substantial differences in the physical characteristics between the former set of crops and strawberries. Therefore, as an extension of the "youth-in-agriculture" line of monitoring studies we will attempt to determine the nature and extent of pesticide exposure suffered by children or youths harvesting these crops. This information will be compared and contrasted with like information for corresponding groups of adults. 2) It is of considerable general interest to compare the excretion of pesticide metabolites with whatever measures of dermal exposures that can be made on workers. Toward that end, two groups of subjects will be monitored in each crop type. One group will be monitored for dermal exposure to one or more pesticides, while the other group will give urine samples for metabolite analysis. In each study both groups will engage in both activities so that they will act as their own controls. As usual cognizance will be taken of age, height, weight and sex of the individual subjects in these studies.

Since the pesticides under consideration are generally compounds with low volatility (e.g., captan), exposures are expected to result from dermal contact; consequently, this route of exposure will be given major emphasis in the contemplated field studies. Dermal dosimeters currently in use in this laboratory consist of 12-ply, 3 x 3 inch surgical sponge (gauze pad) backed by a polythylene

moisture shield enclosed in a paper envelope that has a circular face opening

to expose 28 cm^2 (4.3 in^2) of the gauze pad. This configuration allows for

rapid assembly of the dosimeter and easy attachment to carrier garments such

as T-shirts. The potential for inhalation exposure will not be ignored,

however. Both aerosol and vapor samplers will be placed in the field for

general monitoring. At least two of the subjects will carry "breathing zone"

personal aerosol monitors. These monitors will be rotated among the subjects

at two hour intervals.

Since urine grab samples are of limited utility in interpreting metabolite

outputs, complete urine collections will be requested of the cooperating sub-

jects over the desired monitoring period. These will be done in as close to

12 hour blocks ("day" and "night") as the subjects can manage.

Environmental samples will be comprised of foliar leaf discs (48 x 3 cm

diameter punches per sample), soil samples (6 scoops of 8 x 10 x 1 cm deep

making in all some 600-800 g of soil) representative crop samples and area

aerosol collections which are backed up with charcoal tube vapor traps. All

environmental samples will be collected in the vicinity of the workers who are

being monitored.

All samples will be placed on dry ice immediately after they have been

collected. At the completion of sample collection they will be transported on

dry ice to the laboratory, transferred to a freezer and maintained at -10°C or

colder until just prior to extraction.

4. PROJECT ORGANIZATION

The following chart shows the organizational structure for developing and implementing QA Project Plans within the Berkeley PHAP. Acceptable QA procedures will be developed in cooperation with, and under the supervision of, the OPP Quality Assurance Officer. It is understood that the EPA project officer (Dr. C.W. Miller) will function as the Quality Assurance Officer in terms of:

1) providing guidance to the project on QA,

2) facilitating interlaboratory QA, and,

3) approving QA project plans.

The responsibility for the design and implementation of acciptable QA procedures lies with the Project Director of the Berkeley PHAP.


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┌─────────────────────┐
│ Quality Assurance   │
│  Officer OPP/HEB    │
└─────────────────────┘
          │
┌─────────────────────┐
│ EPA Project Officer │
│    NPHAP/HEB        │
└─────────────────────┘
          │
┌─────────────────────┐
│  Project Director   │
│   Berkeley PHAP     │
└─────────────────────┘
          │
┌─────────────────────────┐
│    Committee for the    │
│ Protection of Human     │
│      Subjects           │
└─────────────────────────┘
          │
┌──────────────┐  ┌──────────────┐  ┌──────────────┐
│ Chief Chemist│  │ Statistician │  │ Field Studies│
│              │  │              │  │  Supervisor  │
└──────────────┘  └──────────────┘  └──────────────┘
```
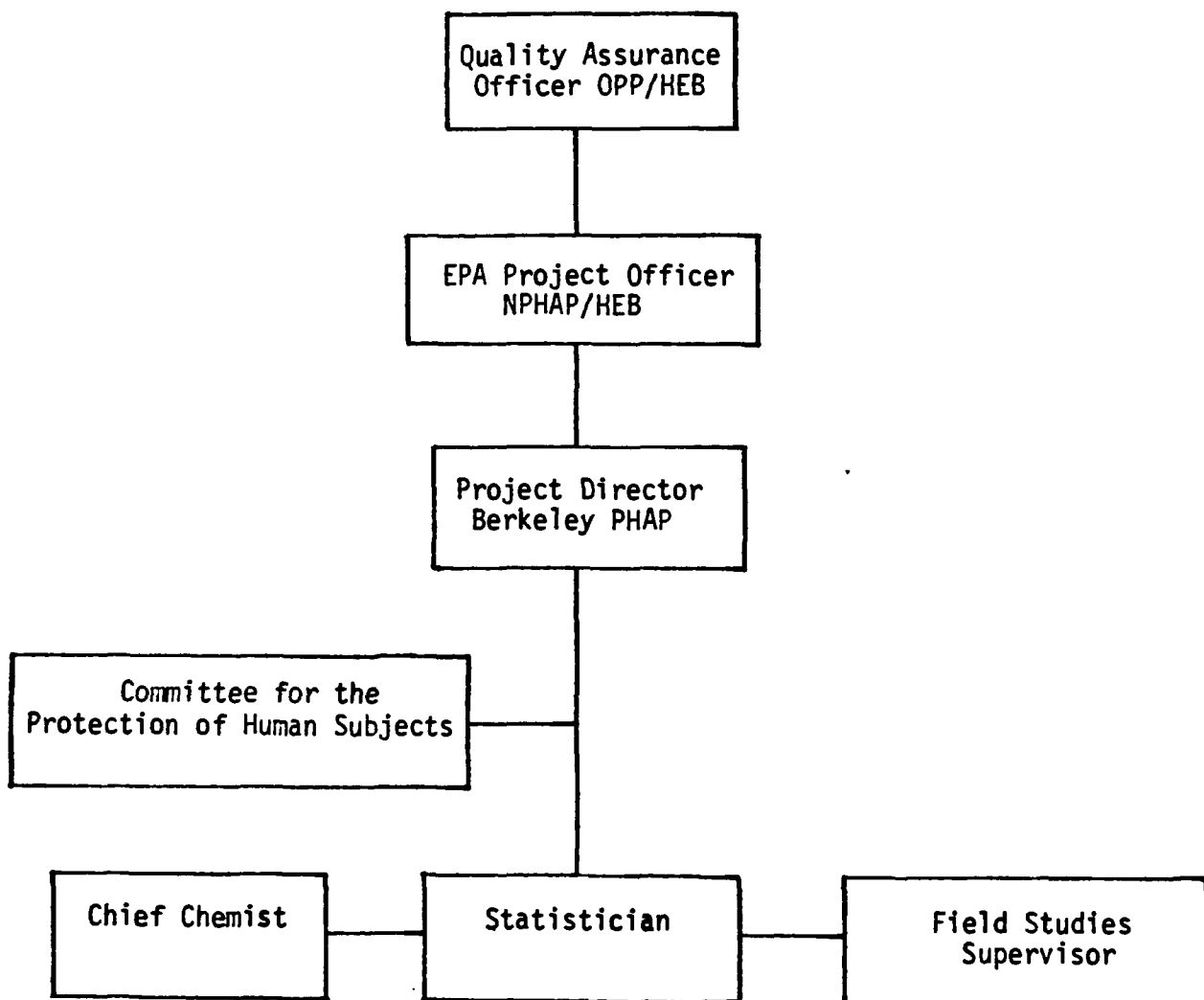
The Chief Chemist, with guidance and concurrence of the Project Director, is responsible for the design and implementation of QA procedures within the laboratory. He is responsible for superivising the laboratory's participation in any interlaboratory quality control programs. He also must design, schedule and evaluate interlaboratory QA procedures to insure confidence in the methodology and facilities used for all analyses.

5. QUALITY ASSURANCE OBJECTIVES

The measurements to be attempted in this study center on the estimation of dermal exposure of pesticides undergone by workers harvesting cane-, bush- and trailing berries. Since there is no standardized methodology for accomplishing this task, it is impossible to estimate accuracy. However, components of the method can be tested for precision and accuracy by employing the device of spiked blanks. These components include recovery of pesticide from gauze patches, gloves, aerosol and vapor samplers, and the analytical procedures used to assay the recovered residues.

For environmental samples, accuracy can be gauged by the taking of replicate samples. Spiked blanks are required here, as well, to determine precision and accuracy. Table 1.5 shows the best current estimates for the QA objectives for the measurements to be made during the berry harvester studies.

In reference to Table 1.5, since this study does not focus on only one pesticide or class of pesticides, the detailed methods of extraction and analysis cannot be foretold, and, in fact, can be developed and validated only after the exact combination of pesticides applied to a given field (to be monitored) have been reported. In general, however, the following references are applicable to Dermal Dosimeters:

1) McLean, H. R.; Futagake, S.; and Leffingwell, J. T.
   Loss of Paraoxon in aqueous acetonitrile extractions. Bull.
   Environ. Contam. & Toxicol. 18:247, 1977.

2) Popendorf, W.
   Exploring citrus harvesters exposure to pesticide contaminated
   foliar dust. Am. Industr. Hyg. Assoc. J. 41:652, 1980.

to Aerosol Monitors and Vapor Traps (for total dust and various pesticides):

National Institute for Occupational Safety & Health
NIOSH Manual of Analytical Methods, 2nd Ed.

vol. 1   DHEW (NIOSH) Publ. No. 77-157-A
     2   "   "   77-157-B
     3   "   "   77-157-C
     4   "   "   78-175
     5   "   "   79-141
     6   "   "   80-125

to Soils:

1) Spencer, W. F., Cliath, M. M., Davis, K. R., Spear, R.C., and
    Popendorf, W. J.
    Persistence of Parathion and its oxidation to paraoxon on the soil
    surface as related to worker reentry into treated crops. Bull.
    Environ. Contam. Toxicol. 14:265, 1975.

2) Spencer, W. F., Iwata, Y., Kilgore, W. W., and Knaak, J. B.
    Worker reentry into treated crops II: Procedure for the deter-
    mination of pesticide residues on the soil surface. Bull. Environ.
    Contam. Toxicol. 18:656, 1977.

to Foliar Surface Residues:

1) Iwata, Y., Knaak, J. B., Spear, R. C., and Foster, R. J.
    Worker reentry into pesticide treated crops I: Procedure for the
    determination of dislodgeable pesticide residues. Bull. Environ.
    Contam. Toxicol. 18:649, 1977.

2) Popendorf, W. J., and Leffingwell, J. T.
    Procedures for the determination of dislodgeable dust on foliage as
    related to worker reentry hazards. Bull. Environ. Contam. Toxicol.
    18:787, 1977.

to Body Surface Area:

1) Popendorf, W. and Leffingwell, J. T.
    Regulating OP pesticide residues for farmworker protection. Residue
    Reviews 82:125, 1982.

TABLE 1.5

Quality Assurance of Objectives

Measurement Parameter	EPA Reference	Experimental Conditions	Precision (RSD)	Accuracy	Completeness
Dermal Dosimeters					
Gauze		Spiked Blanks	± 5%	—	—
Gloves		Spiked Blanks	± 5%	—	—
Aerosol Monitors		Spiked Blanks	± 5%	—	—
Vapor Traps		Spiked Blanks	± 5%	—	—
Soils		Spiked Blanks	± 10%	± 10%	—
Foliar Surface Residues		Spiked Dust	± 5%	—	—
Urine		Spiked Blanks	± 10%	—	—
Body Surface Area			—	± 20%	—
Time Of Exposure			± 5 Min. (2%)	± 15 Min. (5%)	—

6. SAMPLING PROCEDURES

6.1 Dermal Exposure to Pesticides

This project employs a gauze pad as a dermal dosimeter for all areas of the worker's body except the hands. This dosimeter consists of a 12-ply 3 x 3 inch gauze surgical sponge. A polyethylene "moisture barrier" is placed on the side of the pad facing the skin of the subject. All of this is held in a glossy paper envelope. The side of the envelope facing away from the skin has a circular hole 60 mm in diameter exposing 28 cm^2 of the gauze pad.

Body locations for mounting the gauze pad dosimeters are as follows:

Head -- mounted on the side of the head, roughly over one ear, either stapled to a stretchable head band or taped to the inside of the brim of the subject's hat (1);

Chest -- mounted over sternum between the pectoral muscles (1);

Back -- mounted over backbone between the scapulae (1);

Upper Arm -- mounted over the deltoid muscles (2);

Lower Arm -- mounted roughly midway between the elbow and wrist on the dorsal surface (2);

Upper Leg -- mounted roughly midway between the hip and the knee on the anterior surface (2);

Lower Leg -- mounted roughly midway between the knee and the ankle on the anterior surface (2).

For ease of mounting and dismounting the patches, the chest, back and upper arm dosimeters are stapled to T-shirts which are dispensed to the subjects at the beginning of the work period and collected at the end. The T-shirts are to be worn next to the skin of the subject so that the dosimeters will be exposed to

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only that portion of the residues that would eventually reach the skin. Lower

arm and upper and lower leg patches are taped directly to the skin in the appro-

priate location after the T-shirt is donned. The subjects then wear whatever

clothing they would normally wear while working, except that if they were to strip

to the waist (which some male workers in California do) they would continue to

wear the T-shirt bearing the dosimeters. A hand dosimeter consists of a light-

weight cotton glove.

6.2 Personal Aerosol Monitors

Personal breathing zone air samples will be taken on at least two subjects

each working period of two hours. An open-face, 37 mm Millipore cassette

(0.8 μ pore size) is mounted in a subject's breathing zone and is aspirated at

2.0 $\pm$ 0.2 Lpm with a belt-mounted portable pump.

6.3 Area Aerosol and Vapor Monitors

An open face 37 mm Millipore cassette (0.8 μ pore size) will be stationed

centrally in an area of the field under harvest by our cooperative subjects.

This cassette will be backed up by a charcoal tube vapor trap as insurance against

vapor break-through from the filter.*

6.4 Foliar Samples

Foliar sampling is accomplished by using a leaf punch equipped with a 3 cm

diameter die. The punch-through action of the device pushes the leaf disk into

a 4-oz wide-mouth jar which is attached to the punch and which subsequently serves

as the sample storage container. The punch is also equipped with a resettable

counter.

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*It should be noted that the experience of this laboratory is that Millipore filters
possess an appreciable capacity for absorption of pesticide vapors. However, since
the vapor retention characteristics of the filter for the particular pesticides
being studied here are unknown, a back-up charcoal tube (#226-01, SKC-West, Inc.)
is employed.

Sample collection is accomplished by striking out diagonally across the area to be sampled, stopping every three or four rows to take a single leaf sample. The sampling points are to be distributed throughout the areas of the plants that the harvester will actually contact. This includes all parts of the plant, both outer and inner canopy leaves, from either side of the row, and from the center. The standard sample size is 48 disks. If the edge of the field is reached before the full complement of leaf disks has been obtained, the person collecting the sample merely reflects back into the field on a new diagonal.

6.5 Soil Samples

The soil sampling device has two parts: a three-sided form 10 cm long by 8 cm wide and 8 cm high, which when pressed into the soil surface blocks out an area 80 cm^2; and a small rectangular shovel which fits just inside the form and has a 1 cm high rim around the sides and back. See Figure 6.1

Sampling is accomplished by first shoving the form into the soil several centimeters. The shovel is then inserted vertically into the soil at the open face of the form, likewise, several centimeters; and the soil is scraped away from the form with it to a depth of several centimeters. The shovel is then run into the form horizontally so that it picks up a layer of surface soil the area of the form and 1 cm deep. The sampling pattern utilized for taking soil samples is the same as for taking foliage samples, being collected on a diagonal across the area being harvested by the cooperating pickers. However, since there are only six "scoops" taken, rather than the 48 sampling sites for the leaf punches, samples are taken every 8 to 10 rows. Furthermore, samples are taken in the area between the planted rows, which is where pickers are physically located, and where they contact the soil. Soil samples are held in a paper sack (#4 lunch bag) which is in turn placed in a plastic bag to reduce moisture loss in frozen storage.

Figure 6.1: Soil Sampler
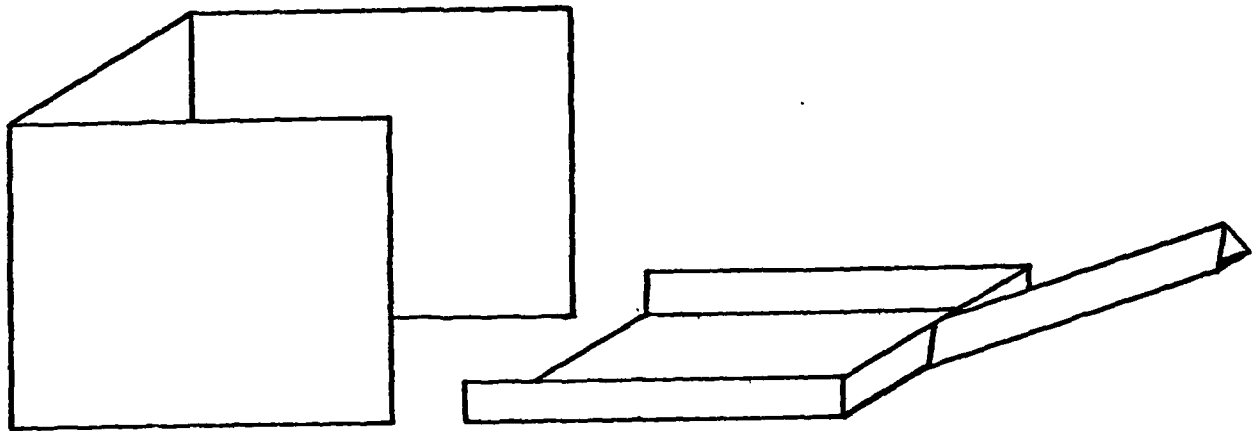
6.6 Urine Samples

Subjects are requested to give all of their urine in approximately 12 hour segments for at least 72 hours after exposure has terminated. Initially they are supplied with three wide-mouth, 500 mL Nalgene bottles: 1) One for the first period of collection; 2) one for the next 12 hour period; 3) and one back-up for the event that it is ever needed. The bottles are labeled with the subject's name, and those that are intended for a specific time period have the proper date and the designation "day" or "night" on them. In addition, there is label space for the subject to write the actual times of first and last use on the label. Thus, each subject should have a full 24 hour's worth of bottles and a back-up to start out.

The subjects are instructed to fill out the label on each bottle as it is used in its appropriate time period and to either bring the bottle to project staff or to store it refrigerated until they can do so. Each subject is given a new set of bottles to replace the ones brought in to project personnel until

the 72 hour time period is exhausted.

Bottles are prepared by washing in hot water with a strong laboratory detergent. After appropriate water rinsing, the bottles may be rinsed with dilute hydrochloric acid if visual inspection shows deposits. Finally, they are rinsed with acetone to remove traces of soluble organic material, air-dried and returned to service.

6.7 Sample Preservation

All samples, regardless of type, are placed on dry ice as sampling is completed. They are kept thus in ice chests until they are delivered to the laboratory, where they are transferred to a standard freezer chest maintained at -10°C. Samples are generally hand delivered to the laboratory by the field study personnel (which often includes laboratory personnel). If the samples cannot be inventoried by the laboratory personnel immediately upon arrival, the samples are stored until the next working day in a different freezer from the one customarily used for sample storage. This procedure minimizes the possibility of not logging a sample entering the sample storage freezer.

In the unexpected event that samples are shipped by common carrier rather than being hand carried by project personnel, arrangements will be made between the person(s) shipping the samples and the laboratory to reduce the chance of losing samples en route. For short distances, our laboratory has found that the "next bus out" service of Greyhound Package Express is reliable and provides overnight (cool) service from anywhere in Northern California. For longer distances an appropriate air courier service is chosen. Once the shipment has been made and the laboratory has been telephoned to confirm that face, the Chief Chemist arranges for someone to meet the shipment at its expected time of arrival.

Samples are removed from the storage freezer only for the purpose of inventorying and analysis. During inventories, small numbers of samples are removed at one time to prevent their thawing during identification and counting. When samples are removed for analysis, they are withdrawn from the freezer in groups only the size of the numbers of samples to be extracted, allowing the minimum thawing time needed for room temperature equilibration.

6.8 Forms, Notebooks, Recordkeeping

A form has been developed in this laboratory to record pertinent field data on cooperating harvesters, and is included here as Appendix A. This form records a subject's personal data such as age, height, weight, his/her clothing, work habits, and production (yield). The form also provides for accumulation of exposure data (contact time, times and flow rate for air samplers, and for comments on irregularities in sampling, or subject's work).

A field notebook is maintained as well as individual data sheets on the subjects. This book records the time, location, and quantity of all environmental samples taken, including data on all foliar, soil, and area air samples, regardless of whether they were taken before, during, or after a harvester exposure study.

7. SAMPLE CUSTODY

7.1 Field Sampling Operations

A. Preparation of Sampling Supplies

1) Preparation of the dermal dosimeters is described in Section 3 of this document. The gauze sponges are preextracted by soxhlet in order to eliminate possible interferences which this laboratory has previously encountered with some batches of the sponges. Once the samplers are assembled they are labeled with their sample identifying code and stapled, when appropriate, to the T-shirt carrier. All head, lower arm, and leg patches must be attached to the subject as he/she is about to enter the study. Lower arm and leg patches are taped in place. Head patches are either taped to the subject's hat, if one is worn, or stapled to a project-supplied hat or head band which is worn as a carrier.

2) The Millipore filters used both for personal samplers and for area monitoring are prepared as follows:

Pre-weighing Procedure

--Prior to use in the field, the filters are weighed in order to establish initial weights. Six control filters are weighed at the same time in order to quantify weight gained due to moisture in the laboratory.

--The test filters are removed from the sealed packaging and allowed to sit out on the laboratory bench for approximately 10 to 20 minutes, in order to equilibrate with room moisture. A paper is placed over the filters to prevent any dust from settling on them. The control filters are prepared for weighing in the same manner. The cassette

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holders are prepared at this time and an identification number is assigned to each one. Once the filters are placed in the cassettes they will be referenced by this number.

--An automatic electro balance having a digital readout in milligrams with four significant figures is used to weigh the filters to ± 5 micrograms. The balance is calibrated using a standard 20 mg weight prior to any filter weighing. The calibration is repeated intermittently during the weighing of both the control and test filters to assure an accurate reading. The filters are handled with blunt-tipped forceps. The weights for both the test and the control filters are recorded and logged into a laboratory notebook. The test filters are entered and referenced by the number given to the cassette in which they will be placed. The control filters are referenced by a number on the petri dish in which they are stored. After the weight has been recorded the filters are assembled into the cassettes and are then ready for field use.

Transport From Field

--At the completion of aerosol sampling the cassettes are placed upright in a styrofoam holder to prevent loss of dust from the filter. The holder is placed in an ice chest with dry ice which is then transported to the laboratory.

Post Weighing

--The post-weighing procedure is identical to the pre-weighing procedure with the exception that the filters are placed in individual, dessicating jars which contain anhydrous calcium sulfate.

After removal of the moisture caused by the refrigeration process, the filters are placed on the laboratory bench and allowed to equilibrate with the room moisture. The control filters are prepared in the same manner. The difference in weight between pre- and post-weighing are logged into the notebook for each filter. The same is done for the control filters. The resulting dust weights are obtained by the difference in the pre- and post-weight minus the average weight gain for the six control filters. The filters are then placed back in their cassettes and held in the freezer to await chemical analysis.

3) Leaf punches are cleaned of the build-up of leaf debris and dirt which accumulates on the punch and die while a sample is being collected. This cleaning is performed with a household scouring pad made of either copper or stainless steel turnings. Cleaning is performed between samples and reduces chances of any cross contamination between samples.

4) Vapor samplers are obtained commercially and are opened only as they are to be used. They are resealed immediately after sampling with the caps provided by the supplier.

B. Procedures and forms for Recording Sample Acquisition Data

This information is put forth in Section 6.

C. Documentation of Specific Sample Preservation Methods ᵃⁿᵈ 6.7

Sample preservation methods are described in Sections 3 of this document.

D. Sample Labeling

Each study is preassigned a "field" or study number. This number, combined with the year, yields a unique study number. Appendix B is the document supplied to the field personnel describing label generation.

E. Field Tracking Forms

The subject data sheet and the field notebook act as field tracking devices.

7.2 Laboratory Operations

A. Laboratory Sample Custodian

The Chief Chemist is the laboratory sample custodian and as such is responsible for inventorying samples held for analysis or other processing and for maintaining all necessary documents pertaining to sample custody. These documents include any shipping receipts or bills of lading and a sample log book (see Appendix C).

The sample log book provides for the notation of sample identity, date of sampling if known, date recieved, date extracted, and date analyzed. Sample numbers used within the laboratory are those assigned in the field since those identifiers are unique and specify useful and pertinent data about the sample as well (i.e., days post application, sample type).

Sample flow through our laboratory, and thereby sample custody, follows the general pattern discussed hereinafter: when samples first arrive at the laboratory they are placed in a specified freezer, "A", until they can be logged into the laboratory log book. After they are logged in they are transferred to a second freezer, "B". The person responsible for extraction pulls batches of samples from freezer "B", noting this in the log book, performs the appropriate extraction procedure, prepares the sample for analysis, and turns the batch over to the analyst. The analyst is responsible for proper documentation of the chromatograms and maintenance of sample integrity while he/she has possession of them. The anaylst also must note the date of analysis in the log book. When analysis of the batch is complete, the samples are

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returned to the person who performs the extraction and the samples are

prepared for archival storage and replaced in freezer "B".

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8. CALIBRATION PROCEDURES AND FREQUENCY

8.1 Field Equipment

A. Personal Sampling Pumps

The personal sampling pump shall be calibrated before and after each day of sampling.

1) Allow the pump to run 5 minutes prior to voltage check and calibration. Check the voltage.

2) Assemble the polystyrene cassette filter holder using the appropriate filter for the sampling method. Ensure that the luer adaptor does not come in contact with the back-up pad.

3) Connect the collection device, tubing, pump and calibration apparatus. The length of hose should be the same as that used in the sampling train (approximately 1 meter).

4) Check the seals on all Tygon tubing connections.

5) Wet the inside of a 1-liter buret with a soap solution.

6) Turn on the pump and adjust the pump rotometer to the appropriate flow rate setting.

7) Momentarily submerge the opening of the buret in order to capture a film of soap.

8) Draw two or three bubbles up the buret in order to ensure that the bubbles will complete their run.

9) Visually capture a single bubble and time the bubble from 0 to 1000 mL.

10) The timing accuracy must within $\pm$ 1 second of the time corresponding to the desired flow rate.

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11) If the time is not within the range of accuracy, adjust the flow rate and repeat steps 9 and 10 until the correct flow rate is achieved.

12) Steps 9 and 10 shall be performed at least twice.

13) While the pump is still running, mark the position of the pump rotometer.

14) A calibration curve can then be calculated. The flow rate in LPM is placed on the x-axis and the rotometer reading on the y-axis.

B. Other Field Equipment

In general, the relatively crude measurements taken in the field, such as height and weight of subjects, and time worked, are effected with devices whose calibration are not checked. This includes carpenter's rule, a bathroom scale, and various researchers' wrist watches. The thermometers of the psychrometers, the thermo-anemometer and any other meterological instruments are used generally uncalibrated, as well, since their data is used only for background information to describe the quality of the working conditions.

8.2 Laboratory Equipment

A. Balances

1) Electrobalance: the electrobalance used to weigh membrane filters for aerosol monitoring is calibrated as described in Section 7 of this document.

2) Analytical Balance: the balance used to weigh analytical standards and smaller samples ($\leq$10g), when necessary, is a Mettler Model B-6 which is good on its vernier to at least 0.02 mg. It is kept in a balance room out of normal traffic flow and laboratory activities. The laboratory which houses PHAP activities contracts for an annual cleaning and calibration from a private contractor.

B. Volumetric Glassware

Whenever practical or necessary, volumetric glassware is Class A or

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Class A serialized quality. Further calibration is not attempted. In

non-critical applications such devices as tilt-dispensers and graduated cylinders are employed.

C. Analytical Instruments

The chromatographs are checked continually as they are used by injection of standards. When manual injections are done, more frequent standardization is required (every three to five samples) than when a mechanical injection device is used. Furthermore, the analyst is required to choose standards that closely match the samples being injected. When automatic injection is being done, less frequent standardization is called for (every ten samples).

D. Calibration Standards

Chromatographic standards are obtained, whenever possible, from the EPA repository at Research Triangle Park, NC. Failing that, they are obtained from the following sources in the order of preference listed:

1) Commercial suppliers (e.g., Chem. Services, Westchester, PA) as crystalline solids or neat liquids.

2) Pesticide manufacturers as crystalline solids or neat liquids.

3) Commercial suppliers as a solution in organic solvent (e.g., Nanogens, Supelco, Varian Associates, etc.).

4) Pesticide manufacturers as technical grade materials.

5) Pesticide manufacturers as formulated pesticides.

Standards, unless obtained as a solution, are weighed out with an accuracy sufficient to give at least four significant figures. Dilutions are made in hydrocarbon solvents, at least for the concentrated standards. This is done to minimize the possibility of chemical reactions between solvent and solute. If reactive solvents, such as ketones, alcohols, or nitrogen containing compounds, are required by the analytical method being used, they are used only to make up the working standard.

As few dilution steps as possible are used to obtain a working standard, thus reducing errors inherent in such operations.

9. SAMPLE PREPARATION PROCEDURE

9.1 All Samples

Sample preparation date and extraction volume are entered in the spaces provided in the sample log book.

9.2 Gauze Pads

Samples consist of one or two pads (one for main trunk or two for limb sample sites) stapled inside paper application packs and stored in an RPE Zip-lock bag in the freezer. After the staples are removed, the pad together with the plastic moisture barrier is transferred to a 125 mL LPE wide-mouth bottle. Thirty mL of toluene, some of which is used to rinse the bag, are added and the sample is shaken at about 200 Hz for one hour. A ten mL aliquot of the analyte is reserved in a glass polyseal vial and an auto-sampler vial is prepared from the remainder.

9.3 Glove Samples

These are treated in a manner similar to the patches. The gloves are frozen one pair to a sample bag and 100 mL of toluene is used to extract a pair. If a subject wore more than one pair, the solvent is increased only to the extent that an aliquot can be easily removed and the actual amount of solvent is noted.

9.4 Aerosol Samples

These are Millipore disposable cassettes with 37 mm membrane filters. An extraction bottle is chosen so that the filter can be dropped directly in from the cartridge without handling. Loose dust is washed off the cassette with hexane because the plastic is soluble in toluene. The hexane is allowed to evaporate and the pesticide extracted with 30 mL of toluene. The sample is stored as above under the procedure for gauze pads.

9.5 Leaf Punch Samples

The standard leaf punch sample consists of 48 - 3 cm leaf disks frozen in a glass jar with a water-tight plastic cap. After a half-hour thawing period, the leaves are dumped into a one pint square Mason jar with the standard lid and ring closure. Six drops of a 20 mg/L solution of dioctyl sodium sulfosuccinate is added to the sample jar. The surfactant and dust are transferred quantitatively to the Mason jar with 100 mL of distilled water. The leaves are shaken for 30 min. on a shaker table at about 140 Hz and the liquid decanted into a 500 mL separatory funnel containing 50 mL methylene chloride (dichloromethane), using a narrow-stemmed funnel to avoid transferring leaves. The process of washing the leaf disks with surfactant and water is repeated twice more. Then the leaves are counted and discarded. The separatory funnel is shaken 30 times and the organic layer is drained through a small funnel plugged with glass wool and filled with anhydrous sodium sulfate into a 500 mL round-bottomed ʃ 24/40 flask. The extraction procedure is repeated twice more with fresh 50 mL aliquots of solvent and the combined solvent is rotary evaporated to about 1 mL. Ten mL of toluene is added and evaporated. This process is repeated twice more. The final residue is quantitatively transferred to a 10 mL volumetric flask and made up to volume. The sample is ready for gas chromatographic analysis.

The dust which was washed from the leaf surfaces remains in the interfacial layer in the separatory funnel. This material is filtered onto a pre-weighed glass fiber filter, dried at 110°C overnight and cooled in a dessicator. Post-weighing of the filter yields the foliar dust weight.

9.6 Soil Samples

The sample is weighed and sifted through a #10 sieve (2 mm hole size) to break up lumps and remove rocks, twigs and leaves. The trash is weighed. The sifted

sample is mixed and a 250 mL portion is transferred to a tared beaker and weighed; the beaker is then placed in an ambient-temperature vacuum desiccator and dried for 24 hours or more and reweighed until the residual moisture is less than 0.5%. A glass soxhlet thimble is prepared by placing 1.5 cm of acetone washed sand in the bottom to protect the extra-course frit from fouling by soil fines. The thimble is tared and about 30 gm of desiccated soil is added, the weight being taken to four significant figures. The thimble is then placed in a 250 mL soxhlet extractor and cycled for four hours. The solvent is azeotropic acetone-hexane (59% - 41%). After extraction the solvent is removed by rotary evaporation and replaced by a solvent compatible with the analytical method to be used - toluene for GC only, acetronitrile for GC plus HPLC. This method is applicable only to those low-volatility chemicals expected to be found during this study.

9.7 Urine Analysis

A. Captan

Tetrahydrophthalimide (THPI) is the major urinary metabolite of captan, with tetrahydrophthalamic acid being a closely related minor metabolite. There are two analytical methods for THPI. The former Idaho PHAP project developed a method (Brokopp, C.D. Annual Progress Report, Idaho Epidemiologic Studies Program, EPA Cooperative Agreement, #78-CX-0363, April 1980) and a newer version is being published by Schoen and Winterlin (Schoen, S.R. and W.L. Winterlin. "Gas Chromatographic Determination of the Captan Metabolite Tetrahydrophthalimide (THPI) in Urine," submitted for publication, 1982.

The major difference between the methods is the fact that the THPI is derivatized for EC analysis in the former, while in the latter, the metabolite is analyzed as underivatized THPI on a nitrogen-phosphorous detector equipped gas chromatograph. The clean-ups for the two methods diverge somewhat due to

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the facts that they were developed for analysis on different detectors and that they were developed in different laboratories. We will develop the Shoen-Winterlin method in our laboratory first, given that the elimination of a derivatization step simplifies the procedure.

B. Organophosphate Insecticides

There are six alkyl phosphate metabolites commonly observed as a consequence exposure organophosphate pesticide. One or two of these are possible from any given OP compound, depending on its structure. Reid and Watts have published a method for derivatizing these metabolites without the use of the explosive and powerfully carcinogenic reagents (diazoalkanes) required by older methods [Reid, S.J. and R.R. Watts. "A Method for Determination of Dialkylphosphate Residues in Urine." J. Anal. Toxicol., 5, 126 (1981)].

10. DATA REDUCTION, VALIDATION
AND REPORTING

10.1. Agricultural Chemical Samples

Most samples yield four (4) data items:

1) Sample vol., is the final amount of solvent in which the entire amount of analyte from the sample is contained. This number is determined by the technician who prepares the sample and records it with the extraction date in the sample log.

2) Injection vol., is the amount of sample actually injected into the GC or HPLC. This number is recorded by the instrument operator along with the sample number on the recording tape of the HP3390A (GC) or the Water's Data Module (LC) Integrator, i.g., 2 μL of a 1:1000 dilution are injected, the operator records, inj. vol. = 0.002 μL.

3) Counts per injection: This is the area under the peak in μV-sec. as determined by the integrator for each injection.

4) Response factor: This is an arithmetical expression of the sensitivity of the entire analytical system to the injection of a standard of known volume and concentration and has the units- $R = C/ng$. If $\bar{C}$ is the average count for 2 or more identical standard injections with a RSD < 5% then $R = \bar{C} \div$ inj. vol. $\div$ std. conc. proof:

$$\frac{\bar{C}}{inj} \times \frac{inj}{\mu L} \times \frac{\mu L}{ng} = \frac{\bar{C}}{ng}$$

At the conclusion of a day's run the integration record is logged in thus: The values for each standard are entered, averaged and the RSD verified. The response value is calculated.

The sample number, injection volume and the replicate peak areas are recorded, then the sample number is looked up in the sample log and the analysis date recorded there, finally the extraction volume is transferred from the log to the laboratory notebook. Since we want the final result to be in µg of analyte per sample the following formula is used:

$$\frac{C}{inj} \div inj \text{ volume} \div resp \text{ factor} \times ext \text{ volume} = \frac{\mu g}{sample}$$

Note that prior to multiplication by the extraction volume ng/µL convert per acidens to µg/mL. Proof:

$$\frac{C}{inj} \times \frac{inj}{\mu L} \times \frac{ng}{C} \times \left(\frac{1\mu g}{10^3 ng} \times \frac{10^3 \mu L}{1mL} \right) \frac{mL}{samp} = \frac{\mu g}{Sample}$$

The principal criteria used to validate data integrity will be agreement between the records and calculations and transfer checks done by the analytical chemist on randomly selected samples.

For the purpose of this study, an outlier is defined as an analytical data set with a relative standard deviation greater than 10%. Because several samples are taken from different parts of each subject's body, the unacceptable sample is held until the rest are completed and the whole body dose calculated. The effect of the uncertainty on the whole body dose can then be estimated and a proper decision made as to whether the sample must be cleaned and concentrated.

The following data flow and reporting scheme refers to the Sample/Data Flowchart, Figure 10.1.

Figure 10.1:   Sample/Data Flowchart
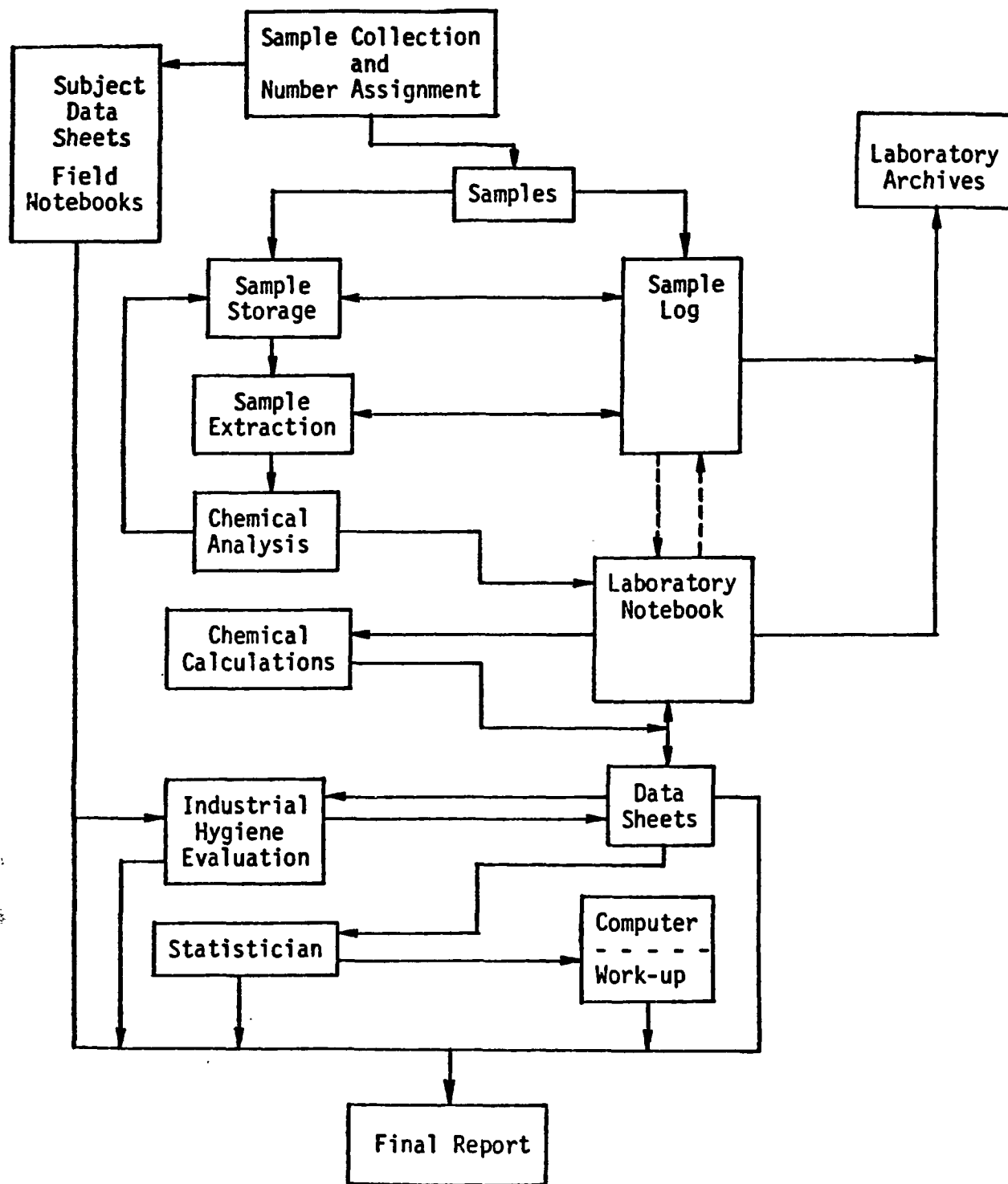
The process begins in the field when the industrial hygienist fills out a field data sheet on each worker and assigns a subject number to him/her. A specimen field data sheet is in Appendix A. As each sample is collected a number is assigned to it in accordance with the protocol described in Appendix B. The samples are placed in dry-ice chests for the trip to the laboratory. The field data sheets and the spray history are given to the senior scientist for later use.

Upon arrival at the laboratory, the samples are transferred to the deep-freeze for storage and the sample log is filled out through the storage date column. The Chief Chemist and the analytical chemist later verifying the log against the samples with a physical inventory. The samples are turned over to the technician who organizes them by type for extraction. As each sample is extracted the date and volume is entered in the log and the extracts are turned over to the analyst. After the extracts have been run, they are returned to the technician for storage. The raw data is transferred from the instrument print-out to the laboratory notebook, and the printout is dated, coded and filed. The extraction volume and any special data (e.g. crop weight) are entered into the laboratory notebook from the sample log and the analysis date entered in the log book. The calculations are performed and the results entered in the laboratory notebook and the data sheets (see Appendix D). The data sheets are checked against the laboratory notebook by the analytical chemist and given to the senior scientist who uses the field data sheets to perform additional calculations. The completed data sheets are turned over to the statistician who enters the data on the computer and does the statistical work-ups. The computer output and all the data sheets finally go to the Project Director for use in preparing the final report.

The field notes, data sheets, and laboratory notebooks are retained by the senior project chemist or/and project director for seven years.

11. INTERNAL QUALITY CONTROL CHECKS

As many samples as possible are collected in duplicate. However, the majority of the personal monitoring samples are unique. Leaf punch, and soil and airborn pesticide samples are regularly collected in duplicate or more.

In the laboratory, method checks are conducted by analysis of replicated spiked samples and blanks. These method checks are employed during routine analysis, as well as regular calibrations described in Sections 7 and 8 of this document. Reagent (solvent blanks) are also a regular feature of the internal checks employed by this laboratory.

Replicates and frequent calibrations are the backbone of our quality assurance program for chromatographic analysis. At least duplicate injections are used whether manual or automatic sample introduction is used. The analyst is required to check results for each sample for reproducibility and if the relative standard deviation exceeds 10% (5% is the laboratory goal) then additional injections are required until satisfactory results are achieved.

Spiking leaf punches, soil samples, and to some extent, dermal dosimeters, will be accomplished by the use of pesticide-laden dust. This material will be formulated by dosing a quantity of pre-sieved soil dust which has been checked for freedom from residues of the compound(s) of interest. In this way a supply of dust carrying a known and verified concentration of pesticide(s) can be kept on hand for spiking into the various substrates which will be analyzed. A supply of unspiked dust from the same source will be kept on hand for blanks.

This technique offers advantages over spiking pesticides carried in organic solvent, especially in the case of checking foliar dislodgeable residue methodology.

The schedule of internal quality assurance samples to be run varies for different types of samples. The bulk of the samples to be analyzed are dermal pads. They are run in batches of 30 samples at a time and two of those samples will be either a blank and a spiked blank or two spikes. Since aerosol samples are extracted and analyzed in an identical fashion as gauze pads, they will be included with the gauze pads for quality assurance purposes.

Since soil sample processing is not consistently a batching process, a target of 10% of those processed will be QA samples. Leaf punches are run in batches of up to fifteen samples in number, and one of each batch, at least, will be either a blank or a spiked blank. Since only two or three vapor traps are extracted at a time, at least one spiked blank will have to be included in the process.

The results of these quality assurance sample analyses will be accumulated in a laboratory notebook especially set aside for this purpose. A summary of these results will be reported monthly along with the regular monthly reports forwarded to the EPA project officer.

12. PERFORMANCE AUDITS

A plan for external performance audits is currently being developed
with the cooperation of the chemists at the Pesticide Hazard Assessment Project
located at the University of Iowa, and under the guidance of our Project
Officer. When this plan is complete, it will be forwarded for inclusion in
this document.

13. PREVENTIVE MAINTENANCE

13.1 Field Equipment

Generally, cleaning and recalibration (for air sampler pumps) provides project personnel an opportunity to inspect field sampling equipment for deficiencies before use. Leaf punches require sharpening at long intervals (once every two or three seasons) in order that they continue to cut the tough fibers in xeomorphic leaves (e.g., citrus). This is performed on an as needed basis.

13.2 Laboratory Equipment

The analytical balance used by the project received an annual cleaning and recalibration (see Section 8).

Gas chromatographs are maintained in the following ways: All carrier gases are passed through moisture and oil traps to prevent fouling the columns and detectors, and the trap elements are changed every four (250 SCF) cylinders. Carrier gas intended for electron capture detectors is passed through an oxygen scrubber, as well, which is changed after six cylinders of gas have passed through it. Electronics are checked by performing an electrometer zero and noise check monthly or whenever a new method is set up. The voltage profile for the ECD is also checked and recorded.

The digital integrator-printer-plotters used by the project perform a self check every time they are turned on. They require a cleaning of paper debris each time a new role of plotter paper is installed.

The auto sampler is operated on compressed air which is passed through a particulate and water trap before use. The performance of the auto sampler is checked daily by careful examination of results obtained from calibration standards and solvent blanks which are interspersed among samples.

The liquid chromatograph automatically does a self diagnostic test when powered up. Solvents are prefiltered through a 0.22 μ filter to prevent particulate damage to the system.

13.3 Spare Parts Inventory

Air monitoring pumps use rechargeable battery packs which periodically fail, so spare battery packs are kept on hand.

The gas chromatographs have spare EC power supplies (3), a fan motor, heater cartridges for detectors, and injectors and an FPD igniter coil. There are three spare tritium ECD cells of unknown condition. Regular supplies such as septa, columns, and packings, are procured as necessary on an ongoing basis.

The integrators have ho spare parts, except the thermal printer/plotter paper they consume.

The auto sampler is backed up with extra syringes and needles, air filter cartridges and consumable (vials, caps, and septa).

The liquid chromatograph has a spares kit supplied by the manufacturer which is kept up when pieces are used.

14. SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

14.1 Field Sampling

Standardized sampling procedures are employed to assure accurate environmental monitoring (i.e., respirable dust and pesticides, dislodgeable residues, soil residues, crop residues, and meteorological conditions). The patch technique used as a dermal dosimeter is unproven, although it is generally accepted as the best technology available at present. Therefore, the accuracy of the data generated by the technique is unknown.

14.2 Laboratory Analyses

All chromatographic analyses are run **at least** in duplicate. Relative standard deviations are calculated and any samples giving greater than 10% RSD are re-analyzed. At the discretion of the analyst, a lower RSD criterion may be used. The general precision goal for the laboratory is five percent. Standards are weighed by the most experienced chemist in the group. Working standards are cross-checked against one another.

Calculations are recorded in the laboratory notebook assigned to the project and are double checked by the analyst as he/she performs them by re-calculating every third or fourth sample. The data is then triple-checked by another person by their recalculating 10% of the samples.

An absolute quality criteria is used independent of any statistical test, viz., any recovery and duplicate analyses not meeting the objectives specified in Section 5 will cause the corrective actions described in Section 15 to be initiated.

14.3 Further Data Reduction

Results in term of mass of target chemical (pesticide) reported by the laboratory are then transcribed into computer-readable format for further calculations. This operation is also double checked either on a 10% or 100% basis depending upon the computer employed. Finally, the results are transcribed onto appropriate data sheets and forms as indicated by Appendices F through J for aerosol, leaf punch, soil, crop, and meteorology data, respectively. The dermal data reduction sheet was previously shown in Appendix D.

15.   CORRECTIVE ACTION

Whenever any evidence appears to indicate trouble or insufficiency in sampling, analytical or data reduction activities or equipment, efforts are mounted to trouble shoot and correct any problem to the satisfaction of responsible project personnel. Specific procedures depend upon the nature of the problem and the ability of the personnel dealing with it to interpret the symptons.

Acceptable limits for the performance of equipment, and thereby the data produced by it, is described in other sections of this document. The responsible person for initiating corrective action is that person who detects the problem, be it malfunctioning equipment or data that does not appear correct or consistent. Of course, the ultimate responsibility lies in the hands of the Chief Chemist and the Project Director.

16.   QUALITY ASSURANCE REPORTS TO MANAGEMENT

Quality assurance results will be accumulated in a QA notebook. These results will be summarized in the Monthly Report format which is sent to the PHAP Project Officer (see Appendix E). Monthly reports are prepared jointly by the Project Director and the Chief Chemist.

The final report will include a QA section which summarizes the Monthly Reports and discusses any QA issues which come from an analysis of the QA data.

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University of California
School of Public Health
Biomedical and Environmental Health Sciences
Berkeley, CA 94720

Field Personnel Sampling Form

ame and Number of Experiment:

te of Experiment:

Subject Name	Subject Number	Sex	Age	Weight	Height

ration of Exposure:

Time In: Time Out: Time In: Time Out: Total Hours:

lothing Description (type, parts of body not covered, hat, etc.):

ork Habits: (Working position, observed foliar contact, etc.)

nusual Observations:

ampling Patches (Nos.):

ead   _____
hest   _____
ack   _____
pper arm   _____ (L) _____ (R)
ower arm   _____ (L) _____ (R)
pper leg   _____
ower leg   _____ (L) _____ (R)
ands (gloves)
ther

Pump No.: _____

Collector Type

Flow Rate: m^3/hr

_____
Name of Recorder (Observer)

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UCB SAMPLE IDENTIFICATION CODE

$$\underbrace{\text{— —}}_{\text{Year (a)}} \quad \underbrace{\text{— —}}_{\text{Plot (b)}} \quad \underbrace{\text{— —}}_{\text{Sample Type (c)}} \quad \underbrace{\text{— —}}_{\substack{\text{Days Post-}\\\text{Appl. (d)}}} \quad \underbrace{\text{—}}_{\text{Replicate (e)}}$$

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(a) Last two digits of year, e.g., 80, 81, or 82

(b) Plot number (2 digits) assigned by project supervisor

(c) Sample Type

    A = aerosol

    C = crop sample

    P = punch sample

    S = soil

    V = charcoal or other vapor collector

    Patches, etc.

H = head	Ch = chest
UA = upper arm	UL = upper leg
LA = forearm	LL = lower leg
St = stomach	Sh = shoulder
	LB = lower back

(d) Days post application, 0 = day of application, 1 = first day after, etc., (PA is preapplication).

(e) Replicate number for duplicate sample, different people, etc., as necessary and recorded in field notes.

Laboratory Sample Log

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YEAR FIELD TYPE	DAYS POST APPLICATION	REPLICA OR SUBJECT #	SIZE OR POSITION	AMOUNT	SAMPLE DATE	STORAGE DATE	EXTRACTION DATE	ANALYSIS DATE	LAB BOOK AND PAGE #	MISCELLANEOUS	EXTRACTION VOLUME
8013I	14.5	U A	2	7-12	7-13	8-5	8-7	K-61		30
8013C	14.1	W F	14	7-12	7-13	8-21	8-23	L-6	175g	100
8013A	14.2	4m	250L	7-12	7-13	8-16	8-17	K-89	27.3 mg	30

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(7/81) DERMAL DATA SHEET

STUDY:_____ COMPOUND:_____
DATE:_____
LAB LOG:_____ Pad Area:_____cm^2 (a)

cation/ID	(b) chem. mass (g)	# pads n	(c) time hours	(d)=(a)(c) hr-cm^2	(e=(b)/(d) rate density (g/hr.cm^2)	(f) LOC AREA cm^2	(h)=(e)(f) rate (g/hr)
HD						1075	
neck						230	
*						*1300	
SH						1305	
BA						1540	
**BA						**2190	
CH						1540	
St						720	
**CH						**2190	
hips						1750	
UL						3460	
LL						2590	
*						*6050	
feet						1230	
UA						1860	
LA						1290	
GL						1075	

*Indicates area as sum of previous two locations.
**Areas to be used where no shoulder or stomach pads included.

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Date Report Prepared:_____

MONTHLY LABORATORY STATUS REPORT

~ticipating Pesticide Hazard Assessment Projects_____

:le of Study/Investigation:_____

~iod of Report:_____ to _____

Substrate (List chemical residue to be analyzed for or test to be performed)	Number of Samples on Hand	Number of Samples Received or Collected During Report Period	Total Number of Samples to be Analyzed	Number of Samples Completely Analyzed During Report Period	Numbers of Samples Remaining to be Analyzed

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Date Report Prepared:_____585

STUDY/INVESTIGATION MONTHLY STATUS REPORT

Title of Study/Investigation:_____

Participating Pesticide Hazard Assessment Project_____

Period of Report_____ to _____ Prepared by_____

Cognizant HEB Staff Member_____

I. List Tasks Completed During Report Period:

II. List Tasks Started on Schedule During Report Period:

II. Tasks Behind Schedule:

IV. Why are Tasks Behind Schedule? — Account for each Task:

V. Action or Assistance Needed to Complete Tasks — Include New Start and/or
   Completion Dates.

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Aerosol Data Form

Study ID#_____/Chemical_____

| PERSONAL ID# | SAMPLE ID# | TIME | VOL AIR (L) | DUST | | PESTICIDE | | POOLED GROUPS |
				Wt(mg)	CONC. mg/m^3	Wt(g)	CONC. g/m^3	

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School of Public Health
Biomedical and Environmental Health Sciences

Leaf Punch Data Sheet

Study ID#_____/Chemical _____

(Area of 3 cm punch = 7.07 cm^2)

I. Preapplication Samples:

SAMPLE ID#	DATE	# OF PUNCHES	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	DUST mg/cm^2	CONC. ON DUST, ppm

II. Post Application

1. Interim Decay Samples

SAMPLE ID#	DATE	# OF PUNCHES	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	DUST mg/cm^2	CONC. ON DUST, ppm

2. Field Study Samples

SAMPLE ID#	DATE	# OF PUNCHES	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	DUST mg/cm^2	CONC. ON DUST, ppm

3. Post-Field Study Samples

SAMPLE ID#	DATE	# OF PUNCHES	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	DUST mg/cm^2	CONC. ON DUST, ppm

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School of Public Health
Biomedical and Environmental Health Sciences

Soil Sample Data Sheet

Study ID#_____

(Area per scoop = 77.4 cm^2)

I. Pre Application Samples

SAMPLE ID#	DATE	NO. OF SCOOPS	SOIL WT.(g)	% H_2O	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	PPM

II. Post Application

1. Interim Decay Samples

SAMPLE ID#	DATE	NO. OF SCOOPS	SOIL WT. (g)	% H_2O	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	PPM

2. Field Study Samples

SAMPLE ID#	DATE	NO. OF SCOOPS	SOIL WT. (g)	% H_2O	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	PPM

3. Post Field Study Samples

SAMPLE ID#	DATE	NO. OF SCOOPS	SOIL WT. (g)	% H_2O	AMOUNT OF PESTICIDE	CONC. $\mu g/cm^2$	PPM

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School of Public Health
Biomedical and Environmental Health Sciences

Crop Sample Data Sheet

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Study ID#_____/Chemical _____

. Preapplication Samples

SAMPLE ID#	DATE	NO. OF FRUITS	FRUIT WT. (g)	PESTICIDE (g)	µg/cm^2	PPM

. Post Application

1. Interim Decay Samples

SAMPLE ID#	DATE	NO. OF FRUITS	FRUIT WT. (g)	PESTICIDE (g)	µg/cm^2	PPM

2. Field Study Samples

SAMPLE ID#	DATE	NO. OF FRUITS	FRUIT WT. (g.)	PESTICIDE (g)	µg/cm^2	PPM

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University of California
School of Public Health
Biomedical and Evironmental Health Sciences

Meteorology Data Form

Study ID#_____

Section No. ___K___
Revision No. ___0___
Date: __November 10, 1982__
Page_____ of_____
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```
           M    D    Y
DATE____/____/____
```

	Wind			Temperature			
TIME	*DIRECTION	AVG. SPEED	RANGE FPM	WET F	DRY F	HUMIDITY %	SUN CON- DITION

*NOTE relation to work operation

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APPENDIX B

CORRESPONDENCE REGARDING URINARY

METABOLITE ANALYSES

14 December 1984

Dr. Geraldine Fristrom
FSSP Laboratory Coordinator
EAB/HED/OPP   (TS-769-C)
United States Environmental Protection Agency
401 M Street, SW
Washington, D.C.   20460   RE: CR-810691-02-0

Dear Gerrie:

    Your letter of 10 October 1984 was appreciated; it is essentially correct.   Here is a summary of progress to date.

    Save for some ironing out of a few minor quality assurance issues, I feel that we have run the benomyl environmental and personal samples in sufficient numbers to know exactly what we have.   All of the 8301 and 8302 glove samples were positive, though low.   The 8301 samples ranged from about 50 to 1000 micrograms, while the 8302 gloves were 200 to 2000.   Recall that the gloves from the strawberry fields where benomyl was applied ran in the vicinity of 10 to 30 milligrams.   A selection of 48 patches from the 8302 study   (40%) resulted in no detectable (not "too low to quantitate") residues. All the air samples from both the studies gave the same result. Finally, all the leaf punch samples from the two benomyl studies (8301 and 8302) have been completed, along with all the associated quality assurance samples.

    I feel that we could safely expect that there is no further use in analyzing any more of the patches.   The indications to me are that there will probably be no detectable metabolites in the urines, as well.   However, as we have discussed by telephone, John Tessari's laboratory will select a few samples based on the glove data and verify this prediction.

    The mesurol urinary metabolite method that we have been putting together has proved itself reasonably reliable with spikes and standards, so far; and, although it is getting close to the deadline, I remain optimistic that we will be able to complete that task satisfactorily.   Only one experiment remains to be done before the actual samples go into the system.   That one is to determine whether or not we must hydrolyze conjugates as a first step in the sample work-up.

    I looked into the issue of instrument rentals.   It turns out that there is one major purveyor of rental equipment in this area,

named USI; and they handle most major manufacturers. When one looks at short-term rentals, as opposed to leases of a year or more (usually with purchase options), there are some interesting, though logical, restrictions applied. If one goes into a long-term arrangement, you can get a system configured any way you want, because the lessor will go out and buy exactly what you stipulate. On the other hand, the short-term renter takes what they have "on the shelf." What they stock for rental customers is the top of the line equipment. This way, they minimize their inventory; the fanciest equipment is the most versatile, and that minimizes their capital outlay. Anyway, the upshot of all this is that it would cost us approximately $1700 per month to rent a High Pressure Liquid Chromatograph to do the analyses we presently are carrying out. That is at the academic rate of 5% of the retail price per month instead of the 10% charged to industrial clients.

That is generally quite a bit more than I have been paying in for the upkeep of the present equipment. I do not see being able to afford such an expense, and the machines have hung in there the last few months with only minor troubles.

I spoke with Dr. Zweig some time back, now, and he informed me that he will not be working under Dave Severn; rather, he is now assigned to a one-year project in Registrations. That creates a problem here in the final report department, because, as I pointed out previously, there is no way of our getting these analyses all completed in time to have final reports written prior to the termination date. I am sure that no one has a taste for these data to go uninterpreted. Dr. Spear and I have discussed this issue, and we have agreed to submit a request for a no-cost extension under separate cover.

However, the funds are, in fact, coming out close to the budget, and it certainly would improve the situation here if there could be some supplementary funding from the PHAP program to facilitate the last steps of finishing the reports and seeing to the transfer of equipment to Jim Seiber's shop.

Sincerely

John T. Leffingwell, Manager
California PHAP

cc   R.C. Spear

17 December 1984

Dr. Geraldine Fristrom
FSSP Laboratory Coordinator
EAB/HED/OPP   (TS-769-C)
United States Environmental Protection Agency
401 M Street, SW
Washington, D.C.   20460   RE: CR-810691-02-0

Dear Gerrie:

Attached is a preprint of a manuscript titled, "The Relationship Between Dermal Pesticide Exposure By Fruit Harvesters And Dislodgeable Foliar Residues." It will be appearing shortly in The Journal of Environmental Science and Health, Part B. It contains a wrap-up of much of the work that we have conducted under the aegis of the Youth in Agriculture program, summarizing most of the dermal exposure data collected over the last four years.

Incidentally, the Mesurol (methiocarb) dermal data is included in this paper, and the write-up will serve as the basis of our final report on the 1983 blueberry study.

Sincerely

John T. Leffingwell, Manager
California PHAP

11 January 1985

Dr. Geraldine Fristrom
FSSP Laboratory Coordinator
EAB/HED/OPP (TS-769-C)
United States Environmental Protection Agency
401 M Street, SW
Washington, D.C. 20460   RE: CR-810691-02-0

Dear Gerrie:

Developments in the matter of mesurol metabolite analysis are such that I deem it desirable to report them to you in some detail and seek relief in the deadlines we face at present.

As you know from previous telephone conversations and correspondence, we were required in 1983 to change the proposed work plans which we had submitted to the NPHAP staff to drop the idea of doing more work on strawberry harvesters in favor of workers in three other berry crops. This meant that we would have to focus on populations of workers and crops that were quite distant from our laboratory and of which we knew almost nothing. The consequence was that almost all control over such critical factors as the choice of the field site and the timing of our studies in relationship to pesticide applications was lost to us. In fact, when we left for Oregon in July 1983, we even had not been able to determine what pesticides we would be working with.

As good fortune would have it, the blueberry grower who was cooperating with us happened to be treating one plot of his farm with mesurol just days before we were to begin our study, and he allowed our group of harvesters to work in that newly treated plot (it was a legal reentry). In due course we collected the urine samples according to the approved protocol, along with other personal and environmental samples needed to complete the study.

Since we did not know what pesticide(s) to expect, we could not have methods of analysis developed and in place at our laboratory before the collection of samples. Consequently, we preserved the urine samples in a manner consistent with our previous experience; namely, we took 20 mL aliquots of the urines, dosed them with 1.5 mL of concentrated hydrochloric acid and sealed them in 25 mL ampules. This style of preservation had worked excellently for urines containing p-nitrophenol.

Alternate methods of preserving urine samples were not acceptable to me. The use of sodium fluoride would cause severe problems with subsequent acid hydrolysis of conjugates. The use of thymol promised to give massive interference in the analysis of phenolic metabolites (such as those of mesurol). And, we could not handle the logistics of freezing, shipping and storing the hundreds of urine samples that were to be generated in the 1983 studies.

This last Fall, as you already know, we began development work on an analytical method to deal with the realities of mesurol metabolism {It leads to three related phenols: 3,5-dimethyl-4-methylthiophenol, 3,5-dimethyl-4-methylsulfinylphenol (the sulfoxide) and 3,5-dimethyl-4-methylsulfonylphenol (the sulfone), reflecting step-wise oxidation of the sulfur.} and the (acid) state of the one hundred plus samples on hand. My approach was to oxidize the three metabolites all to the last one and analyze for it by HPLC.

The development process started from the sulfone; with standards from the manufacturer in hand, we first confirmed that we could analyze that compound by HPLC. then, we worked on oxidation procedures that would take the methylthioether and the sulfoxide to the sulfone. Finally, having done that, we had to anticipate that these phenols could be present in the urines as conjugates with glucose or sulfate and would require hydrolysis prior to analysis. This is the stage where we were just prior to the Christmas break.

It was possible that conjugate hydrolysis had already occurred spontaneously during the samples' standing for over one year at a pH of less than 0.1. The only way we could test for the necessity of a hydrolysis step was to heat an aliquot of one or more actual samples and compare them to aliquots that had not been subjected to this treatment. The results of that experiment was zero in all samples, even the spikes run for quality assurance. Subsequent experiments with spiked samples, including p-nitrophenyl-β-D-glucuronide and p-nitrophenyl sulfate as surrogates, showed that the hydrolysis of the conjugates works perfectly; however, serious, if not complete, loss of the sulfoxide and sulfone occurred (0 to 40% recoveries, respectively).

A review of the chemistry of this type of sulfur compound indicates that treatment with strong acid causes the aromatic carbon-sulfur bond to be hydrolyzed, such that we could expect to have 3,5-dimethylphenol as a product (either conjugated or not). To confirm this hypothesis, samples of acid-treated standards have been submitted to the analytical services laboratory of the College of Chemistry on the Berkeley Campus for GC-MS analysis. We are expecting results back by the middle of this month.

The set-back that this development represents means that we are nearly back to square one in the analysis of the mesurol metabolite samples. If our hypothesis holds, and 3,5-dimethyl-phenol is our analyte, there is a whole new set of parameters to pin down. What method of chromatography (gas or liquid)? If capillary gas chromatography is the separation method of choice, what detector? This compound has no substituents that are amenable to detection with the ECD, FPD or NPD, and would require derivatization with a halogen or phosphorous containing reagent. Will clean-up be required to remove interferences?

To resolve these questions and run the pending samples, we will need time beyond our current ending date of 31 January 1985, as well as salary and supply money for the laboratory personnel who will be needed to complete the work. If all the steps fell into place, the minimum time to implement a method would be a month form now. Analysis of the samples would take another month. A reasonable estimate of completion of these tasks would be the end of March 1985.

Sincerely

John T. Leffingwell, Manager
California PHAP

cc   R.C. Spear
      Marion Lentz

24 January 1985

John Tessari, Manager
Colorado Pesticide Hazard Assessment Project
Colorado State University
Fort Collins, CO
80523

Dear John:

Enclosed are three standards for your use in working with the analysis of Benomyl urinary metabolites: Carbendazim and benomyl from the EPA Standards Repository, and 5-hydroxy-2-benz-imidazolecarbamate from du Pont. The later is the metabolite of interest, although, I am surprised that the carbamate moiety is still intact at the 2 position.

The first two are different forms of the active fungicide; benomyl decomposes rapidly in the environment and in protic solvents, as well, to carbendazim. Carbendazim can be converted to benomyl by reacting it with n-butylisocyanate. This technique is useful in manipulating these compounds for HPLC analysis; benomyl elutes substantially later than carbendazim on a reverse phase C_{18} column, and changing the elution time of the analyte has been useful in eluding interfering peaks. I presume that the same reaction would go with the 5-hydroxy-2-benzimidazolecarbam-ate. For the carbendazim/benomyl analysis, we use an acetoni-trile-water mixture (65:35) @ 2.0 ml per minute on a 25 cm C_{18} column. The butylisocyanate has to be present in the sample at about 2 to 5 ppm to maintain the compound as benomyl. Detection is by UV at 292 nm.

Good luck!

Sincerely

John T. Leffingwell, Manager
California PHAP

cc: G. Fristrom

25 January 1985

Dr. Geraldine Fristrom
FSSP Laboratory Coordinator
EAB/HED/OPP   (TS-769-C)
United States Environmental Protection Agency
401 M Street, SW
Washington, D.C.   20460   RE: Mesurol Metabolite Analysis

Dear Gerrie:

The answer has come back from the GC/MS lab that the only thing found in the treated standard we took them was a dimethylphenol. Given that we started with 3,5-dimethyl-4-methylsulfinylphenol, it is reasonably safe to infer that the product of the decomposition is 3,5-dimethylphenol.

Since we have been following Reed and Watts' method for urinary alkyl phosphates using pentafluorobenzylbromide (PFBB) as a derivatizing reagent in conjunction with our work on the fluorescent tracer project, and since PFBB is reputed to be an excellent derivatizing agent with phenols for electron capture detection, we have undertaken to develop a method utilizing this reagent.

As way of background, 10 mL of the acidic urine samples will be diluted with 5 mL of water and heated to liberate any conjugates. The 3,5-dimethylphenol will be extracted into methylene chloride. The derivatization reaction is carried out in a polar solvent, such as an alcohol, acetone or acetonitrile; so, we will convert the methylene chloride to acetonitrile. Catalysts for the reaction are solid anhydrous potassium carbonate and 18 crown 6 ether; the former generates the potassium salt of the phenol, while the later solvates the potassium ion away from the phenolate ion, promoting its reactivity toward the benzylbromide.

Before he started, Mr. McLean contacted a technical person at Supelco, our supplier of PFBB, to obtain advice on approaches to removing the unused derivatizing reagent from a sample after reaction with the analyte of interest has been completed. PFBB is a neutral molecule; and, as such, cannot be separated from the derivative of the phenol by commonly employed extraction techniques, such as manipulation of pH or use of adsorbents to differentiate between polar and non-polar species. Furthermore, it is highly electron capturing (response factor of about 10 counts

per femptogram on our GC at present), and it will be present in great excess over the analyte of interest. Therefore, an unusual approach is needed in order to utilize this reagent with an ECD that was not needed with the alkyl phosphate analyses using the flame photometric detector.

The Supelco person recommended that we use a strong cation exchange resin in the acid form. The free PFBB would react with the benzene sulfonate groups on the resin and would be, thereby, removed from the sample. The Supelco person had in mind that we would use that company's disposable solid phase extraction/clean-up cartridges loaded with HPLC-type strong cation exchange packing. Since we did not have this item in hand ($2.00 ea. in packages of 50), but did have a good quality cation exchange resin (Bio-Rad AG 50W-X8). For ease of sample handling, we decided to try the resin as a slurry, rather than in a column.

It did not work. No matter how much resin was put in the sample, no reduction in the quantity of PFBB was seen. We even set up a resin column, and saw no reduction. So, back to our contact at Supelco, and his reaction was that he had assumed that we would be working in an aqueous medium. Now, he and another person at Supelco have given us a new procedure.

The treated sample in acetonitrile is to be diluted with water and extracted with hexane. The hexane extract is to be put onto a silica gel extraction/clean-up cartridge, eluted with additional hexane to remove all PFBB and then eluted with 20% hexane in toluene to elute the derivatized phenol. Mr. McLean is attempting this new procedure as of this writing.

If you think that there is a particularly knowledgeable person within EPA or the NPHAP group, I would be glad to talk with them by telephone. I am afraid that by the time copies of this letter get around, and interested parties take time to respond with their ideas, it will be much too late for us to effectively put them into practice. Give me a call when you have read through this and have an idea or two about people I might contact directly for additional suggestions. Thanks.

Sincerely

John T. Leffingwell, Manager
California PHAP

14 March 1985

Dr. Geraldine Fristrom
FSSP Laboratory Coordinator
EAB/HED/OPP (TS-769-C)
United States Environmental Protection Agency
401 M Street, SW
Washington, D.C.   20460   RE: CR-810691-02-0

Dear Gerrie:

It has been some time, now, since we last talked by telephone. I did promise you an update on the Mesurol urinary metabolite methods development work.

As explained in earlier correspondence, we had developed a method for the analysis of mesurol metabolites based on the literature, which indicated that the compounds to be anticipated were threefold: Mesurol phenol (3,5-dimethyl-4-methylthiophenol), the sulfoxide (3,5-dimethyl-4-methylsulfinylphenol) and the sulfone (3,5-dimethyl-4-methylsulfonylphenol). The last step in the method development showed that not only did real samples lack any of these phenols, but spiked blanks lacked them, as well. A review of the chemical literature on sulfur containing phenols led us to believe that the strong acid conditions we used to preserve the samples cleaved the sulfur-carbon bond at the ring. Subsequent GC/MS analysis of a treated spike confirmed that hypothesis.

Work on a second method was undertaken during January, but had to be terminated when Mr. McLean had to be laid off due to lack of funds. The approach we were taking was to derivatize the 3,5-dimethylphenol with something that would allow it to be analyzed with a gas chromatograph equipped with an element-specific detector, eg. electron capture or flame photometric detectors. The ultra-violet spectrum of 3,5 dimethylphenol did not give any distinct peaks at which we could set the variable wavelength detector for the HPLC, rendering that analytical technique of questionable applicability for this problem.

Since we have had relatively good success with the use of pentafluorobenzylbromide in conjunction with the malathion urinary metabolite work that we have been doing of late, we decided to give that a try; we were fairly familiar with its chemistry and we had a stock of the necessary reagents on hand. However,

contrary to the malathion metabolite work, which was done on the flame photometric detector, this work would be done on the electron capture detector; and we would have to devise a scheme to purge the samples, once treated, of excess reagent, which, itself is extremely electron capturing, and renders the detector useless for hours if passed through it in any quantity.

As described in earlier correspondence, we sought advice from our supplier (Supelco) on approaches to handling this problem, since they tout the material as a good derivatizing agent for phenols. Most of the problems were worked out successfully using blanks and spikes, and we had a reasonably good clean-up for clean samples with about a 90% recovery. However, at the point where we had to terminate our work we were experiencing disturbing occurrences of excessive contamination in a large proportion of our blanks. The few spiked urines we had attempted to run through the procedure had chromatograms similar to the contaminated blanks making it impossible to tell whether the urines were contaminated as well, or whether the procedure was simply inadequate for treating urine samples.

Under the circumstances, the only position that I could take was that we might have a usable method, but that it is quite possible that more or different clean-up would be necessary. Worse yet, an entirely new approach to the problem might be required if what we saw in the spiked urine was not an artifact similar to what had appeared in many of the blanks.

At this point, I think it is urgent that we discuss whether or not I will be taking the samples to John Tessari in Colorado. Time is running short for me in the near future, since I will be leaving for a field study late in May. I have most of the reagents in hand for continuation of the Mesurol methodology, if the chemists at the Colorado PHAP wish to continue along that line.

Sincerely

John T. Leffingwell, Manager
California PHAP

cc: John Tessari

26 April 1985

John Tessari, Manager
Colorado Pesticide Hazard Assessment Project
Colorado State University
Fort Collins, CO
80523

Dear John:

Enclosed is a copy of the provisional mesurol metabolite method, as it stood at the point where we had to quit working on it. If it works out that I shall bring the samples to you, I do have PFBB and 18 crown 6 ether (hexaoxacyclooctadecane) that I could bring along, as well as potassium carbonate and the phenol, itself. However, as my letter to Gerri Fristrom points out, this method may yet be a blind alley, and an entirely new approach may be required, to include the possibility of running these samples on a capillary/FID set-up. I do not think that the uv spectrum of the 3,5-dimethylphenol is good enough to do it by HPLC; although, I would not shy away from re-running the spectrum of it again, just in case my crew blew it in preparing the standard for the spectrophotometer.

Sincerely

John T. Leffingwell
University of California
Bldg. 112, Richmond Field Station
47th & Hoffman Blvd.
Richmond, CA 94804

Tessari3.ltr

MESUROL URINARY METABOLITES

Notes

The pertinent analytical methods in the literature were for the simultaneous determination of Mesurol and its two oxidized forms as Mesurol sulfone. Our goal was to apply this type of analysis to Mesurol phenol and its two oxidized forms as they would be found in urine.

Our first findings indicate that the potassium permanganate oxidation method used by Mobay quantitatively destroys MP (mesurol phenol), MPX (mesurol phenol sulfoxide) and MPN (mesurol phenol sulfone).

We next found that the m-chloroperoxybenzoic acid (mCPBA) oxidation method recovered both MP and MPX as MPN. The recovery was low, but no lower than for MPN, itself, which led us to suspect the extraction rather than the oxidation.

The pH of the extraction solution turned out to be the problem. Mesurol has no ionizable molecular site, so that drastic methods could be used to prevent co-extraction of unwanted acidic materials. Up to 40% of the MPN can be lost at the high pH values used for extraction of oxidized mesurol. By using magnesium sulfate solution to slightly lower the pH, recoveries very close to 100% have now been obtained.

Analytical Method

Equipment and Reagents

a) Tilt dispensers: 1 X 10 mL
1 X 15 mL
2 X 20 mL
1 X 25 mL
b) 1 mL high speed pipettor (Brand).
c) Rotary evaporator with water bath.
d) 13 X 100 mm screw-top culture tube with teflon lined cap (1 per sample).
e) Test tube rack for 13 mm tubes.
f) 125 mL separatory funnel with LPE stopper and teflon plug (1 per sample).
g) Separatory funnel rack.
h) 250 mL, ₴ 24/40 Round-bottom flasks (2 per sample).
i) ₴ 24/40 Stoppers (2 per sample).
j) 117 mm OD X 60 mm ID Cork rings (1 per sample).
k) 35 mm Polypropylene analytical funnel (2 per sample).
l) Small volumetric flasks with LPE stoppers (1 X 10 mL or 1 X 5 mL per sample).
m) 4 Dram vials with teflon lined caps (1 per sample).

n) 10 mL Volumetric pipets (1 per sample).
o) Wash bottle for methylene chloride.
p) Wash bottle and dropper bottle for acetonitrile.
q) Glass wool.
r) Pasteur pipets (2 per sample).

Reagents

All solids are Analytical Grade; all liquids are HPLC Grade.

a) CH_2Cl_2 - Methylene Chloride.
b) CH_3CN - Acetonitrile.
c) H_2O - Class ?? Reagent Grade Water (Milli-Q).
d) mCPBA - 1% in CH_2Cl_2.
e) $MgSO_4$ - 250 g/L in H_2O.
f) $NaHCO_3$ - Aqueous Saturated Solution.
g) Na_2SO_3 - Aqueous Saturated Solution.
h) Na_2SO_4 - Anhydrous crystals.
i) Dry ice and coolant (2-propanol) for rotary evaporator.

Procedure

Pipet 10 mL of prepared urine* into a 125 ml separatory funnel; then add 15 mL $MgSO_4$ and 20 ml $NaHCO_3$. Extract sequentially with 3 X 25 mL portions of CH_2Cl_2, filtering each through a 35 mm funnel plugged with glass wool and containing Na_2SO_4 into a 250 round bottom flask, stopper and set aside for rotary evaporation.

Rotovap sample to ˜ 0.25 to 0.50 mL final volume. Transfer to a culture tube with a pasteur pipet using 4 X 1 mL portions of 1% mCPBA to rinse the flask. Seal the tube and allow the contents to react at room temperature for at least 20 minutes, but no more than 30 minutes.

Quantitatively transfer the tube contents to a 125 mL separatory funnel containing 20 mL Na_2SO_3 solution and shake well to destroy any remaining organo-peroxide. Then add 15 mL saturated Na_2SO_4 and 20 mL $NaHCO_3$. Extract with CH_2Cl_2 as described above.

Rotovap to ˜ 0.5 mL and add 10 mL CH_3CN. Repeat twice more. Transfer with CH_3CN and pasteur pipet to a small volumetric flask (5 or 10 mL) and make up to volume. Shake well and put in a 4 dram vial with proper label. Turn the sample over to the HPLC operator for analysis of total MPN.

Mesurol Urinary Metabolite
Analytical Method

A Provisional Method Using
Pentafluorobenzylbromide
to Derivatize
3,5-Dimethylphenol

Introduction

      While at the field study site, I decided to store the
urines in a fashion that had served us well in the past when we
were dealing with phenolic urinary metabolites: We placed dupli-
cate 20 mL aliquots of each subject's urine samples in 20 mL
ampules, adding 1.5 mL of concentrated hydrochloric acid as a
preservative. This approach to storage obviates the need for
refrigeration, eliminates leak-prone screw-cap closures, and sets
the sample up for future hydrolysis of conjugates. However, good
evidence exists to show that the storage of urine samples con-
taining metabolites of mesurol [mesurol phenol (3,5-dimethyl-4-
methylthiophenol), the sulfoxide (3,5-dimethyl-4-methylsulfinyl-
phenol) and the sulfone (3,5-dimethyl-4-methylsulfonylphenol)] in
strong acid causes these compounds to undergo a reaction that
cleaves the sulfur-carbon bond, leaving the product, 3,5-dimeth-
ylphenol.

      In an attempt to produce an analyte that could be quanti-
tated by gas chromatography, I decided to derivatize with penta-
fluorobenzylbromide (PFBB) and utilize the electron capture de-
tector. I recognize that this approach is fraught with many
pitfalls; ECD's are notoriously sensitive to many extraneous
materials that might be present in the urine samples, and rea-
gents used to hang a handle on an otherwise non-capturing mole-
cule usually derivatize many unwanted compounds, as well. It is
possible that a good quality flame ionization detector coupled
with a capillary column would give sufficient sensitivity for
underivatized 3,5-dimethylphenol to eliminate the need for the
ECD and its attendant hypersensitivities. I did not have such a
set-up; so, decided to press on with the PFBB procedure.

Materials and Methods

      The first step is taken to hydrolyze any remaining conju-
gates of the phenol. Ten mL of urine is transferred to a 20 mL
ampule and 5 mL of water is added. The ampule is sealed and
heated under pressure (15 lb. in a standard household pressure
cooker or 20 lb. in a laboratory or clinical autoclave) for 2 hr.
The ampule is opened and the contents are quantitatively trans-
ferred to a 125 mL separatory funnel with about 40 mL of water.
Extract three times with about 25 mL of methylene chloride.

      At this point the methylene chloride can be removed and
replaced with acetonitrile by rotary evaporation. (With care not
to let the solvent go completely dry, good recoveries of the

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relatively volatile phenols can be realized doing a solvent volume reduction on a rotary evaporator.) It has not been tested, yet, to determine whether or not the derivatization reaction can be carried out in the methylene chloride, either with or without a prior drying step. At this point, the conversion to acetonitrile is compatible with the subsequent clean-up procedure utilizing hexane/water partitioning.

Whether the reaction is to be carried out in methylene chloride or in acetonitrile (It will also go equally well in acetone.), the volume of the sample should be brought to about 1 mL. Add 20 µL of pentafluorobenzylbromide, 20 mg potassium carbonate and 20 mg 18 crown 6 ether. Seal (We use Teflon-lined, screw-capped culture tubes.) and heat 2 hours at 100° C. Add 10 mL of hexane and shake well. Add 5 mL of water and, again, shake thoroughly; then allow to settle.

Pre-clean a silica gel Sep-Pak by running 10 mL of HPLC or pesticide grade hexane through it. Draw off a 3 mL aliquot of the hexane layer of the sample with a gas tight syringe and push very slowly through the pre-cleaned silica gel Sep-Pak. Follow it with 5 mL of clean hexane. Discard the eluate; it contains about 90% of the residual PFBB. Finally, elute the Sep-Pak with 5 mL of a toluene/hexane mixture (70/30 v/v). Collect the eluate; bring it to a convenient volume; and analyze for the derivative of the phenol by EC gas chromatography. We found the HP-5880A, using a 50 micron Megabore capillary column, gave us a very nice peak with 4 to 10 femptograms of the derivative. Unfortunately, the same holds true for the PFBB, as well; so, it is important to have most of the reagent removed before the sample hits the ECD.

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APPENDIX C

DATA FILES RELEVANT TO.

URINARY METABOLITE ANALYSES

APPENDIX C

Urine Volumes

TABLE 1

Raspberry Study, Pre-Exposure Urine Samples*

Sample ID	Subject ID	Group	Volume
8301-U-60.	1	A	170
8301-U-60.	2	A	208
8301-U-60.	3	A	630
8301-U-60.	4	A	230
8301-U-60.	5	B	380
8301-U-60.	6	A	300
8301-U-60.	7	A	177
8301-U-60.	8	B	190
8301-U-60.	9	B	209
8301-U-60.	10	B	480
8301-U-60.	11	B	680
8301-U-60.	12	A	310
8301-U-60.	13	A	186
8301-U-60.	14	B	230
8301-U-60.	15	A	630
8301-U-60.	16	A	380
8301-U-60.	17	A	310
8301-U-60.	18	A	252
8301-U-60.	19	A	186
8301-U-60.	20	A	214
8301-U-60.	21	B	300
8301-U-60.	22	B	146
8301-U-60.	23	B	210

* First morning void prior to entry into the field, 11 July 1983.

TABLE 2

Raspberry Study, First Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8301-U-61/62.	1	A	790
8301-U-61/62.	2	A	305
8301-U-61/62.	3	A	790
8301-U-61/62.	4	A	620
8301-U-61/62.	5	B	380
8301-U-61/62.	6	A	680
8301-U-61/62.	7	A	550
8301-U-61/62.	8	B	234
8301-U-61/62.	9	B	530
8301-U-61/62.	10	B	740
8301-U-61/62.	11	B	740
8301-U-61/62.	12	A	730
8301-U-61/62.	14	B	710
8301-U-61/62.	15	A	450
8301-U-61/62.	16	A	380
8301-U-61/62.	17	A	515
8301-U-61/62.	18	A	620
8301-U-61/62.	19	A	415
8301-U-61/62.	20	A	290
8301-U-61/62.	21	B	290
8301-U-61/62.	22	B	335

* Overnight samples, Day Two to Day three, 12 to 13 July 1983.

TABLE 3

Raspberry Study, Second Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8301-U-62.	1	A	194
8301-U-62.	2	A	104
8301-U-62.	3	A	216
8301-U-62.	4	A	100
8301-U-62.	5	B	124
8301-U-62.	6	A	N/S
8301-U-62.	7	A	N/S
8301-U-62.	8	B	N/S
8301-U-62.	9	B	N/S
8301-U-62.	10	B	224
8301-U-62.	11	B	280
8301-U-62.	12	A	172
8301-U-62.	14	B	114
8301-U-62.	15	A	150
8301-U-62.	16	A	410
8301-U-62.	17	A	175
8301-U-62.	18	A	N/S
8301-U-62.	19	A	N/S
8301-U-62.	20	A	N/S
8301-U-62.	21	B	N/S
8301-U-62.	22	B	N/S

* Samples collected during working hours of Day Three, 13 July 1983.

TABLE 4

Raspberry Study, Third Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8301-U-62/63.	1	A	770
8301-U-62/63.	2	A	345
8301-U-62/63.	3	A	710
8301-U-62/63.	4	A	270
8301-U-62/63.	5	B	470
8301-U-62/63.	6	A	221
8301-U-62/63.	7	A	153
8301-U-62/63.	8	B	138
8301-U-62/63.	9	B	300
8301-U-62/63.	10	B	700
8301-U-62/63.	11	B	570
8301-U-62/63.	12	A	655
8301-U-62/63.	14	B	435
8301-U-62/63.	15	A	550
8301-U-62/63.	16	A	285
8301-U-62/63.	17	A	730
8301-U-62/63.	18	A	865
8301-U-62/63.	19	A	240
8301-U-62/63.	20	A	281
8301-U-62/63.	21	B	274
8301-U-62/63.	22	B	Lost by Subject

* Overnight sample, 13 to 14 July 1983.

TABLE 5

Raspberry Study, Fourth Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8301-U-63.	1	A	123
8301-U-63.	2	A	190
8301-U-63.	3	A	280
8301-U-63.	4	A	92
8301-U-63.	5	B	138
8301-U-63.	6	A	400
8301-U-63.	7	A	265
8301-U-63.	8	B	80
8301-U-63.	9	B	170
8301-U-63.	10	B	430
8301-U-63.	11	B	380
8301-U-63.	12	A	72
8301-U-63.	14	B	232
8301-U-63.	15	A	156
8301-U-63.	16	A	190
8301-U-63.	17	A	170
8301-U-63.	18	A	250
8301-U-63.	19	A	132
8301-U-63.	20	A	170
8301-U-63.	21	B	214
8301-U-63.	22	B	218

* Samples collected during working hours of Day Four, 14 July 1983.

TABLE 5

Raspberry Study, Fourth Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8301-U-62.	1	A	123
8301-U-62.	2	A	190
8301-U-62.	3	A	280
8301-U-62.	4	A	92
8301-U-62.	5	B	138
8301-U-62.	6	A	400
8301-U-62.	7	A	265
8301-U-62.	8	B	80
8301-U-62.	9	B	170
8301-U-62.	10	B	430
8301-U-62.	11	B	380
8301-U-62.	12	A	72
8301-U-62.	14	B	232
8301-U-62.	15	A	156
8301-U-62.	16	A	190
8301-U-62.	17	A	170
8301-U-62.	18	A	250
8301-U-62.	19	A	132
8301-U-62.	20	A	170
8301-U-62.	21	B	214
8301-U-62.	22	B	218

* Samples collected during working hours of Day Four, 14 July 1983.

TABLE 6

Blackberry Study, Pre-Exposure Urine Samples*

Sample ID	Subject ID	Group	Volume
8302-U-17.	1	A	615
8302-U-17.	2	A	390
8302-U-17.	3	A	740
8302-U-17.	4	A	235
8302-U-17.	5	A	277
8302-U-17.	6	A	306
8302-U-17.	7	A	224
8302-U-17.	8	A	275
8302-U-17.	9	A	930
8302-U-17.	10	A	950
8302-U-17.	11	A	515
8302-U-17.	12	A	178
8302-U-17.	13	B	264
8302-U-17.	14	B	204
8302-U-18.**	15	B	335
8302-U-18.**	16	B	450
8302-U-17.	17	***	110
8302-U-17.	18	***	254
8302-U-17.	21	B	395
8302-U-18.**	22	B	255
8302-U-17.	23	B	430
8302-U-17.	24	B	366
8302-U-17.	28	B	260
8302-U-17.	29	B	390

* First morning void prior to entry into the field, 18 July 1983.
** Subjects 15,16, and 22 joined the study on Day 2.
*** Subjects 17 and 18 were dropped from the study.

TABLE 7

Blackberry Study, First Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8302-U-18/19.	1	A	930
8302-U-18/19.	2	A	780
8302-U-18/19.	3	A	750
8302-U-18/19.	4	A	400
8302-U-18/19.	5	A	148
8302-U-18/19.	6	A	266
8302-U-18/19.	7	A	182
8302-U-18/19.	8	A	224
8302-U-18/19.	9	A	800
8302-U-18/19.	10	A	584
8302-U-18/19.	11	A	1040
8302-U-18/19.	12	A	242
8302-U-18/19.	13	B	130
8302-U-18/19.	14	B	160
8302-U-18/19.	15	B	720
8302-U-18/19.	16	B	380
8302-U-18/19.	21	B	470
8302-U-18/19.	22	B	580
8302-U-18/19.	23	B	960
8302-U-18/19.	24	B	326
8302-U-18/19.	28	B	455
8302-U-18/19.	29	B	480

* Overnight samples, Day Two to Day Three, 19 to 20 July 1983.

TABLE 8

Blackberry Study, Second Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8302-U-19.	1	A	290
8302-U-19.	2	A	730
8302-U-19.	3	A	102
8302-U-19.	4	A	345
8302-U-19.	5	A	32
8302-U-19.	6	A	144
8302-U-19.	7	A	214
8302-U-19.	8	A	180
8302-U-19.	9	A	175
8302-U-19.	10	A	870
8302-U-19.	11	A	172
8302-U-19.	12	A	230
8302-U-19.	13	B	55
8302-U-19.	14	B	160
8302-U-19.	15	B	190
8302-U-19.	16	B	135
8302-U-19.	21	B	358
8302-U-19.	22	B	N/S
8302-U-19.	23	B	138
8302-U-19.	24	B	290
8302-U-19.	28	B	378
8302-U-19.	29	B	N/S

* Samples collected during working hours of Day Three, 20 July 1983.

TABLE 9

Blackberry Study, Third Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8302-U-19/20.	1	A	650
8302-U-19/20.	2	A	670
8302-U-19/20.	3	A	405
8302-U-19/20.	4	A	228
8302-U-19/20.	5	A	254
8302-U-19/20.	6	A	258
8302-U-19/20.	7	A	328
8302-U-19/20.	8	A	250
8302-U-19/20.	9	A	N/S**
8302-U-19/20.	10	A	N/S**
8302-U-19/20.	11	A	N/S**
8302-U-19/20.	12	A	N/S**
8302-U-19/20.	13	B	N/S**
8302-U-19/20.	14	B	N/S**
8302-U-19/20.	15	B	840
8302-U-19/20.	16	B	760
8302-U-19/20.	21	B	860
8302-U-19/20.	22	B	495
8302-U-19/20.	23	B	800
8302-U-19/20.	24	B	520
8302-U-19/20.	28	B	335
8302-U-19/20.	29	B	660

* Overnight samples, Day Three to Day Four, 20 to 21 July 1983.
** Subjects 9, 10, 11, 12, 13 and 14 dropped out of the study.

TABLE 10

Blackberry Study, Fourth Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8302-U-20.	1	A	178
8302-U-20.	2	A	N/S
8302-U-20.	3	A	248
8302-U-20.	4	A	256
8302-U-20.	5	A	126
8302-U-20.	6	A	178
8302-U-20.	7	A	228
8302-U-20.	8	A	305
8302-U-20.	15	B	195
8302-U-20.	16	B	130
8302-U-20.	21	B	700
8302-U-20.	22	B	66
8302-U-20.	23	B	220
8302-U-20.	24	B	190
8302-U-20.	28	B	365
8302-U-20.	29	B	430

Samples collected during working hours of Day Three, 20 July 1983.

TABLE 11

Blackberry Study, Fifth Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8302-U-20/21.	1	A	375
8302-U-20/21.	2	A	800
8302-U-20/21.	3	A	790
8302-U-20/21.	4	A	355
8302-U-20/21.	5	A	220
8302-U-20/21.	6	A	210
8302-U-20/21.	7	A	176
8302-U-20/21.	8	A	315
8302-U-20/21.	15	B	588
8302-U-20/21.	16	B	740
8302-U-20/21.	21	B	820
8302-U-20/21.	22	B	315
8302-U-20/21.	23	B	730
8302-U-20/21.	24	B	710
8302-U-20/21.	28	B	1040
8302-U-20/21.	29	B	810

* Overnight samples, Day Four to Day Five, 21 to 22 July 1983.

TABLE 12

Blackberry Study, Sixth Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8302-U-21.	1	A	172
8302-U-21.	2	A	360
8302-U-21.	3	A	160
8302-U-21.	4	A	166
8302-U-21.	5	A	110
8302-U-21.	6	A	43
8302-U-21.	7	A	140
8302-U-21.	8	A	66
8302-U-21.	15	B	80
8302-U-21.	16	B	80
8302-U-21.	21	B	410
8302-U-21.	22	B	N/S
8302-U-21.	23	B	220
8302-U-21.	24	B	610
8302-U-21.	28	B	420
8302-U-21.	29	B	370

* Samples collected during working hours of Day Four, 21 July 1983.

TABLE 13

Blueberry Study, Pre-Exposure Urine Samples*

Sample ID	Subject ID	Group	Volume
8303-U-2/3.	1	B	126
8303-U-2/3.	2	A	190
8303-U-2/3.	3	A	230
8303-U-2/3.	4	A	140
8303-U-2/3.	5	A	690
8303-U-2/3.	6	A	154
8303-U-2/3.	7	A	510
8303-U-2/3.	8	A	830
8303-U-2/3.	9	A	390
8303-U-2/3.	10	A	810
8303-U-2/3.	11	A	640
8303-U-2/3.	12	A	820
8303-U-2/3.	14	B	226
8303-U-2/3.	15	B	320
8303-U-2/3.	16	B	460
8303-U-2/3.	17	A	265
8303-U-2/3.	18	B	305
8303-U-2/3.	19	B	250
8303-U-2/3.	20	B	130
8303-U-2/3.	21	B	340
8303-U-2/3.	22	B	410
8303-U-2/3.	23	B	340
8303-U-2/3.	25	B	380
8303-U-2/3.	26	A	N/S**

* First morning void prior to entry into the field, 11 July 1983.
** Subject 26 was the same person as Subject 24 in the Blackberry Study (8302); therefore, use sample 8302-U-21.24 as this person's pre-exposure sample for this study.

TABLE 14

Blueberry Study, First Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8303-U-4/5.	1	B	77
8303-U-4/5.	2	A	270
8303-U-4/5.	3	A	330
8303-U-4/5.	4	A	700
8303-U-4/5.	5	A	440
8303-U-4/5.	6	A	266
8303-U-4/5.	7	A	540
8303-U-4/5.	8	A	355
8303-U-4/5.	9	A	490
8303-U-4/5.	10	A	480
8303-U-4/5.	11	A	620
8303-U-4/5.	12	A	810
8303-U-4/5.	14	B	350
8303-U-4/5.	15	B	640
8303-U-4/5.	16	B	990
8303-U-4/5.	17	A	590
8303-U-4/5.	18	B	800
8303-U-4/5.	19	B	360
8303-U-4/5.	20	B	700
8303-U-4/5.	21	B	430
8303-U-4/5.	22	B	920
8303-U-4/5.	23	B	1340
8303-U-4/5.	25	B	670
8303-U-4/5.	26	A	860

Overnight samples, Day Two to Day Three, 26 to 27 July 1983.

TABLE 15

Blueberry Study, Second Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8303-U-5.	1	B	260
8303-U-5.	2	A	640
8303-U-5.	3	A	240
8303-U-5.	4	A	N/S
8303-U-5.	5	A	N/S
8303-U-5.	6	A	N/S
8303-U-5.	7	A	N/S
8303-U-5.	8	A	N/S
8303-U-5.	9	A	N/S
8303-U-5.	10	A	N/S
8303-U-5.	11	A	172
8303-U-5.	12	A	300
8303-U-5.	14	B	N/S
8303-U-5.	15	B	194
8303-U-5.	16	B	N/S
8303-U-5.	17	A	N/S
8303-U-5.	18	B	N/S
8303-U-5.	19	B	320
8303-U-5.	20	B	340
8303-U-5.	21	B	N/S
8303-U-5.	22	B	760
8303-U-5.	23	B	910
8303-U-5.	25	B	380
8303-U-5.	26	A	810

* Samples collected during working hours of Day Three, 27 July 1983.

UNIVERSITY OF CALIFORNIA

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COLLEGE OF ENGINEERING
SANITARY ENGINEERING
RESEARCH LABORATORY

RICHMOND FIELD STATION, BLDG. 112
47TH & HOFFMAN BLVD.
RICHMOND, CALIFORNIA 94804
415-231-9400

GROUP B

INSTRUCTIONS FOR PARTICIPANTS IN UNIVERSITY STUDY

You have volunteered to participate in an important field study in which we are trying to investigate the absorption of pesticides through the skin of persons working in fields which have been sprayed with pesticides. As fruit pickers, you may have been exposed to very small quantities of pesticides which may remain on leaves and fruit from a previous spray to control insects or plant diseases.

Both Group B, to which you belong, and Group A (the other participants) will be collecting their urine throughout the study.

The study in which you are participating will commence on Sunday night and will be completed at the end of the work day on Friday of that week. It is important that you follow these instructions and that you try to complete ALL SIX DAYS of the study. If you must drop out of the study for one reason or another, please notify your foreman or any of the University people who will be working with you during this week. But, we

urge you to try to work with your fellow participants and tough it out!

Here then are the simple instructions which we will ask you to follow. Again, if you have any questions or run into any trouble, please contact your foreman or any of the University people right away.

Sunday Night and Monday

At the end of this briefing you will receive 2 plastic bottles. One has black markings (Night Bottle) and the other is a collapsible container marked "Specimen Storage Container" (Overflow Container). We will now demonstrate how to assemble the Overflow Container.

On Sunday night before you go to bed and on Monday morning as you wash up, we want you to collect **all** of your urine into your black-marked Night Bottle. If your Night Bottle ever becomes full, deposit all excess urine into your Overflow Bottle. Please store these bottles in a cool place (for example, in your refrigerator). Bring both of your bottles into the field on Monday morning and give them to the University person in charge of bottle collecting.

Tuesday

At the end of your work day, return to the Control Station where we shall give you a new Night Bottle and a new Overflow Bottle to take home. Please collect ALL OF YOUR URINE into these bottles, storing them in a cool place, just like before. When you return to work on Wednesday morning, bring both of these bottles

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with you and hand them to the personnel at the Control Station.

Wednesday, Thursday, & Friday

On the mornings of each of these three days, before you enter the field, please give your Night and Overflow bottles, which you have brought with you from home, to the University person on duty. You will then be handed a new white plastic bottle (your Day Bottle) which will be marked with your name and number. We want you to collect all of your urine into this bottle during the time that you are in the field. Next to the toilet facilities, we have provided several ice chests in which we want you to store your Day Bottle while not in use.

At the end of the work day on Wednesday and Thursday, we will issue you a new Night Bottle and a new Overflow Bottle in which we want you to collect all of your urine until you return to the field in the morning with the bottles, just like before.

On Friday, the experiment will be over at the end of the work day. At that time you give your last Day Bottle to us.

IF YOU HAVE ANY QUESTIONS, PLEASE ASK ANY OF THE UNIVERSITY PERSONNEL, AND THEY SHALL GLADLY ANSWER ANY AND ALL OF YOUR QUESTIONS.

Thank you very much for agreeing to participate in this important study which is significant for the health of all agricultural field workers in Oregon and across the country.

State University of Oregon, Corvallis
University of California, Berkeley

TABLE 16

Blueberry Study, Third Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8303-U-5/6.	1	B	148
8303-U-5/6.	2	A	62
8303-U-5/6.	3	A	430
8303-U-5/6.	4	A	910
8303-U-5/6.	5	A	420
8303-U-5/6.	6	A	N/S**
8303-U-5/6.	7	A	214
8303-U-5/6.	8	A	174
8303-U-5/6.	9	A	400
8303-U-5/6.	10	A	580
8303-U-5/6.	11	A	480
8303-U-5/6.	12	A	590
8303-U-5/6.	14	B	330
8303-U-5/6.	15	B	450
8303-U-5/6.	16	B	630
8303-U-5/6.	17	A	1010
8303-U-5/6.	18	B	1030
8303-U-5/6.	19	B	188
8303-U-5/6.	20	B	122
8303-U-5/6.	21	B	960
8303-U-5/6.	22	B	430
8303-U-5/6.	23	B	660
8303-U-5/6.	25	B	230
8303-U-5/6.	26	A	1000

* Overnight samples, Day Three to Day Four, 27 to 28 July 1983.
** Subject 6 dropped out of the study.

TABLE 17

Blueberry Study, Fourth Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8303-U-6.	1	B	N/S
8303-U-6.	2	A	N/S
8303-U-6.	3	A	N/S
8303-U-6.	4	A	N/S
8303-U-6.	5	A	N/S
8303-U-6.	7	A	266
8303-U-6.	8	A	154
8303-U-6.	9	A	330
8303-U-6.	10	A	270
8303-U-6.	11	A	N/S
8303-U-6.	12	A	380
8303-U-6.	14	B	N/S
8303-U-6.	15	B	N/S
8303-U-6.	16	B	N/S
8303-U-6.	17	A	N/S
8303-U-6.	18	B	190
8303-U-6.	19	B	N/S
8303-U-6.	20	B	N/S
8303-U-6.	21	B	N/S
8303-U-6.	22	B	N/S
8303-U-6.	23	B	N/S
8303-U-6.	25	B	159
8303-U-6.	26	A	N/S

* Samples collected during working hours of Day Four, 28 July 1983.

TABLE 18

Blueberry Study, Fifth Urine Sample Collection*

Sample ID	Subject ID	Group	Volume
8303-U-6/7.	1	B	395
8303-U-6/7.	2	A	447
8303-U-6/7.	3	A	152
8303-U-6/7.	4	A	940
8303-U-6/7.	5	A	435
8303-U-6/7.	7	A	1010
8303-U-6/7.	8	A	635
8303-U-6/7.	9	A	298
8303-U-6/7.	10	A	608
8303-U-6/7.	11	A	146
8303-U-6/7.	12	A	595
8303-U-6/7.	14	B	505
8303-U-6/7.	15	B	620
8303-U-6/7.	16	B	415
8303-U-6/7.	17	A	685
8303-U-6/7.	18	B	1015
8303-U-6/7.	19	B	120
8303-U-6/7.	20	B	235
8303-U-6/7.	21	B	425
8303-U-6/7.	22	B	780
8303-U-6/7.	23	B	1230
8303-U-6/7.	25	B	750
8303-U-6/7.	26	A	805

* Overnight samples, Day Four to Day Five, 28 to 29 July 1983.

Sample Volumes marked "N/S" mean that no sample was collected for that time period. This was the case for many subjects who did not urinate during the "Work" period. Thier total urine out-put was collected, but in the "Night" or "Off Work" period.

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Table 19

ABSTAT 3.00 RASPBERRY STUDY, TIME WORKED DATA FILE: 8301-B REV#11

COMMAND: PRINT DATA

MISSING VALUE TREATMENT: INCLUDE

VARIABLES:

CASE	1 SUBJECT	2 GROUP	3 HOURS1	4 HOURS2	5 HOURS3	6 HOURS4
1	1.00000	1.00000	5.00000	5.40000	3.70000	4.50000
2	2.00000	1.00000	5.00000	5.40000	3.70000	4.50000
3	3.00000	1.00000	5.00000	5.40000	3.70000	4.50000
4	4.00000	1.00000	5.00000	5.40000	3.70000	4.50000
5	6.00000	1.00000	5.00000	MISSING	3.70000	4.50000
6	7.00000	1.00000	5.00000	5.40000	3.70000	4.50000
7	12.0000	1.00000	5.00000	5.40000	3.70000	4.50000
8	15.0000	1.00000	5.00000	5.40000	3.70000	4.50000
9	16.0000	1.00000	5.00000	5.40000	3.70000	4.50000
10	17.0000	1.00000	5.00000	5.40000	3.70000	4.50000
11	18.0000	1.00000	5.00000	5.40000	3.70000	4.50000
12	19.0000	1.00000	5.00000	5.40000	3.70000	4.50000
13	20.0000	1.00000	5.00000	MISSING	3.70000	4.50000
14	5.00000	2.00000	5.00000	5.40000	3.70000	4.50000
15	8.00000	2.00000	5.00000	5.40000	3.70000	4.50000
16	9.00000	2.00000	5.00000	5.40000	3.70000	4.50000
17	10.0000	2.00000	5.00000	5.40000	3.70000	4.50000
18	11.0000	2.00000	5.00000	2.30000	3.70000	4.50000
19	13.0000	2.00000	5.00000	5.40000	3.70000	4.50000
20	14.0000	2.00000	5.00000	5.40000	3.70000	4.50000
21	21.0000	2.00000	5.00000	5.40000	3.70000	4.00000
22	22.0000	2.00000	5.00000	5.40000	3.70000	4.50000
23	23.0000	2.00000	5.00000	5.40000	3.70000	4.50000

Table 20

ABSTAT 3.00   BLACKBERRY STUDY, TIME WORKED DATA   FILE: 8302-B   REV# 7

COMMAND: PRINT DATA

MISSING VALUE TREATMENT: INCLUDE

VARIABLES:

CASE	1 SUBJECT	2 GROUP	3 HOURS1	4 HOURS2	5 HOURS3	6 HOURS4	7 HOURS5
1	1.00000	1.00000	6.50000	4.83300	5.75000	6.50000	4.50000
2	2.00000	1.00000	6.50000	4.83300	5.75000	6.50000	4.50000
3	3.00000	1.00000	5.83330	4.83300	5.75000	6.50000	3.83300
4	4.00000	1.00000	6.83300	4.83300	5.75000	6.50000	4.50000
5	5.00000	1.00000	6.83300	4.83300	5.75000	6.50000	4.50000
6	6.00000	1.00000	5.83300	4.83300	5.75000	6.50000	4.50000
7	7.00000	1.00000	6.50000	4.83300	5.75000	6.50000	4.50000
8	8.00000	1.00000	6.83300	4.83300	5.75000	6.50000	4.50000
9	9.00000	1.00000	5.83300	3.33300	4.00000	MISSING	MISSING
10	10.0000	1.00000	5.50000	3.75000	4.00000	MISSING	MISSING
11	11.0000	1.00000	5.50000	3.75000	4.00000	MISSING	MISSING
12	12.0000	1.00000	5.50000	3.75000	4.00000	MISSING	MISSING
13	13.0000	2.00000	5.50000	3.80000	4.10000	MISSING	MISSING
14	14.0000	2.00000	5.50000	3.80000	3.90000	MISSING	MISSING
15	15.0000	2.00000	0.00000	4.90000	2.60000	4.60000	2.70000
16	16.0000	2.00000	0.00000	5.00000	2.80000	5.10000	2.70000
17	21.0000	2.00000	5.20000	0.00000	6.40000	4.10000	4.80000
18	22.0000	2.00000	0.00000	5.00000	2.80000	5.10000	1.40000
19	23.0000	2.00000	5.20000	0.700000	6.40000	4.30000	4.90000
20	24.0000	2.00000	4.60000	1.00000	4.70000	MISSING	3.10000
21	28.0000	2.00000	6.50000	6.50000	7.80000	5.90000	5.10000
22	29.0000	2.00000	6.50000	6.50000	7.80000	5.90000	5.10000

Table 21

ABSTAT 3.00   BLUEBERRY STUDY, TIME WORKED DATA   FILE: 8303-BY   REV# 9

COMMAND: PRINT DATA

MISSING VALUE TREATMENT: INCLUDE

VARIABLES:

CASE	1 SUBJECT	2 GROUP	3 HOURS1	5 HOURS2	7 HOURS3	9 HOURS4
1	2.00000	1.00000	7.27000	7.28000	0.750000	3.00000
2	3.00000	1.00000	6.40000	6.57000	0.750000	2.90000
3	4.00000	1.00000	4.85000	5.75000	0.500000	MISSING
4	5.00000	1.00000	7.67000	6.28000	1.00000	6.45000
5	6.00000	1.00000	4.88000	6.02000	1.00000	MISSING
6	7.00000	1.00000	7.72000	7.62000	3.50000	7.33000
7	8.00000	1.00000	4.98000	5.77000	3.42000	8.22000
8	9.00000	1.00000	7.55000	7.42000	3.50000	7.33000
9	10.0000	1.00000	7.52000	7.75000	3.50000	7.33000
10	11.0000	1.00000	5.98000	5.68000	3.42000	7.16000
11	12.0000	1.00000	4.98000	5.70000	3.17000	7.33000
12	17.0000	1.00000	4.93000	6.37000	0.300000	5.35000
13	26.0000	1.00000	6.80000	7.28000	1.25000	3.25000
14	1.00000	2.00000	7.27000	2.50000	0.00000	MISSING
15	14.0000	2.00000	7.89000	7.18000	1.34000	6.45000
16	15.0000	2.00000	7.58000	7.95000	0.00000	6.45000
17	16.0000	2.00000	7.73000	7.08000	1.58000	4.87000
18	18.0000	2.00000	7.77000	MISSING	0.330000	4.87000
19	19.0000	2.00000	7.73000	7.50000	MISSING	MISSING
20	20.0000	2.00000	7.67000	7.37000	MISSING	MISSING
21	21.0000	2.00000	7.73000	8.00000	3.25000	6.22000
22	22.0000	2.00000	7.65000	7.17000	2.75000	MISSING
23	23.0000	2.00000	7.65000	7.17000	2.75000	MISSING
24	25.0000	2.00000	7.60000	8.50000	2.58000	5.87000

Table 22

ABSTAT 3.00   BLUEBERRY STUDY, YIELD DATA   FILE: 8303-HY   REV# 9

COMMAND: PRINT DATA

MISSING VALUE TREATMENT: INCLUDE

VARIABLES:

CASE	1 SUBJECT	2 GROUP	4 YIELDKG1	6 YIELDKG2	8 YIELDKG3	10 YIELDKG4
1	2.00000	1.00000	41.9501	46.2585	2.49433	24.7166
2	3.00000	1.00000	19.0476	17.9138 ·	1.36054	13.1519
3	4.00000	1.00000	46.7120	43.7642	0.00000	MISSING
4	5.00000	1.00000	32.1996	14.5125	MISSING	46.7120
5	6.00000	1.00000	42.6304	47.1655	MISSING	MISSING
6	7.00000	1.00000	91.8368	98.6395	58.5034	99.7733
7	8.00000	1.00000	32.3129	43.5374	MISSING	68.0272
8	9.00000	1.00000	66.6667	68.7075	56.6893	75.7370
9	10.0000	1.00000	94.7846	84.1270	54.4218	95.0114
10	11.0000	1.00000	21.5420	21.7687	MISSING	29.4785
11	12.0000	1.00000	32.3129	43.5374	MISSING	58.9570
12	17.0000	1.00000	17.6871	29.0250	MISSING	MISSING
13	26.0000	1.00000	45.5782	59.4105	MISSING	22.6757
14	1.00000	2.00000	22.6757	18.1406	0.00000	MISSING
15	14.0000	2.00000	36.0544	31.9728	MISSING	40.1361
16	15.0000	2.00000	61.6780	58.0499 ·	0.00000	53.7415
17	16.0000	2.00000	55.3288	29.0250	0.00000	MISSING
18	18.0000	2.00000	77.3243	MISSING	MISSING	MISSING
19	19.0000	2.00000	45.5782	46.2585	2.49433	26.9841
20	20.0000	2.00000	52.1542	54.8753	4.30839	31.9728
21	21.0000	2.00000	91.8368	102.494	60.7710	108.617
22	22.0000	2.00000	45.3515	36.2812	MISSING	MISSING
23	23.0000	2.00000	38.5488	36.2812	MISSING	MISSING
24	25.0000	2.00000	47.8458	49.4331	16.7801	MISSING

APPENDIX D

CONSENT FORMS AND

INSTRUCTIONS FOR PARTICIPANTS

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COLLEGE OF ENGINEERING   RICHMOND FIELD STATION, BLDG. 112
SANITARY ENGINEERING   47TH & HOFFMAN BLVD.
  RESEARCH LABORATORY   RICHMOND, CALIFORNIA 94804
                                                415-231-9400

STUDY OF PESTICIDE EXPOSURE AMONG
BERRY HARVESTERS
CONSENT TO ACT AS SUBJECT FOR RESEARCH AND INVESTIGATION

Subject's Name_____Date_____

1. The Pesticide Hazard Assessment Project at the University of
   California wishes to study the amount of dust and pesticides in
   your workplace. We want to measure your level of exposure to
   pesticide residues and to evaluate its health hazard. If you
   agree to participate, we will ask you to wear some sample col-
   lectors during your workday. We will provide you with:

   (1) gauze patches taped to an arms and legs like small
       bandages,
   (2) a T-shirt with patches attached,
   (3) cotton work gloves, and, perhaps
   (4) a pump worn on your belt with a dust collector on your
       shoulder.

   This study also calls for the collection of all of each person's
   urine for a maximum of four days. If you choose to participate
   in the study, you will be provided with containers and be given
   thorough instructions for their use.

   After your work, we will collect these samples and take them
   back to our laboratory for analysis. We will then evaluate
   these measurements as they might affect your health, or that of
   your co-workers. Therefore, we ask for your cooperation. Your
   participation in this study is purely voluntary. It will have
   no effect on your employment status here this summer. We would
   like to sample for nearly the whole workday, but you can end
   your participation at any time.

2. I understand that the study in which I am participating
   involves:

   a. The wearing of patches that act as collectors of dust and
      pesticides as they fall on me while I work.

   b. The possibility of wearing a small portable air sampling
      device while working during the study period.

   c. The collection of urine samples for up to 4 days.

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3.   I hereby authorize _____, or other such
      qualified assistants, as may be selected by Dr._____,
      to collect urine, patch and air samples.

4.   The procedures and investigation in which I am participating
      have been explained to me by_____.

5.   I understand that the urine, patch and air sampling procedures
      may involve some annoyance or inconvenience.

6.   I understand that Dr._____and/or such
      qualified assistants as may be selected by him will answer any
      questions I may have at any time concerning the study. I under-
      stand that I may withdraw from the study at any time. I also
      understand that if I do withdraw, it will in no way jeopardize
      my employment.

7.   I understand that no unusual or extraordinary pesticide applica-
      tions have been made for the purposes of this study.

8.   I understand that I will be paid a bonus of $20.00 for the
      completion of urine sampling over a maximum of four days.

9.   I understand that my name will not be used in any context or in
      any way connected with the use of results from any of the col-
      lection procedures.

                         _____
                                   Subject's Signature

                         _____
                               Parent or Guardian's Signature

                         _____
                                        Witness

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COLLEGE OF ENGINEERING
SANITARY ENGINEERING
  RESEARCH LABORATORY

RICHMOND FIELD STATION, BLDG. 112
47TH & HOFFMAN BLVD.
RICHMOND, CALIFORNIA 94804
415-231-9400

GROUP A

INSTRUCTIONS FOR PARTICIPANTS IN UNIVERSITY STUDY

You have volunteered to participate in an important field study in which we are trying to investigate the absorption of pesticides through the skin of persons working in fields which have been sprayed with pesticides. As fruit pickers, you may have been exposed to very small quantities of pesticides which may remain on leaves and fruit from a previous spray to control insects or plant diseases.

In order to measure concentration of pesticides on the skin, Group A, to which you belong, will be fitted with cotton gloves for hand exposure and cotton patches for exposure to the rest of the body. Both Group A and Group B (the other participants) will be collecting their urine throughout the study.

The study in which you are participating will commence on Sunday night and will be completed at the end of the work day on Friday of that week. It is important that you follow these instructions and that you try to complete ALL SIX DAYS of the study. If you must drop out of the study for one reason or

another, please notify your foreman or any of the University people who will be working with you during this week. But, we urge you to try to work with your fellow participants and tough it out!

Here then are the simple instructions which we will ask you to follow. Again, if you have any questions or run into any trouble, please contact your foreman or any of the University people right away.

Sunday Night and Monday

At the end of this briefing you will receive 2 plastic containers. One is a bottle with black markings (Night Bottle) and the other is a collapsible container marked "Specimen Storage Container" (Overflow Container). We will now demonstrate how to assemble this container.

On Sunday night before you go to bed and on Monday morning as you wash up, we want you to collect **all** of your urine into your black-marked Night Bottle. If your Night Bottle ever becomes full, deposit all excess urine into your Overflow Container. Please store the containers when used in a cool place (for example, in your refrigerator). Bring your Night Bottle into the field on Monday morning and give it to the University person in charge of specimen collecting. (If you had to use the overflow container, bring that with you into the field.)

We will issue you a pair of white cotton gloves which may decrease your dermal pesticide exposure. When the gloves become too dirty or wet, please go to the Control Station (a University

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vehicle) but <u>do not try to remove your gloves</u>. We will remove your gloves and issue you another, new pair.

Tuesday

Before you go into the field to pick berries on Tuesday, go to the Control Station and you will be issued gloves, just like on Monday, and you will be outfitted with cotton patches on different parts of your body. You will keep the patches on all day since they will not become too soiled. If, however, a patch should come loose, please notify your foreman or University personnel. We'll be there to help you! If the gloves become too dirty or wet, please notify us, and we shall issue a new pair of gloves to you. Do not try to remove the gloves yourself! During your lunch hour, let us remove your gloves, and we shall issue you a new set of gloves when you return to work after lunch.

At the end of your work day, return to the Control Station, and we shall remove your gloves and patches for the day Just before you go home, we shall give you a new Night Bottle and a new Overflow Bottle to take home. Please collect ALL OF YOUR URINE into these bottles, storing them in a cool place, just like before. When you return to work on Wednesday morning, bring both of these bottles with you and hand them to the personnel at the Control Station.

Wednesday, Thursday, & Friday

On Wednesday morning, before you enter the field, please give your Night and Overflow bottles, which you have brought with you from home, to the University person on duty. Again, you will

be issued gloves and patches just like on Tuesday. In addition, on each of these three days you will be handed a new white plastic bottle (your Day Bottle) which will be marked with your name and number. We want you to collect all of your urine into this bottle during the time that you are in the field. Next to the toilet facilities, we have provided several ice chests in which we want you to store your Day Bottle while not in use.

Gloves will be changed by us at the lunch break, and new gloves will be issued to you if needed, just like before. On Thursday and Friday you will only be issued gloves and not patches.

At the end of the work day on Wednesday and Thursday, we will issue you a new Night Bottle and a new Overflow Bottle in which we want you to collect all of your urine until you return to the field in the morning with the bottles, just like before.

On Friday, the experiment will be over at the end of the work day. At that time you give your last Day Bottle to us.

IF YOU HAVE ANY QUESTIONS, PLEASE ASK ANY OF THE UNIVERSITY PERSONNEL, AND THEY SHALL GLADLY ANSWER ANY AND ALL OF YOUR QUESTIONS.

Thank you very much for agreeing to participate in this important study which is significant for the health of all agricultural field workers in Oregon and across the country.

State University of Oregon, Corvallis

University of California, Berkeley

UNIVERSITY OF CALIFORNIA, BERKELEY

BERKELEY • DAVIS • IRVINE • LOS ANGELES • RIVERSIDE • SAN DIEGO • SAN FRANCISCO   SANTA BARBARA • SANTA CRUZ

SANITARY ENGINEERING AND ENVIRONMENTAL
   HEALTH RESEARCH LABORATORY
     COLLEGE OF ENGINEERING
     SCHOOL OF PUBLIC HEALTH

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RICHMOND, CALIFORNIA 94804-4603
(415) 231-9449

24 October 1985

Dr. Geraldine Fristrom
FSSP Laboratory Coordinator
EAB/HED/OPP   (TS-769-C)
United States Environmental Protection Agency
401 M Street, SW
Washington, D.C.   20460   RE: CR-810691-02-0
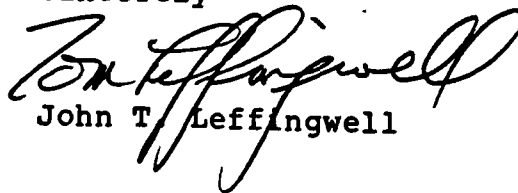
Dear Gerrie:

Attached is a corrected page five for Appendix C of the final report we just handed you. While working over some of the files that had gone into the production of the report, I discovered that this one table had the incorrect Sample ID; so, I have corrected it in all copies but yours.

I hope your trip to West Coast is considered successful. I presume that you have things at Davis all squared away, and that both you and Jim are happy.

                 Sincerely

                 John T. Leffingwell

Encl.

An Assessment of Exposure of Okra Harvesters
   to Carbaryl

Research performed by

Texas Tech University
San Benito, TX   78586

February 28, 1986

In behalf of the Texas PHAP the undersigned have reviewed and approved the report draft entitled "An Assessment of Exposure of Okra Harvesters to Carbaryl."

_____   28-Feb 1986
Quality Assurance Officer   Date

_____   2-28-86
Project Director   Date

TABLE OF CONTENTS

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Abstract. Human exposure to residues of carbaryl (1-Naphthyl N-methylcarbamate) was assessed in a study group of individuals re-entering a 10 acre field of okra immediately after an aerial application of a wettable powder formulation. Deposition of carbaryl was examined on artificial substrates, elevated panels, as well as on foliage and soil. Residues of carbaryl appeared to be uniformly distributed over the foliage canopy. The mean concentration detected on panels (6.04 $\pm$ 3.35 ug/cm^2) elevated within the canopy was not significantly different than the mean concentration detected in leaves (9.37 $\pm$ 5.24 ug/cm^2). Concentrations detected in leaf samples collected near the canopy were not signficantly different than concentrations detected in leaf samples obtained from below the canopy. The lowest mean concentration was detected in soil (0.408 $\pm$ 0.297 ug/cm^2). The transfer of residues to the workers was assessed through the examination of residue concentrations on sampling devices, 100 cm^2 gauze patches, located on outside and inside sleeves and the chest pockets of cotton chambray shirts worn by the subjects. Significantly greater concentrations of carbaryl were detected on outside sleeves (8.61 $\pm$ 2.59 ug/cm^2) than on chest patches (3.06 $\pm$ 1.38 ug/cm^2). Concentrations of carbaryl detected on outside sleeves were not signficantly different than concentrations detected on inside sleeves (5.53 $\pm$ 3.35 ug/cm^2). Residues of carbaryl appeared to accumulate on outside arm patches and penetrate the cotton chambray shirt. Urine samples analyzed for the metabolite of carbaryl, 1-napthol, indicated dermal absorption of carbaryl (0.037 $\pm$ 0.005 ug/mg creatinine/ml). Immediate health effects from this level of exposure appeared remote. The burden on metabolic and excretory processes from such an exposure for an extended period might require further investigation.

AN ASSESSMENT OF EXPOSURE OF OKRA HARVESTERS TO CARBARYL

INTRODUCTION

Occupational exposure to carbaryl has been extensively reviewed by the National Institute of Occupational Safety and Health (NIOSH, 1976) and the World Health Organization (WHO, 1982). NIOSH (1976) estimated that 10,000 workers in the U.S. may be exposed to carbaryl every year including agricultural crop workers, farmers, plant nursery workers and spray pilots. A case study (NIOSH, 1976) of agricultural workers exposed to carbaryl in the Soviet Union (Yakim, 1967) indicated no change in physiological functions before or after work, although whole blood cholinesterase activity was depressed 11-22% in individuals involved in loading to a high of 30% in aerial signalers. Airborne concentrations of carbaryl were contrasted among the loading site (2 mg/M^3) and the concentrations (4 mg/M^3) detected in the fields where signalers were exposed and within the aerial applicators cabin (7 mg/M^3). Concentrations detected in the cabin of aircraft used to spray carbaryl exceeded threshold limits (5 mg/M^3) most recently utilized by the American Conference of Governmental Industrial Hygienists (ACGIH, 1984). Although concentrations appeared to exceed threshold limits within the aerial applicators workspace, the origin of the residues and the extent of exposure to the pilots was not given (NIOSH, 1976).

In another assessment of risk to workers occupationally exposed to carbaryl, Comer et al. (1975) determined that workers involved in mixing and bagging dust formulations of carbaryl were subjected to greater risk of dermal exposure than field workers. Spraymen working in fruit orchards were exposed to 59.0 mg/hr compared to 73.9 mg/hr for factory workers. Urine samples obtained from factory workers contained an average of 8.9 ppm and a high of 65 ppm of the principal metabolite of carbaryl, 1-naphthol. Accepting these values and those reported by Best and Murray (1962) as representative of possible daily exposures to carbaryl, a 70 Kg worker may be expected to be exposed to concentrations well above the acceptable daily intake (ADI) of 0.01 mg/Kg set by the Food and Agricultural Organization of the United Nations (FAO) and the World Health Organization (Kuhr and Dorough, 1976). Although exposure of workers to carbaryl would be expected to be greater than the general population (Kuhr and Dorough, 1976), the work related studies reported by NIOSH (1976) did not indicate serious health effects related to enhanced exposure.

Maitlen et al. (1982) observed that nearly 100% of the exposure to aerial applicators occurred through the hands as a result of manual adjustment of spray nozzles. A similar route of exposure was observed for workers involved in ground application. Individuals involved in handgun application received more uniform exposure. Applicators received considerably less exposure than individuals involved in mixer-loader operations.

By considering many of the facets of pesticide application to fruit orchards, Maitlen, et al. (1982) were able to estimate the extent of exposure to farm workers. Aerial flaggers or signalers had the highest hourly dermal

exposure (HDE). Residues were more evenly distributed over the body compared to mixer-loaders, aerial applicators, or tree thinners. Flaggers received greatest exposure on the face, while workers performing the other duties received greatest exposure through the hands.

Transfer of dislodgable residues of carbaryl onto the hands of workers involved in thinning leaves from the trees (thinners) was also compared with the loss of residues from the leaves (Maitlen et al., 1982). Loss of residues from the leaves followed first order kinetics with a loss of 87% of the residue in the first 8 days. The remainder of the residue was lost more slowly. Maitlen et al. (1982) obtained a significant correlation (r = 0.99) between leaf residue (ug/cm^2) and hourly dermal exposure on the hands of thinners. The pharmacokinetic disposition of the insecticide was not observed.

Dermal exposure to carbaryl by strawberry harvesters was studied by Zweig et al. (1984). They determined that, on this crop at least, dermal exposure is mainly on the hands and forearms and, to a much lesser degree, on the lower legs. They also observed higher exposure levels in the morning than in the afternoon and that younger and/or lighter weight subjects exhibited lower exposures.

Best and Murray (1962) contrasted the exposure of carbaryl-manufacturing plant workers with corresponding blood samples for the determination of cholinesterase activity and urine specimens for the detection of the primary metabolite of carbaryl, 1-naphthol (NIOSH, 1976). The NIOSH document (NIOSH, 1976) which reported the results of Best and Murray (1962) suggested that the cholinesterase data were based on an insensitive method and were not

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representative of exposure as indicated by the concentrations of 1-naphthol detected in urine. An average of 354 ug/l of 1-naphthol was detected in urine collected after completion of the work day during 3.5 months of activity, e.g., production, bagging and shipping of carbaryl. After cessation of activity, urine concentrations of 1-naphthol decreased to 108 ug/l. Upon resumption of work urine concentrations of 1-naphthol rebounded to a high of 10 mg/l in 41% of the 138 urine specimens. Best and Murray (1962) reported a range of air concentrations of carbaryl between 1.23 and 40 mg/M^3 for the study period. Although the air concentration exceeded threshold limit values (5 mg/M^3) and urine concentrations of 1-naphthol indicated exposure, the employees studied did not demonstrate clinical evidence of intoxication (NIOSH, 1976).

Carbaryl (1-naphthyl N-methylcarbamate) is a widely used monomethyl carbamate insecticide with reasonably well understood acute toxicological properties (NIOSH, 1976 and Kuhr and Dorough, 1976). Exposure to the many formulations of carbaryl may be detected through examination of serum or red blood cell (RBC) cholinesterase (ChE) activity and metabolites of carbaryl in blood or urine. Associations between dermal exposure and biological activity may be useful in the preparation of worker protection standards (NIOSH, 1976). Because of the rapidity of hydrolysis of carbaryl, depression of ChE activity may not be sensitive enough to measure exposure (NIOSH, 1976). Detection of concentrations of metabolites in urine may prove more quantitative.

This study was designed to estimate exposure of okra harvesters to dislodgable residues of carbaryl (Sevin[R] 50-W) following an aerial application at the maximum labeled rate (4 lbs/acre). Exposure was to be

assessed by making comparisons of concentrations of carbaryl metabolites
detected in urine of workers to concentrations of residues of carbaryl found
in dermal exposure patches and the associated substrates, okra leaves and soil.

BACKGROUND

Okra is an important fresh market and processing market crop grown in Texas primarily on 400 to 800 acres of the Lower Rio Grande Valley (LRGV) (Sikes et al., 1980). At maturity, okra grown in South Texas reaches a height of one to two meters. The leaves are relatively large and the foliage is heavy. The pods mature rapidly, requiring a daily harvest to maintain uniform sizes. Harvesting is done early in the morning to allow for easy manipulation of the pods at maximum freshness.

Harvesters may be expected to contact residues of carbaryl when handling the pods through the lush foliage. Continuous exposure to carbaryl may be expected as the harvest continues. Okra is picked over a period of many days according to sizing requirements of the grower. Applications of carbaryl may be repeated in accordance with insect pest pressures. Additionally, workers may influence their own exposure through the clothing they wear (barriers), through personal behavior (eating habits, smoking), and the speed with which they work. Harvesters are usually paid by the amount of okra picked.

Both youth, 17 years of age and younger, and adult farmworkers are engaged in the harvest of okra. In addition, children of migrant farmworkers frequently enter the fields with their parents (Spear, 1982). Youths involved in the harvest of okra may be expected to come into contact with pesticide residues at the same level as adults. Munn et al. (1985) observed that youths

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may experience a higher absorbed dose because of lower body weights. This study was originally designed to examine the exposure of youth and adult farmworkers to carbaryl while harvesting okra. The aim of the study was to estimate the level of exposure between youths and adults.

METHODS AND PROCEDURES

A ten acre field near Monte Alto in Willacy County of the Lower Rio Grande Valley (LRGV) of Texas was chosen as the sample site. Deposition of carbaryl was examined on elevated panels, soil, and okra leaves. The elevated panels consisted of three 100 cm^2 gauze patches distributed over a 0.093 m^2 (1 ft^2) surface elevated at the height of the canopy (171 cm). Nine panels were placed within 40 inch wide rows and aligned in a north south direction from the west edge of the field. Each panel was separated by 25 rows (24.6 m). A companion set of nine panels was placed 61.8 m (200 ft.) from the east border and 61.8 m from the first set. The panels aligned in the north-south plane along rows were transected at the middle of the field by another set of 10 panels aligned in the east-west plane.

Sevin 50-W (EPA Reg. No. 264-315) was aerially applied at the rate of 4 lbs. per acre on 20 October 1983. The applicator sprayed in swaths from east to west beginning at the north end traveling south. The applicator made 14 passes with two final passes across each north and south end. The time of application was 1400 hours and the wind velocity was 10-12 miles per hour from the southeast. The temperature at 1300 was $86°$ F. The soil was dry although a percent moisture reading was not taken.

Sample collection started 30 minutes after application and continued for three hours. A single gauze patch was randomly selected from each of the 18

panels for extraction. The remaining patches were stored frozen. The patch selected for extraction was placed in an Erlenmeyer flask with 150 ml methanol. The solution and patch were agitated on a Burrell wrist action shaker for 15 minutes. The extracts from three replications were combined and dried with sodium sulfate. The dried extract was concentrated with a Buchi Rotovapor R110 evaporator and reduced to 5 ml on a nitrogen Meyer N-EVAP analytical evaporator.

Leaf samples were collected from plants along assigned rows in the north-south direction. The samples (5 cm^2) were taken from exposed leaves at the top of the canopy (n = 100) and from covered leaves under the canopy (n = 100). The leaf punches were dropped from the punch into 120 cc plastic urine specimen containers and transported on dry ice to the laboratory. Ten leaf punches were drawn from each of the 100 samples collected in the field. The leaf punches (n = 10) from each of the sampling sites (n = 9) were examined for dislogable residues of carbaryl according to the method of Gunther et al. (1974).

The ten leaf punches (50 cm^2) were placed in 120 cc urine specimen cups for extraction. The sample was extracted with 75 ml deionized water and 50 ul of (0.5%) Witconol NP-100 surfactant at maximum agitation for 15 minutes on a laboratory shaker. The sample was extracted three times. The extracts were collected in a 1000 ml separatory funnel. The volume was adjusted to 600 ml with a 2% solution of sodium sulfate in water. The sodium sulfate acted as a clearing agent to prevent formation of an emulsion upon extraction. The 600 ml solution was extracted three times with 150 ml methylene chloride. The

extract was pooled and dried with sodium sulfate. The dried sample was concentrated to 0.5 ml and the volume adjusted to 5.0 ml with methanol.

Deposition of carbaryl on soil was examined on 400 cm^2 soil pans (n = 4) containing 100 grams of soil at a depth of 0.5 cm. The pans were placed in a row flush with the soil near the center of the field. Soil from the pans was transferred to quart size zip-lock[R] bags and stored frozen until prepared for analysis. The soil (10 g) was extracted three times with 50 ml methanol with vigorous agitation of a Burrell wrist action shaker for 15 minutes. The pooled extract (150 ml) was filtered through Whatman #1 filter paper. The filtrate was concentrated in a Buchi Rotovapor R110 evaporator and reduced to 5.0 ml on a nitrogen Meyer N-EVAP analytical evaporator.

The sample extracts were analyzed by reverse phase high performance liquid chromatography (HPLC) at 280 nm with a Spectra-Physics liquid chromatograph equipped with a Model SP8440 variable wavelength detector, a SP8700 solvent delivery system, and a SP8750 organizer with a 7125RV Rheodyne syringe sample injector with a 10 ul sample loop (Cramer et al., 1982). Samples were separated on an Alltech C18 (250 mm x 4 mm i.d.) column. The mobil phase was 50% acetonitrile and 50% water at a 1 ml/min flow rate. The peaks were integrated and computations quantified by a Hewlett Packard HP9826 desk top micro-computer utilizing the 4400 Series Nelson Analytical Software Program for Chromatography.

A mean concentration of 0.10 $\pm$ 0.03 ug/cm^2 was recovered from panel patches (n=3) fortified with carbaryl (0.10 ug/cm^2). Seventy percent of the fortified concentration (1.3 ug/cm^2) of carbaryl was recovered from leaves. Much higher recovery (143%) was obtained from soil fortified at 1.0 ug/y.

Preharvest urine specimens were obtained from 5 male and 3 female farmworkers. These subjects did not enter the field. Farmworker participation was cancelled because of inclement weather. The study design was amended to utilize urine samples obtained from three of the four male members of the study team before entry into the field and after collection of substrate samples. These study team workers became the test subjects. The harvesters originally recruited as test subjects became the control population. The test subjects were equipped with 4 x 4 gauze sample patches (100 cm^2) on the inside and outside sleeves and on the right and left chest pockets of cotton chambray work shirts. The gauze patches were analyzed for residues of carbaryl according to the method described for panel patches. Urine samples were examined for the metabolite of carbaryl, 1-naphthol, according to the method of Shafik et al. (1971). The minimum detection limits for this method were established by Shafik et al. (1971) at 0.02 ppm. A recovery of 77.0 percent was obtained for a single quality control sample fortified at 20.0 ng/ml.

Urine (1.0 ml) was added to 3.0 ml 4N HCl in 15 ml culture tubes and heated at 32°C for one hour. The hydrolyzed sample was allowed to cool to room temperature and then extracted twice with 5.0 ml methylene chloride. The combined extracts were adjusted to 10.0 ml with methylene chloride and dried with sodium sulfate. The extract was transferred to another 15 ml culture tube. The sodium sulfate was rinsed twice with methylene chloride and the rinsate was added to the combined extract. The residue was exchanged from methylene chloride into acetone and slowly reduced in volume (0.5 ml). The residue in acetone was derivatized in the presence of potassium carbonate and

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a 1.0 percent solution (100 ul) of alpha-Bromo-2,3,4,5,6-pentafluorotoluene (PFB). The 50 ml culture tube was tightly capped and heated at 100°C for one hour. The tubes were allowed to cool and adjusted in volume with benzene extracted redistilled water to 5.0 ml. The sample was extracted twice with 5.0 ml hexane. The combined extracts of hexane (10.0 ml) were dried with sodium sulfate and then reduced in volume to 1.0 ml. The sample (1.0 ml) was applied to a hexane conditioned silica gel column (9mm i.d., 300m long). The 1-napthyl chloracetate derivative was recovered with the 60% benzene/hexane extract (Shafik et al., 1971).

Analysis of 1-napthol was performed on a dual column Tracor MT220 gas chromatograph equipped with a [^{3}H] detector. The instrument parameters were: column temperature, 200°C; inlet temperature, 225°C; detector temperature, 205°C; nitrogen flow, 40 ml/min; 5.0% OV210 and 1.5% OV17/1.95% OV210 columns.

Descriptive statistics were obtained for each data set according to the Univariate procedure, Statistical Analysis System (SAS, 1979). The distribution of sample values was evaluated prior to performing a statistical test of significance. The differences between means were tested for significance at the 5 percent level according to Student's t-test. Three dimensional plots and charts were obtained through SAS (1981).

RESULTS

The deposition of carbaryl was examined on elevated panels, soil, and okra leaves. A test of trend based on Kendalls tau (Conover, 1980) revealed a near uniform deposition of residues on elevated panels placed along the north-south plane in two rows 60 meters (tau = -0.0833, n = 9, P < 0.754) and 120 meters (tau = -0.2500, n = 9, P <0.348) from the west edge of the field (Fig. 1). The deposition of residues detected on panels in the north-south plane was compared to deposition on panels in the east-west plane (Fig. 1). Residue concentrations on panels were found to be independent (tau = -0.4000, n = 10, P < 0.09) of the distance from the north edge of the field. The mean residue concentration on panels arranged in east-west plane (6.70 $\pm$ 4.68 ug/cm^2) was found to be not significantly different (t = 0.2381, P < 0.50, 26 d.f.) than the mean concentration (7.49 $\pm$ 4.82 ug/cm^2) obtained for the north-south direction.

Deposition on panels was compared to deposition on leaves (Table 1). Because leaf samples were collected along rows in a north-south plane, residue concentrations on leaves were compared with residue concentrations on panels in the same direction. The mean residue concentration on leaves (9.37 $\pm$ 5.24 ug/cm^2) near the top of the canopy (n = 6) was found to be not significantly different (t = -1.5062, P < 0.20, d.f. = 13) than the mean concentration (6.04 $\pm$ 3.35 ug/cm^2) found in panel patches (n = 9) along similar rows 60 meters

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from the west edge of the field (Table 1). Mean concentrations of panel patches along rows 60 meters and 120 meters from the west edge of the field were not significantly different (t = -1.2975, P < 0.40, d.f. = 18). The deposition of carbaryl on panel patches and leaves near the top of the canopy appeared to be uniform.

The ranks of residue concentrations on bottom leaves below the canopy (Table 1) were found to be not significantly different (T = 34.5, n = 6, m = 3, P < 0.122) than the ranks of the concentrations on top leaves according to the Mann-Whitney test for two independent samples (Conover, 1980). This test was chosen because of the size of the unbalanced data sets. A paired comparison of leaf samples from plants along similar rows (Table 1) was not significant (t = 1.6609, d.f. = 2, P < 0.40) at the 5% level.

Although residue concentrations on leaves below the canopy did not appear to be significantly different than concentrations on leaves near the top of the canopy, the study design did not permit the evaluation of the distribution of residues through the canopy. The lowest mean concentration of carbaryl residues was detected in soil samples (10 g) collected from 526.5 cm^2 pans (n = 4) placed flush with the soil surface approximately 100 meters from the north edge of the field and 80 to 100 meters from the west edge of the field (Table 2). However, because of the location of the soil samplers, a statistical comparision of residue concentrations between substrates, panels, leaves and soil, could not be made.

Transfer of residues of carbaryl to workers was assessed through the examination of residue concentrations on sampling devices (100 cm^2 gauze patches) located on the outside and inside sleeves and on the chest pockets of

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cotton chambray work shirts worn by members of the sampling team. These workers were engaged in sample collection and not the harvest of okra. Although their activities in some respects mimiced those of the okra harvester, these subjects may be regarded as not-occupationally exposed. The four participants were adult males (age > 17 years).

The paired differences in residue concentrations between outside and inside sleeve patches (Table 3) were found to be not significantly different (t = 1.900, d.f. = 3, P < 0.20). A similar result (t = 1.993, d.f. = 3, P < 0.20) was observed for paired comparisons of inside sleeve patches and chest patches (Table 3). Outside sleeve patches, however, appeared to accumulate greater (t = 7.893, d.f. = 3, P < 0.005) concentrations of carbaryl than chest patches. The workers appeared to accumulate greater residues on the arms than on the chest. In addition, the accumulated residues on the sleeves appeared to penetrate the cotton chambray material.

The transference and possible dermal absorption of carbaryl by workers exposed to dislodgable residues of carbaryl was monitored by examining concentrations of 1-naphthol in urine. Urine samples were provided by the three study team participants before and after entering the field to collect substrate samples (Table 4). A urine specimen was not obtained from subject 12. The eight farmworkers scheduled to participate in the study provided preharvest urine samples. These samples served as controls (Table 4).

1-Naphthol was detected in urine samples from the three participants of the study team after the collection of substrate samples (Table 4). The mean concentration of 1-naphtol was 0.087 ± 0.021 ug/ml. When adjusted to the urinary creatinine concentration, the normalized mean concentration was

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0.037 $\pm$ 0.005 ug/mg/ml. The participants in the study team appeared to accumulate and absorb residue concentrations of carbaryl while collecting the substrate sampling devices.

INTERPRETATION AND ANALYSIS

The aerial application of a wettable powder formulation (Sevin 50-W) of the N-methyl carbamate insecticide carbaryl (1-napthyl N-methyl carbamate) on a 10 acre plot of okra was found to be uniform over artificial sampling devices, elevated panels (Fig. 1), and the foliage canopy (Table 1). Human subjects entering the field to collect environmental samples appeared to accumulate residues on sampling devices located on the outside sleeves and inside sleeves and on the chest of the cotton chambray shirts worn by the workers (Table 3). The concentrations of carbaryl detected on outside sleeve patches were significantly greater than the concentrations detected on chest patches. The motion of arms during work operations may explain the difference between concentrations on outside sleeve patches and patches on the chest. The accumulated residue concentrations on outside sleeve patches were found to be not significantly different than the concentration detected on inside sleeve patches. Residues of carbaryl apppeared to pass through the sleeve of the chambray work shirt. The protective value of the shirt was considered suspect. Indeed, the metabolite of carbaryl, 1-naphthol, was detected in the urine of the three test subjects (Table 4) after three hours of exposure in the field. 1-Naphthol was not detected in urine collected prior to entry to the field. In addition, 1-naphthol was not detected in urine of any of the

members of the control group (Table 4). The test subjects appeared to have dermally absorbed some residues.

Carbaryl has been observed (Feldmann and Maibach, 1974) to be rapidly absorbed upon dermal contact. The rate of absorption appears to be similar over different body regions (Maibach et al., 1971). The concentrations of 1-naphthol in urine of the test workers (Table 4) was well below the urinary output (8.1 ug/ml) from ingestion of a controlled concentration of carbaryl (Knaak et al., 1968). Knaak et al. (1968) observed that concentrations dermally absorbed or transferred did not represent an acute health threat. Similar assessments of possible risk to the occupationally exposed have been offered by Maitlen et al. (1982); Gold, et al. (1982); and Leavitt et al. (1982). However, the long term effects of repeated exposure to these concentrations are less well known (Comer et al., 1975). The burdens on metabolic and excretory systems after repeated exposure to subacute concentrations of carbaryl may require further study (Knaak et al., 1968; Kuhr and Dorough, 1976).

The metabolism of carbaryl is complex (Kuhr and Dorough, 1976, and Menzie 1969, 1974, 1978, and 1980). The hydroxylated metabolites (4-hydroxy-1-napthyl N-methylcarbamate, 5-hydroxy-1-naphthyl N-methyl-carbamate, 1-naphthyl N-hydroxy methylcarbamate and 5, 6-dihydro-5, 6-dihydroxy-1-naphthyl N-methyl-carbamate) may appear in the urine of mammals as glucuronide and sulfate conjugates (Kuhr and Dorough, 1976). Hydroxylation by NADPH dependent microsomal enzymes predominates over hydrolysis to 1-naphthol in most vertebrate species. Because of the predominance of the conjugated hydroxylated metabolites in urine, determination of exposure based on 1-

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naphthol may represent an underestimation of actual exposure. We advocate the examination of blood and urine for total metabolites of carbaryl with values normalized to creatinine clearance. The units would then be expressive of both hepatic and nephritic function.
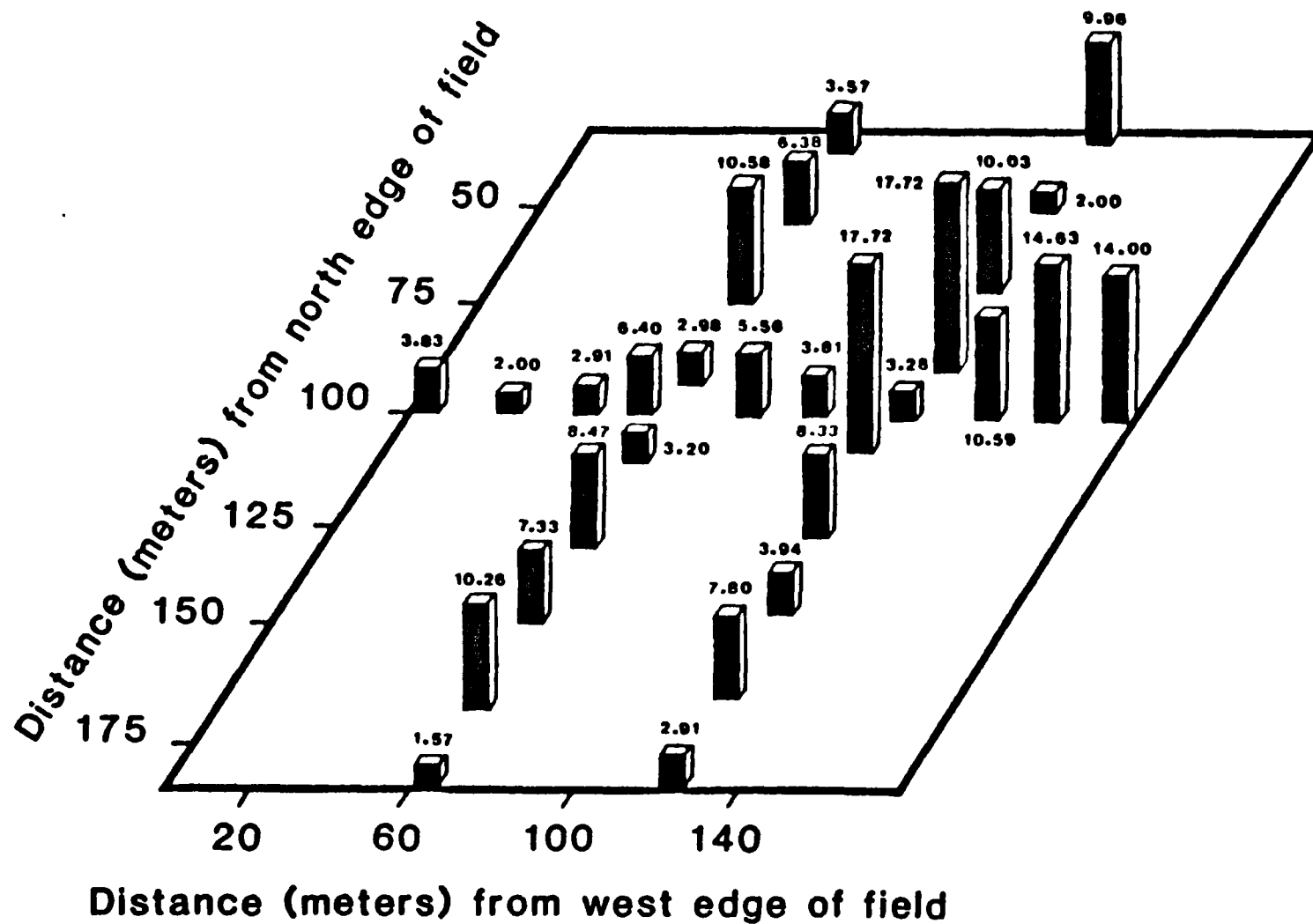
Fig. 1. Distribution of carbaryl residue concentrations (ug/cm^2) detected in 100 cm^2 gauze patches from panels arranged in an east-west plane in a north-south plane.

Table 1. Deposition of aerially-applied carbaryl as Sevin[R] 50-W on panels and okra leaves along rows in the north-south plane.

Distance from north edge of field (m)	Panels[a] 60m	Panels[a] 120m	Leaves Top	Leaves Bottom
34		9.96		
37	3.57			
52		2.00		
56	6.38		13.17	
71		10.03		
75	10.58		11.30	
90		17.72		
94	2.98		13.60	
109		17.72		
112	3.20			
127		8.33		
131	8.47		4.59	1.72
146		3.94		
150	7.33			
165		7.80		
169	10.26		12.49	4.59
184	1.57	2.91		
192			1.07	0.73

a/ Distance of panels in rows 60 and 120 meters from west edge of tne field.

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Table 2. Comparison of the deposition of carbaryl on panels, okra (top and bottom of canopy) and soil.

Substrate	Carbaryl Concentration (ug/cm^2)				
	Lowest Value	Highest Value	Mean	Standard Deviation	Coefficient of Variation
Panels[a]	2.00	14.63	6.70	4.68	0.70
Leaves[b]	1.07	13.60	9.37	5.24	0.56
Leaves[c]	0.73	4.59	2.34	2.00	0.85
Soil[d]	0.129	0.754	0.468	0.297	0.63

[a] Line of panels (n = 10) 100 meters from the north edge of the field 2).

[b] Leaf punches (n = 6) collected from okra leaves at the top of the canopy.

[c] Leaf punches (n = 3) collected from okra leaves below the canopy.

[d] Soil samples (10g) collected from soil pans (526.5 cm^2) located 80 and 100 meters from the west edge of the field and 101.25 meters from the north edge of the field.

Table 3. Accumulation of dislodgable residues of carbaryl as Sevin[R] 50-W on body patches. The means and standard deviations for each sampling device are provided.

Worker Number	Carbaryl concentration (ug/cm^2)		
	Outside Sleeve	Inside Sleeve	Chest Patch
9	9.99	5.41	4.28
10	8.18	2.87	2.19
11	5.16	3.55	1.58
12	11.10	10.30	4.20
	8.61 ± 2.59	5.53 ± 3.35	3.06 ± 1.38

Table 4. Concentrations of the urinary metabolite 1-naphthol detected in urine samples provided by eight control and 3 test subjects. Urine samples were obtained from the test subjects, members of the research team, before and after collection of substrate samples.

Worker Identifier	Hour of Sample Collection	1-Naphthol Concentration (ug/ml)	Creatinine Concentration (mg/ml)	Normalized Concentration 1-Napthol (ug/mg/ml)
Control Group - Did Not Enter Field				
1	1956	ND	2.46	-
2	1956	ND	1.86	-
3	1955	ND	2.80	-
4	1958	ND	1.92	-
5	1958	ND	1.30	-
6	1955	ND	2.41	-
7	1958	ND	3.45	-
8	1956	ND	1.66	-
Test Group - Prior to Entering Field				
9	1430	ND	1.88	-
10	1430	ND	2.79	-
11	1430	ND	1.63	-
Test Group - Three Hour Exposure				
9	1919	0.08	2.26	0.035
10	1800	0.11	2.32	0.043
11	1810	0.07	2.03	0.034

ACKNOWLEDGEMENTS

LITERATURE CITED

American Conference of Government Industrial Hygienists. 1984. Documentation of the threshold limit values for chemical substances in the environment. ACGIH, Inc., Cincinnati, OH. 504 pp.

Best, E. M., Jr. and B. L. Murray. 1962. Observations on workers exposed to sevin insecticide--a preliminary report. J. Occ. Med. 4:507-517.

Comer, S. W., D. C. Staiff, J. F. Armstrong, and H. R. Wolfe. 1975. Exposure of workers to carbaryl. Bull. Environ. Contam. Toxicol. 13(4):385-391.

Conover, W. J. 1980. Practical nonparametric statistics, 2 ed. John Wiley and Sons, NY. 493 pp.

Cramer, P. H., A. D. Drinkwine, J. E. Going, and A. E. Carey. 1982. Determination of carbofuran and its metabolites by high-performance liquid chromatography using on-line trace enrichment. J. Chromatog. 235:489-500.

Feldman, R. J. and H. I. Maibach. 1974. Percutaneous penetration of some pesticides and herbicides in man. Toxicol. Appl. Pharm. 28:126-132.

Gold, R. E., J. R. C. Leavitt, T. Holcslaw, and D. Tuby. 1982. Exposure of urban applicators to carbaryl. Arch. Environm. Contam. Toxicol. 11: 63-67.

Gunther, F. A., J. H. Barkley, and W. E. Westlake. 1974. Worker environment research. II. Sampling and processing techniques for determining dislodgable pesticide residues on leaf surfaces. Bull. Environ. Contam. Toxicol. 12(6):641-644.

Knaak, J. B., M. J. Tallant, W. J. Bartley, and L. J. Sullivan. 1968. The metabolism of carbaryl in the rat, guinea pig, and man. J. Agric. Food Chem. 16:465-470.

Kuhr, R. J. and H. W. Dorough. 1976. Carbamate insecticides: chemistry, biochemistry and toxicology. CRC Press, Inc., Cleveland, OH. 301 pp.

Leavitt, J. R. C., R. E. Gold, T. Holcslaw, and D. Tupy. 1982. Exposure of professional pesticide applicators to carbaryl. Arch. Environ. Contam. Toxicol. 11:57-62.

Maibach, H. I., R. J. Feldman, T. H. Milby, and W. F. Serat. 1971. Regional variation in percutaneous penetration in man. Arch. Environ. Health 23:208-211.

67~

Maitlen, J. C., C. R. Sell, L. M. McDorough, and S. N. Fertig. 1982.
Workers in the agricultural environment: Dermal exposure to carbaryl. 674
Pp. 83-103 in Pesticide residues and exposure, J. R. Plimmer, ed. ACS.
Symposium Series No. 182, American Chemical Society. Washington, D.C.
213 pp.

Menzie, C. M. 1969. Metabolism of pesticides. U.S. Department of the
Interior Fish and Wildlife Service, Special Scientific Report - Wildlife
No. 127, Washington, D.C. 487 pp.

Menzie, C. M. 1974. Metabolism of pesticides, Update I. U.S. Department of
the Interior Fish and Wildlife Service, Special Scientific Report -
Wildlife No. 184, Washington, D.C. 486 pp.

Menzie, C. M. 1978. Metabolism of pesticides, Update II. U.S. Department of
the Interior Fish and Wildlife Service, Special Scientific Report -
Wildlife No. 212, Washington, D.C. 381 pp.

Menzie, C. M. 1980. Metabolism of pesticides, Update III. U.S. Department
of the Interior Fish and Wildlife Service, Special Scientific Report -
Wildlife No. 232, Washington, D.C. 709 pp.

Munn, S., T. J. Keefe, and E. P. Savage. 1985. A comparative study of
pesticide exposures in adults and youth migrant field workers. Arch.
Environ. Health 40(4):215-220.

National Institute for Occupational Safety and Health. 1976. Criteria for a recommended standard: Occupational exposure to carbaryl. DHEW (NIOSH) Publ. No. 77-107. 192 pp.

SAS. 1979. SAS user's guide. 1979 edition. SAS Institute, Inc., Cary, NC. 494 pp.

SAS. 1981. SAS/Graph user's guide. 1981 edition. SAS Institute, Inc., Cary, NC. 126 pp.

Shafik, M. T., H. C. Sullivan, and H. F. Enos. 1971. A method for the determination of 1-naphtol in urine. Bull. Environm. Contam. Toxicol. 6(1): 34-39.

Sikes, V. R., D. McCraw, T. Longbrake, S. Cother, and B. Peavy. 1980. Keys to profitable okra production for food and seed. Texas Agricultural Extension Service, Keys to Profitable Production Series, No. L-1805. 4 pp. (unnumbered).

Spear, R. C. 1982. Farm worker exposure to pesticides residues: reflections on differential risk. Pages 67-76 in V. R. Hunt, M. K. Smith, D. Worth, Eds., Banbury Report II, Environmental Factors in Human Growth and Development, V.R. Hunt, M. K. Smith, D. Worth, Eds., Cold Spring Harbor Laboratory.

675

World Health Organization. 1982. Recommended health-based limits in
occupational exposure to pesticides. Technical Report Series No. 667. 676
WHO, Geneva. 110 pp.

Yakim, V. S. 1967. [The maximum permissible concentration of sevin in the
air of the work zone] Gig. Sanit. 32:29-32.

Zweig, G., R. Gao, J. M. Witt, W. Popendorf, and K. Bogen. 1984. Dermal
exposure to carbaryl by strawberry harvesters. J. Agric. Food Chem.
32(6): 1232-1236.

An Assessment of Exposure of Cucumber
Harvesters to Azinphos-Methyl

Research performed by

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March 31, 1986

In behalf of the Texas PHAP the undersigned has reviewed and approved the report draft entitled "An Assessment of Exposure of Cucumber Harvesters to Azinphosmethyl in South Texas."

_____   3-31-86
Project Director   Date

TABLE OF CONTENTS

ABSTRACT

Occupational exposure of youth (age $\leq$ 17 years) and adult (age > 17 years) farmworkers to residues of azinphosmethyl was assessed in a cohort of individuals harvesting cucumbers from a field in the Lower Rio Grande Valley (LRGV) of South Texas treated with Guthion 2L by aerial application at the rate of 2 pints per acre. Guthion appeared to be uniformly distributed over the field as indicated by the concentrations of azinphosmethyl detected on gauze patches (103.2 cm^2) arranged on panels (929 cm^2) placed within the field. The median concentration on panel patches was (0.57 ug/cm^2). The mean concentration was 0.73 $\pm$ ug/cm^2. The decline or loss of dislodgable residues of azinphosmethyl from foliage was rapid reaching nondetectable levels within two days after application. The half life of azinphosmethyl on soil from a nearby field was estimated to be 2.54 days. Harvesters entered the field 2 days after application of Guthion 2L. The harvesters accumulated significantly greater concentrations of azinphosmethyl on right hand gloves (0.92 $\pm$ 0.54 ug/cm^2) than on outside shirt patches (0.03 ug/cm^2). Farmworkers harvesting cucumbers may be expected to contact residues of azinphosmethyl more readily on their hands rather than their forearms. Residue concentrations did not appear to penetrate protective clothing. Concentrations of dialkyl phosphorous metabolites (DMP and DMTP) of azinphosmethyl were not detected in the urine provided by the workers within a 24 hr period after 3.5 hours of exposure. The 2 day reentry interval appeared to diminish the potential for exposure to azinphosmethyl.

EXPOSURE OF CUCUMBER HARVESTERS TO AZINPHOSMETHYL IN SOUTH TEXAS

INTRODUCTION

In an Interagency Agreement, dated March 17, 1980, officials of the U.S. Department of Labor and the U.S. Environmental Protection Agency pledged their respective organizations to a program of "mutual cooperation in the design and conduct of studies to obtain data on the effects of pesticides on youths employed in agriculture." A comprehensive collection of activities were proposed as tools for examining the present state of knowledge of pesticide effects upon children. One area of investigation was assigned primarily to the national Pesticide Hazard Assessment Projects (NPHAP), the conduction or operation of a series of pesticide exposure studies of both adult and juvenile farmworkers. These studies were intended to provide an assessment of the exposure of harvesters to one or more of the pesticides used to protect these crops from damage by pests or diseases.

The migrant streams of the western United States are comprised mainly of Spanish-speaking peoples. Because of the predominantly Hispanic culture, the Lower Rio Grande Valley (LRGV) of south Texas is home to one of the largest migrant farmworker populations in the United States. During the period September through May of most years, the region provides intermittent work harvesting a wide variety of fruits and vegetables. In the Spring, as the local harvests near completion, the workers will gradually depart to

follow harvests of many of the same crops at progressively more northern latitudes. Workers of the LRGV are the chief component of the central migrant stream that works the Great Plains and the Midwest. However, many will travel directly to Florida or California to work the coastal streams northward.

Because pesticides are applied to virtually all crops grown in the LRGV, residues of the pesticides may represent a health hazard to field workers either through prolonged dermal contact with leaves and fruit or through inhalation or ingestion of dislodgable residues. The kinds of adverse effects that can result from such exposures range from skin or eye irritation to acute intoxication.

The commodities grown in this four-county region are annually treated with perhaps as much as five million pounds of pesticide products, or 25 to 35 percent of all the pesticides used in Texas. Hidalgo County alone, probably the most intensively farmed county in the state, may receive as much as the other three Valley counties combined. Cotton and grains account for possibly the greatest portion of this usage, but they need little human contact during growth or harvest. On the other hand, citrus, many vegetables, and some specialty crops do require hand labor and also require considerable pesticide usage, occasionaly during harvest.

The climate of the Lower Rio Grande Valley (LRGV) has been classified as humid desert. Mid-day relative humidities average 61 percent at Brownsville and decline to about 45-50 percent in Starr County to the west, while mean annual rainfall ranges from 27 to 19 inches in the same direction (U.S. Weather Service, Brownsville, pers. comm.). Summer temperatures frequently exceed 100° F. This climate could influence the formation of oxons from organophosphate insecticides. Oxons are frequently noted as having some importance in poisoning incidents involving harvesters in arid parts in

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California (Maddy and Edmiston, 1982). The combination of both high temperature and high humidity has been observed to promote degradation (Eto, 1979). Most farmworkers in the region are employed in the Fall and Spring. During this period humidity remains relatively high and temperatures are much lower. The rate of degradation of certain pesticides may be subsequently lower than during the summer.

Texas growers will annually plant 7,000-10,000 acres of cucumbers. Over half of this acreage will be in the LRGV. Typically two harvests are made in the LRGV. April through June and September through November. The crop is picked by hand. Since cucumbers do not mature uniformly, several pickings of the same field may be spaced a week or more apart. Frequently mounting insect pressure and changes in market conditions may justify one or more insecticide applications during the harvest period.

The array of pesticides recommended for use on cucumbers up to, and during, harvest (Texas Agr. Ext. Serv., 1980) include several that may represent a considerable risk to the occupationally exposed (Federal Working Group on Pest Management, 1974). The level of exposure may be dependent on the capacity to transfer pesticide residues from leaf or fruit surfaces to a harvester. Cucumbers may represent a low-risk potential because of the low growth habit a property which restricts activities from the breathing zone and exposure to the torso and upper legs and arms. However, hands alone may account for perhaps the largest part of the residues accumulated by workers. The harvesting of cucumbers does require handling of considerable foliage. In addition the picking of cucumbers in early morning when leaves are covered with dew may facilitate both the transfer and uptake of pesticide residues.

The transfer of dislodgable residues of the insecticide azinphosmethyl during the harvest of cucumbers was studied to assess the potential hazard of

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exposure to organophosphorous insecticides. Deposition of a formulation of
azinphosmethyl, Guthion 2L, was examined in conjunction with estimates of
transfer of residues to harvesters. Measurements of residues on articles of
clothing worn by harvesters together with concentrations of metabolites of
azinphosmethyl detected in urine of workers may be useful in assessing the
potential risk of exposure to farm workers harvesting cucumbers.

The organophosphorous insecticide azinphosmethyl (o,o-dimethyl s-[4-
oxo-1,2,3-benzotriazin-3 (4H)-yl) methyl] phosphorodithioate) has been offered
by Mobay Chemical Corporation (Agricultural Chemicals Division, Kansas City,
Mo.) under three formulations (Mobay, 1982) Guthion 2S, Guthion 2L, and
Guthion 50% WP (PVA) for control of spotted and striped cucumber beetle and
western-striped cucumber beetle on cucumbers. The label recommends (Mobay,
1982) complete foliar coverage with sufficient water at the rate of 2 pints of
Guthion 2S and 2L per acre and 1 pound Guthion 50% WP (PVA) per acre. The
labels restrict the use of these formulations of azinphosmethyl to no more
than 3 applications per season. Azinphosmethyl shall not be applied within 1
day of harvest.

Azinphosmethyl is a member of the phosphorodithioate class of
organophosphorous insecticides (O'Brien, 1967 and Eto, 1979). Azinphosmethyl
is soluble in most organic solvents but only slightly soluble in water, 29
ppm at 25^0 C (Eto, 1979). The unformulated compound is subject to hydrolysis
at high temperatures (> 200^0 C) where it decomposes to form a gas (Eto, 1979
and Mobay, 1979). Hydrolysis may be accelerated under aqueous conditions with
increased temperature and pH (Menzie, 1978). The half life of Azinphosmethyl
varied from 5 days under aqueous conditions (40^0 C) to 484 days under dry
conditions at 6^0 C (Menzie, 1978). These values may be contrasted against the
much shorter half life (10.4 hours) reported by Eto (1979) with azinphos-

methyl prepared in ethanol (70° C, pH 6.0). The formulated products remain more stable (Menzie, 1980). The half life of formulations of azinphosmethyl on the foliage of different crops may be variable (Menzie, 1980). The half life of azinphosmethyl on apple trees was 2.6 to 6.3 days (Pree et al., 1976).

The large objective of this work was to estimate the risk of exposure to cucumber harvesters to azinphosmethyl applied to the crop in south Texas. There were also several lesser objectives: (1) to measure the degradation of azinphosmethyl on leaves and soil between the time of application and the time of harvest; (2) to measure the transfer of residues from the crop and soil to the workers during harvest; and (3) to measure the absorbtion of azinphosmethyl by the harvesters.

METHODS

Guthion 2L, a restricted use product of Mobay Chemical Corporation bearing the EPA Registration Number 3125-102 (22.2% azinphosmethyl, 59.8% aromatic petroleum distillates and 18.0% inert ingredients) was ground applied along east-west rows with a boom and tractor assembly at 2 pints per acre to a 9.79 acre plot of cucumbers and squash at 1205 hours on April 7, 1983. The plot was unequally divided between squash (3.10 acres) and cucumbers (6.69 acres). The boom covered 18 rows. The nozzle diameter and conditions of the spray rig were not recorded. Wind velocity at 1700 hours was 10 to 12 miles per hour (mph) from the northeast.

Deposition. Deposition of azinphosmethyl was examined on two panels placed within rows near the middle of the cucumber subplot, approximately 95 meters from the east and west edges of the field and 71.1 and 99.6 meters from the south edge of the field (Fig. 1). Additional depositional data was obtained from panels (n =3) placed within rows of the squash subplot, approximately 92.5 meters from the east and west edge of the field and 4.06, 36.6 and 69.1 from the north edge of the field to the border of the cucumber subplot (Fig. 1). The panels were 12 x 12 cardboard squares (929 cm^2) covered with aluminum foil. The foil was cleaned with acetone before the attachment of three 4 ply 4 x 4 inch (103.2 cm^2) surgical gauze patches. The patches were arranged in a trigonal pattern with two patches in the corners and one patch midway from the opposite corners.

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Deposition and loss of residues of azinphosmethyl were examined on soil and on leaf samples taken from arbitrarily selected cucumber and squash plants. Soil pans were placed flush with the soil surface along rows in close proximity to panels in the cucumber subplot. The soil (100 g) was spread evenly over the bottoms of a series (n = 10) of 9 x 9 inch (522.6 cm^2) aluminum cooking pans aligned in groups of five along rows (Fig. 1). The soil in the interior of the field was Willacy fine sandy loam. The soil along the north and south edges of the field was saline Racombes sandy clay loam. In the squash subplot, soil pans (n = 10) were placed along rows in parallel lines of five (Fig. 1) in close proximity with panels and at three additional locations 32.5, 75.2 and 103.6 meters from the north edge of the field, equal distance from the east and west edges. The soil used in the pans near the north edge of the squash section was Racombes sandy clay loam. The moisture content of the soil was not recorded.

Soil samples were collected from the pans immediately after application (1205 hours April 7, 1983) and at hourly intervals over a seven day period. The soil was collected in resealable quart sized Zip-Lock^R plastic storage bags and transported to the laboratory on dry ice. The samples were stored frozen until analysis.

Leaf samples (n = 100) were collected from cucumber plants across rows within a 28 row section. Samples were obtained from plants within three 28 row sections at different times over the seven day period. In a similar fashion, leaf samples (n = 100) were collected from squash plants across sections (n = 4) of 16 rows. The leaf samples were obtained with a Birkestrand punch (2.5 cm diameter). The leaf punches were dropped from the punch into 120 cc plastic urine specimen containers and transported on dry ice to the laboratory and stored frozen until analysis.

Information to be gained from the study on the deposition and loss of azinphosmethyl from panels, soil, and foliage was to be compared with a companion study designed to assess exposure of cucumber harvesters to azinphosmethyl. Guthion 2L was aerially applied to a 20 acre field of cucumbers at the rate of 1.0 pint per acre at 0930 on 2 May 1983. The aircraft was equipped to cover 20 rows of cucumbers flying at 105 mph with the spray delivered through 8006 nozzles at 35-40 psi. The application along north-south rows was completed at 1000 hours. The temperature at 0930 was 80°F. The wind velocity was 8-10 mph gusting to 22 mph from the southeast.

Deposition of azinphosmethyl was measured on panels placed along rows in a south-north plane (Fig. 2). The panels were designed identically to the previous study. Panel patches were collected in resealable pint sized Zip-Lock[R] storage bags immediately after application. The samples were transported on dry ice to the laboratory and stored frozen until analysis.

Deposition and loss of residues of azinphosmethyl were estimated from soil samples and leaf punch samples. Soil pans similar to those described earlier were placed along rows within a section of 16 rows (Fig. 2). Soil samples were collected as previously described from the pans at various times over a 4 day period. The soil was a Willacy fine sandy loam. The field had been irrigated on 28 April 1983. Moisture content was not measured.

Leaf samples (n = 100) were obtained with a Birkestrand punch (2.5 cm diameter) across rows within a section of 16 rows in accordance with the method previously described. Leaf punches were collected from 8 sections (Fig. 2) immediately after application and Sections 2, 4, 6, and 8 at various times on subsequent days.

Exposure of farmworkers to residues of azinphosmethyl while harvesting cucumbers was assessed by measuring concentrations of azinphosmethyl on

sampling devices worn by the harvesters. In addition, the absorption of residues of azinphosmethyl was estimated from measurements of the concentrations of dialkyl phosphorous metabolites in urine samples provided by the harvesters before, during, and after harvest.

The workers arrived at the field at 0630. After an explanation of the work proposed, the volunteers proceeded through a series of study stations where they signed consent forms and were briefly interviewed. The cohort consisted of 6 females and 22 males (Tables 1 and 2). Average age of the females was 39.3 ± 18.0 years (Table 1). The youngest female was 17 years; the oldest 61 years. A 28 year old subject, worker number 42, (Table 1) was 4 months pregnant. This individual weighed 68 Kg. The average weight of the females was 63 ± 12 Kg. The average height was 1.58 ± 0.06 meters. The average age of the males was 41.5 ± 18.8 years (Table 2). The average height of the males was 1.68 ± 0.06 meters. The average weight of the males was 64 ± 11.2 Kg.

The workers entered the field at 0800. While they were harvesting, a somewhat longer interview (15-20 minutes) of each worker was undertaken to obtain their work history as well as their perception of their own health and medical history (Appendix). During the interview, notes were taken on clothing worn and individual picking practices (Tables 3 and 4). Harvest activities were completed by 1145 hours; harvesters were not in the field longer than four hours. The number of buckets of cucumbers picked by each worker was obtained from the labor contractor (Tables 1 and 2).

Gloves. To estimate the amount of contact with pesticide residues through the hands, 16 subjects were recruited to wear a pair of lightweight 100% cotton twill work gloves with knit wristlets and seamless palms (Sears catalog number 51 K 25915). The average surface area of the gloves (minus the

knit wristlet) was 85.2 in^2 ± 1.29 (549.7 cm^2, n = 3). After the exposure

period, the gloves were sealed in plastic bags and placed on dry ice. The

samples were catalogued and stored frozen until analysis was started.

Air Samples. Seven of the subjects were fitted with DuPont P-4000

Personal Air Sampling Pumps equipped with an air sampling cartridges to assess

the potential for inhalation of airborne residues. The pumps were clipped to

military web belts with the pump positioned to ride at the waist at the small

of the back (Fig. 3). This location caused very little interference with

worker movement. The pumps were set to draw 1 liter/minute. Calibration was

done just prior to sampling and immediately upon returning from the field.

The time that the workers wore the pumps was documented in two ways. First,

each pump had a device to report running time. Second, these values were

compared with the notes on the times the pumps were checked out and checked

in.

The pumps were connected to the cartridges through a 90 cm length of 1/4

inch (inside diameter) x 1/16 inch (thickness) Tygon tubing. The tubing was

adapted to the 4 mm cartridge nipple with a 4 cm length of 1/4 inch (outside

diameter x 1/8 inch (inside diameter) polypropylene tubing. The tubing from

the pump passed between an arm and the torso and cartridge was clipped to the

shirt collar (Fig. 3).

The Bond Elute C18 Bonded Phase Cartridges were obtained from AnalytiChem

International, Harbor City, CA. The 30 cc syringe cylinder was packed with

approximately 1.5 g of Sepralyte Octadecyl C18. Cartridges exposed in the

field were sealed inside a plastic bag and transported on dry ice to the

laboratory. The samples were stored frozen until analysis.

Gauze Patches. To assess the potential for pesticide contact and

absorption through the arms, gauze exposure patches with surface area

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103.2 cm^2 per patch were placed on 25 subjects, one on each forearm outside the shirt, and one on each forearm inside the shirt. Workers performed their normal work activity for 3.5 hours.

Urine. Study subjects were required to contribute urine specimens to measure the concentration of pesticide metabolites which might result from exposure while harvesting cucumbers. Specimens were obtained from each subject. Samples were collected before the subject started to work. Additional samples were collected throughout the day. Subjects were also asked to provide a sample of their first void of the following morning. Urine samples were collected in standard plastic, four-ounce urine specimen containers, and were placed directly on dry ice for immediate transport to the laboratory. The samples were cataloged and kept frozen until analysis.

ANALYTICAL PROCEDURES

Patches. Gauze patches from panels and clothing worn by the workers were extracted in the same fashion. Panel patches were extracted individually (103.2cm²). Right and left forearm patches (206.4 cm²) were extracted together. The patches were extracted three times in a 500 ml Erlenmeyer flask containing 75 ml methanol using a Burrell wrist-action shaker at setting six. The three extracts were combined, filtered through Whatman No.1 paper on a Buchner funnel, dried with anhydrous sodium sulfate, and concentrated to 5 ml on a Buchi Rotavapor R110. Final volume adjustment was made as needed prior to analysis by high performance liquid chromatography (HPLC) for panel patches and gas chromatograph (GC) for clothing patches.

Soil. Soil samples (10.0 g) were extracted three times in acetone with a Burrell wrist-action shaker on setting six. The three extracts were combined, dried with sodium sulfate, filtered through Whatman No.1 paper on a Buchner funnel, and concentrated to 5 ml using a Buchi Rotavapor R110. Adjustments were made to the volume prior to analysis by HPLC. This method was preferred over the method outlined in Sections 11, A and 11, B of the EPA Manual (U.S. E.P.A., 1980). Hexane was found to be a less desirable solvent for extraction of these soils than acetone. A flocculent was formed in the presence of hexane lessening the surface area exposed to the solvent. Substitution of acetone for hexane eliminated the formulation of the flocculent and resulted in a 10 percent improvement in recovery of azinphosmethyl.

<u>Foliage</u>. Leaf punch samples (n = 10) with a combined surface area of of 50.0 cm^2 were extracted according to the method of Gunther et al. (1974) for the measurement of dislodgable residues. The samples were extracted three times for 15 minutes in the presence of 75 ml distilled water containing a 1:50 dilution of the surfactant, Witconol NP-100, on a Kraft shaker-in-the-round (Model S-500) at maximum speed.

The three extracts were collected and tranferred to a 1.0 L separatory funnel and extracted three times with 150 ml methylene chloride. A solution of saturated sodium sulfate in water was used to break up any emulsion that formed. The hexane was dried with anhydrous sodium sulfate and than concentrated with a Buchi Rotavapor R110 to 5 ml. Final evaporation to 0.5 ml was done on a Meyer N-Evap. This volume was adjusted to 5 ml with methanol. Additional volume adjustments were made prior to analysis by HPLC.

<u>Gloves</u>. The gloves were cut into 1 to 2 cm^2 pieces (the knit wristlets were not tested) and placed in a 1.0 l Erlenmeyer flask and extracted three times with methanol on a Burrell wrist-action shaker at setting eight. The pieces were tranferred to a Buchner funnel and washed. The extracts were combined, filtered, and concentrated to 5 ml with a Buchi Rotavapor R110. The volume was adjusted as needed for analysis by HPLC.

<u>Air Samplers</u>. Extraction of the residues from the entrapment medium of the Bond Elute C18 cartridges was accomplished by eluting 150 ml of acetone through the cartridge at approximately 5 ml/min. This solution was dried with anhydrous sodium sulfate and evaporated to 1 ml with a Buchi Rotovapor R110. The extract was analyzed by GC.

<u>Urine</u>. Each specimen was prepared for analysis of dialkyl phosphorous metabolites according to a modified method of the procedures described by Reid and Watts (1981), Takade et al. (1979), and Daughton et al. (1979). A

1.0 ml aliquot of the urine sample was diluted to 20 ml with acetonitrile in a micro impinger tube. Approximately 200 mg NaCl was added to the azeotrope mixture and was evaporated at 90-95° C to near dryness. The concentrate was derivatized for 30 minutes at 90-95° C in the presence of 20 ml of a 5.55 mM solution of 3-benzyl-1-p-toyltriazene prepared in chloroform. The derivatized sample was evaporated to 1.0 ml using a one ball Snyder column. The concentrated sample was diluted with 15 ml of a 10% salt solution (0.57 g NaCl/ml 12N HCl). The diluted sample was extracted three times with 6.0 ml ethyl ether. The organic layer was retained and dehydrated with anhydrous Na_2SO_4 and evaporated to 0.1 ml. The concentrate was adjusted to 1.0 with acetone and prepared for GC analysis.

The concentration of creatinine in the urine samples was measured according to the method of Patel and George (1981). An aliquout of urine (0.50 ml) was diluted with distilled deionized water to 12.5 ml. The diluted urine (0.10 ml) was thoroughly mixed with 0.20 ml acetonitrile. The mixture was centrifuged at 1,000 RPM for 5 minutes to sediment particulate matter. The supernatant was prepared for analysis by HPLC.

Instrumentation. Azinphosmethyl in samples extracted from leaves, panel patches, soil and gloves was detected by reverse phase HPLC at 280 nm on a Spectra-physics high pressure liquid chromatograph equipped with a SP8700 solvent delivery system and a SP8440 variable wavelength detector. The column was a uBondapack C18 (Alltech Associates, Deerfield, IL). The flow rate of the mobil phase (45% acetonitrile, 55% H_2O) was 1.0 ml/min.

A Tracor 222 gas chromtograph was used to assay samples (air cartridges and shirt patches) for azinphosmethyl. Instrument parameters were as follows: detector, FPD in phosphorus mode @ 256 nm; column, 4% SE30/6% OV210 coated with Gas Chrom Q, 80/100 mesh; column temperature,

200°C; detector temperature, 190°C; carrier gasses, nitrogen @ 60 ml/min, hydrogen @ 50 ml/min, and air @ 100 ml/min.

Alkyl phosphate concentrations were detected in urine by gas-liquid chromatography (GC) with a Tracor 222 gas chromatograph equipped with a flame photometric detector (FPD). The instrument was operated in the phosphorus mode (256 nm). A 10% DC 200 column was used to separate the four alkyl phosphates (DMP, DEP, DMTP and DETP) at a flow rate of 50 cc N_2/min and a column temperature of 198°C isocratic.

Creatinine was separated by HPLC on a prepacked uBondapack C_{18} column with an average particle size of 10 u (Alltech Associates, Deerfield, IL). The flow rate of the mobile phase (25% acetonitrile and 75% methanol plus 1 ml NH_4OH) through the column was 1.5 cc/min from a Spectra Physics SP 8700 solvent delivery system. Creatinine was detected with a UV/VIS SP 8440 detector set at 254 nm.

All detectors were interfaced with a Nelson Model 4400 Chromatography Data System. Data were reduced and stored on diskettes.

Recoveries. Recovery of concentrates of azinphosmethyl from fortified quality control samples of the environmental substrates (soil and leaves) and the sampling devices (gauze patches and gloves) was examined to estimate the accuracy and precision of the analytical methods. Accuracy of the data was understood to relate to the relative error of the mean of a series of test results to the expected result, as given by the percent recovery (Anon, 1968; McFarren et al., 1970; Kirchmer, 1983). The precision of the method was given by the percentage of the coefficient of variation (C. V.) or the relative standard deviation (RSD), as an index of dispersion of a series of test results.

A series (n = 8) of 10 g soil samples were fortified with 100 ug of

azinphosmethyl. The mean recovery of the 8 samples was 9.64 $\pm$ 0.37 ug/g

(96.4%) with an RSD of 3.80%. Recovery of azinphosmethyl (1.10 $\pm$ 0.07 ug/cm^2)

in gauze patches (n = 9) was 113.6 percent of the expected fortification level

(100 ug). The recoveries were clustered about the mean (RSD = 6.86%). The

recovery of azinphosmethyl (0.165 $\pm$ 0.012 ug/cm^2) from gloves (n = 6) was 90.7

percent of the expected fortification level (100 ug) and well within control

(RSD = 7.42%), less than 2 standard deviations of the mean. The recovery of

azinphosmethyl (1.66 $\pm$ 0.23 ug/cm^2) from leaves (n = 14) fortified with 100 ug

was more variable (RSD = 13.9%) but within control. The percent recovery was

83.2 perccent.

Recovery of dialkyl phosphorous metabolites was examined in urine samples

fortified with dimethylphosphate (DMP), dimethylthiophosphate (DMTP),

diethylphosphate (DEP) and diethylthiophosphate (DETP). The minimum detection

limit (MDL) for DMP was set at 0.10 ug/ml with 0.087 $\pm$ 0.01 ug/ml (RSD =

9.95%) recovered or 87.7 percent of the expected. Detection of the companion

dimethyl phosphorous metabolite, DMTP, was more variable. The MDL was set at

0.10 ug/ml from observed recovery levels of 0.099 $\pm$ 0.042 ug/ml (RSD = 42.8%).

Recovery of the diethyl phosphorous metabolite, DETP, was quite variable. The

MDL was set at 0.10 ug/ml although the recovery (0.14 $\pm$ 0.06 ug/ml) was more

than expected (RSD = 43.8%). The minimum detection limits for the DEP were

set at 0.25 ug/ml with a recovery of 95.6 ug/ml (RSD = 12.5).

Concentrations of the dialkyl phosphorous metabolites were normalized to

concentrations of urinary creatinine. Recovery of creatinine was examined in

urine samples (n = 8) fortified with 0.50 mg/ml. The recovery of creatinine

(0.54 $\pm$ 0.05) was 109 percent of the expected with an RSD of 8.93 percent.

Analytical Standards. The standards used in the recovery studies were

acquired from the U. S. Environmental Protection Agency, Pesticides and

Industrial Chemicals Repository (MD-8), Research Triangle Park, NC. The
azinphosmethyl (index code number 3820) was from lot number B511 and had a
stated purity of 98.8%. Chlorpyrifos (index code number 2900) was from lot
number A521 and had a stated purity of 99.8%. The latter compound was used
only as a standard for glove and leaf analyses by HPLC while azinphosmethyl
was used as a standard for testing the other substrates.

The specifications for the urinary metabolite standards were as follows:
DMP, dimethylphosphate, index code number 2458, 97.3% pure; DEP,
diethylphosphate, index code number 2386, 98.0% pure; KDMTP, potassium
dimethylthiophosphate, index code number 5734, 98.5% pure; KDETP, potassium
diethylthiophosphate, index code number 5733, purity could not be obtained.
Creatinine (Lot 2173P) as a 1 mg/ml stock prepared in w/10 HCl was obtained
from Harleco[R] Phila., PA.

RESULTS

Deposition of Guthion 2L was examined by detecting residues of azinphosmethyl in a single patch on panels (n = 5) placed within rows of the squash and cucumber subplots in field one (Fig. 1). Additional depositional data was obtained from a companion study of the examination of azinphosmethyl residues on patches of 21 panels placed within rows of a second cucumber field (Fig. 2). The first field was treated with Guthion 2L by ground application at 1205 hours on 7 April 1983. The second field was treated with Guthion 2L by aerial application at 0930 hours on 2 May 1983. Comparisons of the differences in deposition on the sampling devices between aerial and ground application were not attempted because of the differences in the size and location of the fields and the unbalanced nature of the designs. The fields were treated independently.

Patches taken from the apex of the trigonal pattern of three patches were used to estimate deposition. Concentrations detected in the apex patches were compared with patches from a selected corner. A paired comparison of the differences in concentration between apex patches and corner patches was found to be not significant (t = - 0.8848, d.f. = 9, P < 0.40). The deposition of Guthion 2L on the three gauze patches set in a trigonal pattern on the panels was regarded as uniform.

Because of the location of the panels (Fig. 1) and the size of the data sets in the squash (n = 3) and cucumber (n = 2) subplots, the deposition over field one could not be estimated. The mean concentrations of azinphosmethyl

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in panel patches from the squash subplot (0.30 $\pm$ 0.10 ug/cm^2) were found to be not significantly different (t = - 0.2637, d.f. = 3, P = < 0.50) than the mean concentration (0.17 $\pm$ 0.03 ug/cm^2) obtained for the cucumber subplot (Table 5). The concentrations of azinphosmethyl along the midline of field one were regarded as uniform.

The larger sample size (n = 21) and design of the second field (Fig. 4) allowed for an estimation of deposition of Guthion 2L after aerial application. The median concentration of azinphosmethyl detected in panel patches was 0.57 ug/cm^2. The mean concentration was 0.73 $\pm$ 0.44 ug/cm^2. The incomplete rows and column design (Table 6) was partitioned into subsets for treatment according to a two-factor analysis of variance without replication (Sokal and Rohlf, 1969). Missing values for subset 1 (Table 7) were estimated by iteration according to the protocol of Snedecor and Cochran (1976) for two missing values. The variance among columns in the south to north direction were not significantly different ($F_{2,6}$ = 2.6650, P < 0.10). The differences between rows were also not significantly different ($F_{4,6}$ = 0.1633, P < 0.25). Adjustments in the estimation of the error and treatments sums of squares and mean squares with associated degrees of freedom were made according to the protocol of Snedecor and Cochran (1976) for missing values. The one-way analysis of variance with the columns as classes revealed no significant difference ($F_{2,10}$ = 0.4219, P < 0.25) among columns. A similar treatment of inside rows and columns in subset 2 (Table 8) revealed no significant differences among columns ($F_{1,3}$ = 0.0028, P < 0.25) or between rows ($F_{3,3}$ = 0.1518, P < 0.25). The aerial application of Guthion 2L appeared to be uniformly distributed over the panels in field 2.

Deposition and loss of residues of azinphosmethyl were examined in soil samples and foliage from both fields at various times after the application of

Guthion 2L. Residue concentrations in soil within strips of the squash
subplot in field one (Table 9) declined in accordance with a first order rate
of decay (Fig. 5). The half-life for the loss of azinphosmethyl from soil
in strip 1 was estimated to be 2.85 days (Fig. 6) from the slope of the
equation

1. Log (ug/g) = - 0.1056 days + 1.1153

    $r = -0.9429$, $r^2 = 0.8890$, $n = 8$, $P < 0.001$, 6 d.f.

with 88.9 percent of the variablity attributed to the linear regression. A
similar result (t 1/2 = 2.02 days) was obtained for soil from strip 3 (Fig. 7)
according to equation 2 with 95.6 percent of

2. Log (ug/g) = - 0.1490 days + 1.1614

    $r = -0.9827$, $r^2 = 0.9557$, $n = 7$, $P < 0.001$, 5 d.f.

the variability accounted for by the regression. The half-life for the loss
of azinphosmethyl from soils in strip 4 (Fig. 8) was slightly longer (3.60
days).

3. Log (ug/g) = - 0.0835 days + 1.0236

    $r = -0.9430$, $r^2 = 0.8893$, $r = 8$, $P < 0.001$, 6 d.f.

The loss of residues of azinphosmethyl from soil in strips 2 and 3
(Table 10) of the cucumber subplot (Fig. 1) appeared to follow a first order
decay curve (Fig. 9). The half-life (1.78 days) of azinphosmethyl in soil
from strip 2 (Fig. 10) was estimated from the equation

4. Log (ug/cm^2) = - 0.1692 days + 1.2894

   r = - 0.6434, r^2 = 0.4140, n = 7, P < 0.20, 5 d.f.

with 41.4 percent of the variability attributable to the regression. The correlation coefficient (r = - 0.6434) was not significant (t = - 1.8795, P < 0.20, 5 d.f.). The half-life must be viewed with caution.

The half-life (2.66 days) obtained for strip 3 (Fig. 11) was more consistent with the half-life estimates obtained for the squash subplot than for strip 2. The correlation coefficient (r = - 0.9872) was significant (t = - 15.1925, P < 0.001, 6 d.f.) with 97.5 percent of the variability accounted for by the regression equation

5. Log (ug/g) = - 0.1130 days + 0.9598

   r = - 0.9872, r^2 = 0.9747, n = 8, P < 0.001, 6 d.f.

A common slope (b = - 0.1185) was obtained by the analysis of covariance of the slopes of the five regression equations (Snedecor and Cochran, 1967). The slopes of the regression equations were found to be not significantly different $(F_{4,28}$ = 0.8743, P < 0.25). The common half-life of azinphosmethyl in soil from the 5 strips of the squash and cucumber subplots was 2.54 days.

Estimates of the half-life of residues of azinphosmethyl in soil from strips (16 rows) within the second field (Fig. 2) could not be obtained. Samples were taken from soil pans at widely divergent sites within the strips and at different times and dates (Table 11). The study design did not permit the statistical analysis of the data. The median concentration for the samples (n = 12) was 2.03 ug/g.

Unlike the gradual decline of residue concentrations on soils, residue concentrations detected on both squash leaves (Table 12) and cucumber leaves (Table 13) in field one declined rapidly. Half-life estimates of the loss of azinphosmethyl from squash and cucumber leaves were not determined. First samples were obtained approximately 2 hours after completion of the ground application of Guthion 2L. Reentry regulations did not permit sampling immediately after application (Ref   ). The concentrations of azinphosmethyl detected in leaf punch samples (n = 2) obtained from strips within the squash subplot (k = 4), approximately 2 hours after the application of Guthion 2L, were found to be not significantly different ($F_{3,4}$ = 2.3661, P < 0.25). The mean concentration observed for the combined samples from the 4 strips (N = 8) was 1.47 $\pm$ 0.27 ug/cm^2.

Initial leaf punch samples from the cucumber subplot were taken approximately 4 hours after application (Table 13). Because of the differences in sampling times, a comparison of mean concentrations of azinphosmethyl in leaf punch samples from the squash and cucumber subplots was not attempted. The concentrations of azinphosmethyl detected in leaf punch samples (n = 2) from the three sections within the cucumber subplot were found to be not significantly different ($F_{2,3}$ = 1.977, P < 0.25). The mean concentration of azinphosmethyl (3.54 $\pm$ 2.17 ug/cm^2) detected in leaf punch samples from cucumber leaves sampled approximately 4 hrs after application was observed to be greater than the mean concentration (1.47 $\pm$ 0.27 ug/cm^2) observed for leaf punch samples from squash leaves obtained 2 hours after the application.

Leaf punch samples from strips (n = 8) in the second cucumber field sampled on 2 May 1983 were obtained immediately after aerial application. The research team wore protective clothing to obtain the samples. The

concentrations of azinphosmethyl detected in leaf punch samples (n = 100) over the sampling period 2 May 1983 to 6 May 1983 (Table 14) appeared to decline in accordance with a first order decay curve (Fig. 12). Because of the unbalanced nature of the design (Table 14), an estimate of the half-life of azinphosmethyl on cucumber leaves was not determined.

Exposure of cucumber harvesters to residues of Guthion 2L was examined by measuring concentrations of azinphosmethyl on sampling devices worn by the workers and by detecting concentrations of the dialkyl phosphorous metabolites dimethylphosphate (DMP) and dimethylthiophosphate (DMTP) in urine samples provided by the workers. The harvesters entered field 2 (Fig. 2) two days after the aerial application of Guthion 2L and were monitored for three and one half hours for the accumulation of residues of azinphosmethyl on sampling devices, air sampling cartridges (n = 7), gloves (n = 16), and gauze patches worn on the outside (n = 25) and inside forearm sleeves of their work shirts. Azinphosmethyl was not detected in any of the air sampling cartridges (Table 15). The workers did not appear to contact airborne residues. However, the efficiency of the air sampling devices was not established. A more detailed study is required to assess respiratory exposure.

Concentrations of azinphosmethyl were detected in gauze patches (206.4 cm^2) located on the outside (P = 0.60) and inside (P = 0.24) forearm sleeves of workshirts worn by some of the workers (Table 15). Azinphosmethyl was not detected in 40 percent of the outside patch samples (1 - P = 0.40) and 76 percent of the inside patch samples (1 - P = 0.76). Concentrations detected in outside patches were found to be significantly greater (T = 3.241, P < 0.001) than inside patches according to the Wilcoxon signed ranks test for matched pairs (Conover, 1980). This test was preferred over the paired t-test because of the number of zero values. The median

concentration observed for outside patches was 0.03 ug/cm^2; the mean value 0.011 $\pm$ 0.020 ug/cm^2.

Concentrations of azinphosmethyl detected in right hand gloves (0.93 $\pm$ 0.46 ug/cm^2) were found to be not significantly different (t = 0.0082, d.f. = 15, P < 0.001) than concentrations detected in left hand gloves (0.92 $\pm$ 0.54 ug/cm^2) according to the t-test on paired samples (Table 15). The harvesters did not appear to demonstrate handedness while harvesting. The mean concentration observed for right hand gloves (0.92 $\pm$ 0.54 ug/cm^2) was found to be significantly greater (t = 9.805, d.f. = 39, P < 0.001) than the mean concentration obtained for outside arm patches (0.011 $\pm$ 0.20 ug/cm^2). Exposure of harvesters to residues of azinphosmethyl appeared to occur through predominately contact with the hands.

The dialkyl phosphorous metabolite DMTP was detected in morning voids of one female harvester (Table 16) and one male harvester (Table 17) on the second day following harvest of cucumbers in field two. Dialkyl phosphorous metabolites were not detected in the urine of any other subjects. The harvesters did not appear to absorb residues of azinphosmethyl after three and one half hours of work harvesting cucumbers. Concentrations of DMTP, however, did appear in the urine of two subjects 24 hours after entering the field. Excretion of detectable levels of DMP and DMTP may have occurred later. Clinical surveilance of exposure to organophosphorous insecticides by the determination of dialkyl phosphorous metabolites in urine may require a more extended period of monitoring.

INTERPRETATION AND ANALYSIS

Farmworkers entering a field (Fig. 2) located in the Lower Rio Grande Valley (LGRV) of South Texas to harvest cucumbers two days after an aerial application of Guthion 2L accumulated residues of azinphosmethyl on gloves (Table 15) and outside shirt patches (Table 15) but did not appear to absorb residues after three hours and 30 minutes of harvesting (Tables 16 and 17). The deposition of azinphosmethyl on artificial substrates, panels, within the field appeared to be uniform (Fig. 4). Loss of residues of azinphosmethyl from leaves appeared to rapid (Fig. 12). The half-life of azinphosmethyl on soil from an ajoining field was estimated to be 2.54 days. A substantial loss of residues on leaves and soil may be expected prior to reentry.

The harvesters did accumulate residues on gloves at much higher concentrations than on arm patches. This observation appeared to be consistent with the results of Wolfe et al. (1966) and Davis et al. (1983) where hand exposures might range from 20 to 50 percent of the total exposure. Davis et al. (1983) cautioned, however, that residue levels obtained from the use of absorbent gloves might represent an over estimation of potential dermal exposure. Accepting the values obtained for gloves as exaggerated estimates of exposure, the upper limit of dermal exposure of azinphosmethyl on the hands may be extrapolated to be 0.31 ug/Kg/hr using the estimates of body surface area given by Hansen et al. (1978) for the hands (0.082 m^2) of a 70 Kg individual exposed for 3.5 hours.

The concentrations detected in outside shirt patches (Table 15) was considered negligible. In addition, residues of azinphosmethyl did not appear

to penetrate the shirt as indicated by the significantly lower concentrations detected in inside shirt patches (Table 15). A similar result was observed by Hansen et al. (1978) for tractor drivers and sprayers wearing similar clothing but exposed to much higher concentrations of azinphosmethyl for longer periods. Indeed, Hansen et al. (1978) projected from their findings that normal work clothing may be adequate to protect workers exposed to azinphosmethyl in an orchard spray program. Davis et al. (1983) concluded that workers thinning apples may experience little acute or semiacute (subacute) toxic hazard when exposed to residues of azinphosmethyl beyond the 24 hour reentry limit. The dislodgable residues of azinphosmethyl detected on apple leaves by Davis et al. (1983) were far in excess (1.9 ± 0.2 ug/cm²) of the concentrations detected in cucumber leaves (Tables 12 and 13) two days after the aerial application of Guthion 2L at the rate of 1 pint per acre (210 g/acre) may be expected to contact 0.31 ug/kg/hr through the hands while harvesting for 3.5 hours without clinical signs or symptoms or the appearance of metabolites of azinphosmethyl in the urine within 2 days of exposure. Youths (age $\leq$ 17 yrs) may be expected to contact similar levels as adults (age $\geq$ 17) but may experience greater risk of acute intoxication because of lower weights (Munn et al., 1985).

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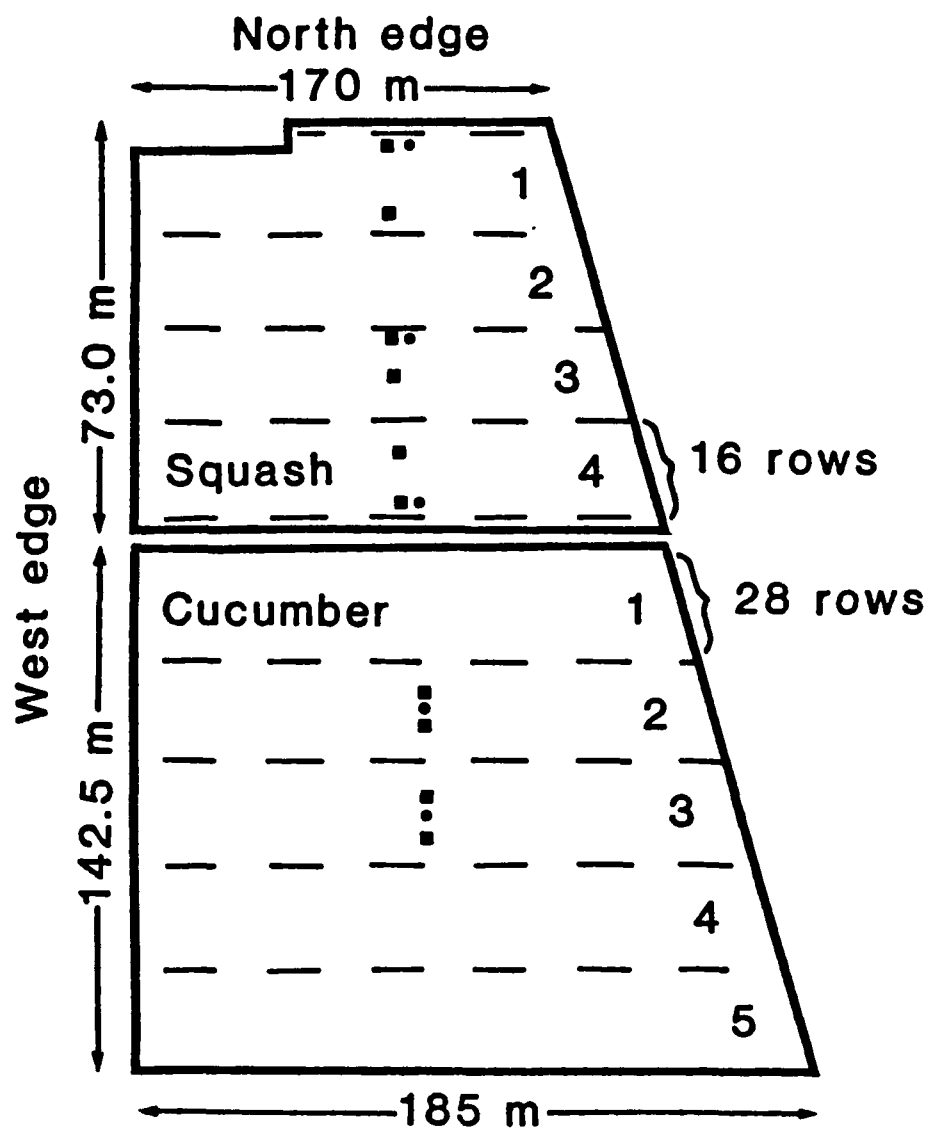
Fig. 1. Schematic representation of the cucumber and squash subplots and the arrangement of soil pans ■ and panels ● within strips in field one. The field was treated with Guthion 2L by ground application on 7 April 1983.
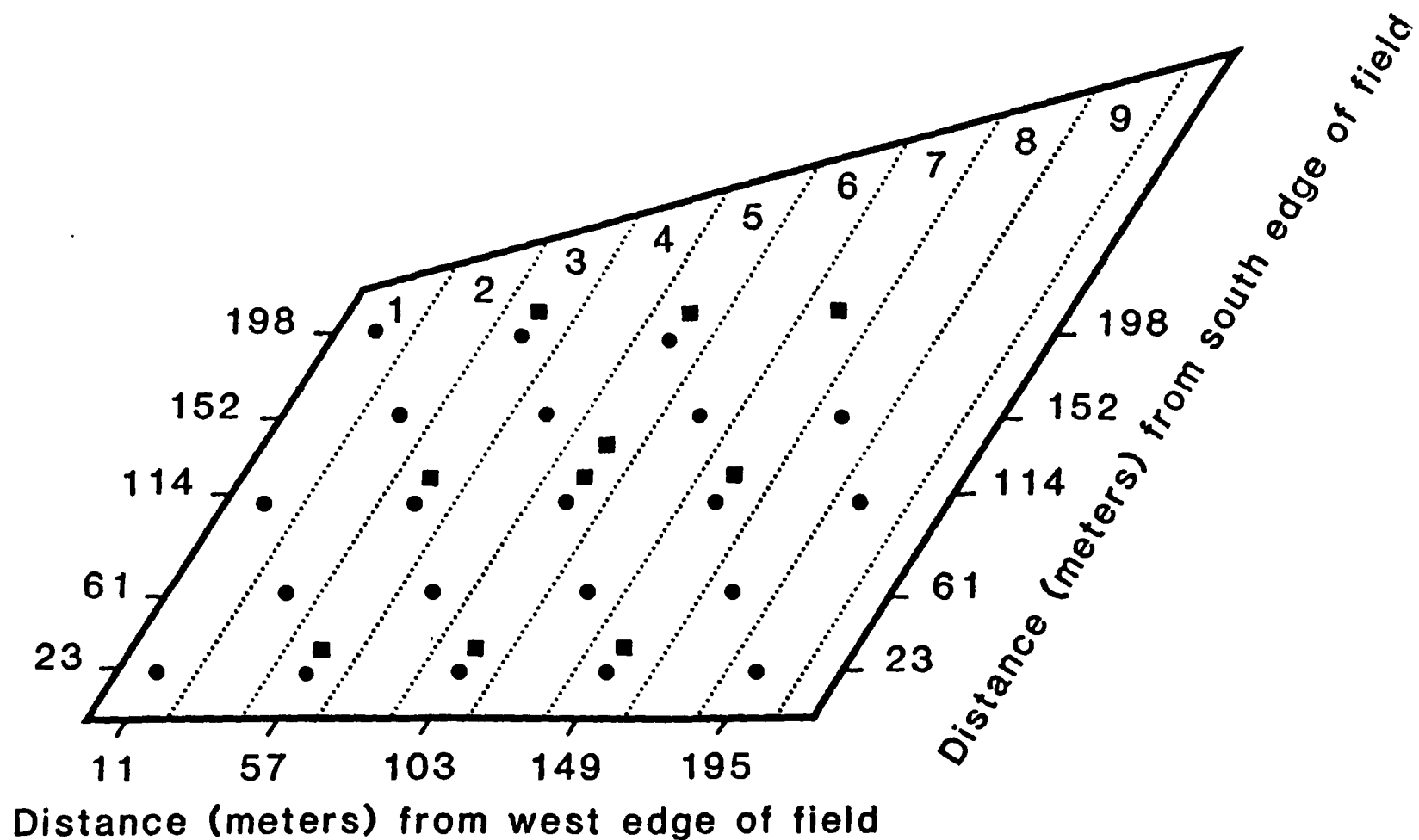
Fig. 2. Schematic representation of cucumber field two and the arrangement of soil pans ■ and panels ● along rows within strips aligned in a south-north plane. The field was treated with Guthion 2L by aerial application on 2 May 1983.
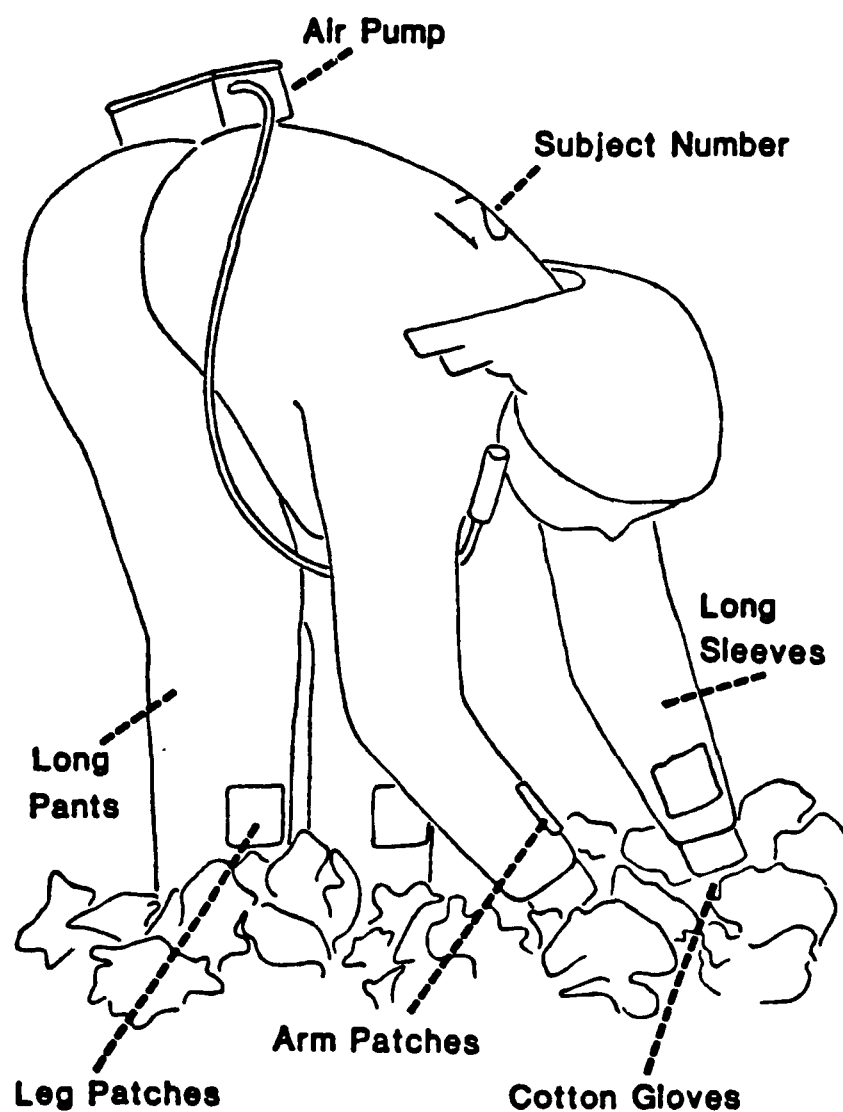
Fig. 3. Positions of sampling devices (air pumps, body patches and gloves) worn by workers harvesting cucumbers treated with a formulation (Guthion 2L) of azinphosmethyl.
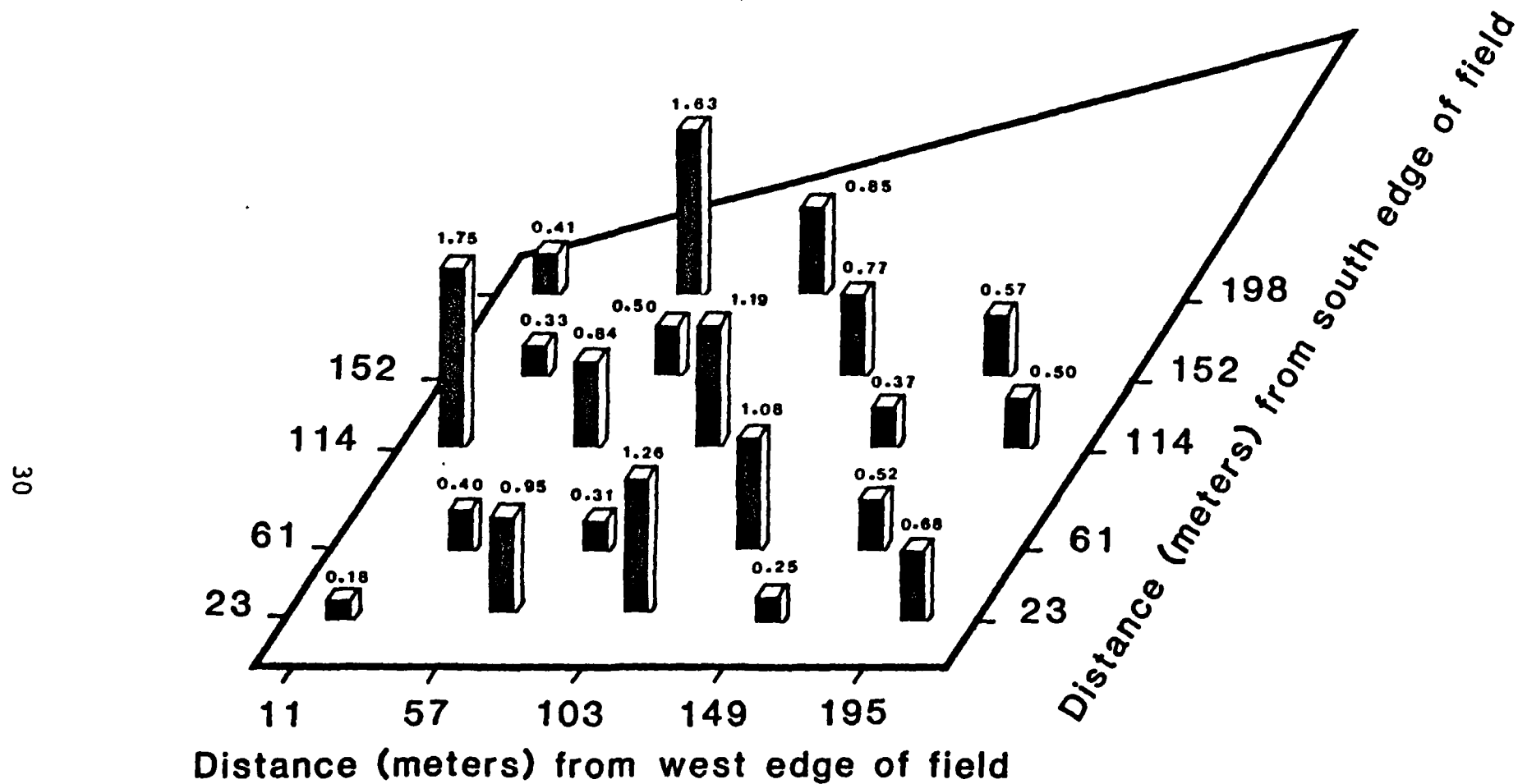
Fig. 4. Deposition of Guthion 2L detected as azinphosmethyl in gauze patches on panels in the second cucumber field.
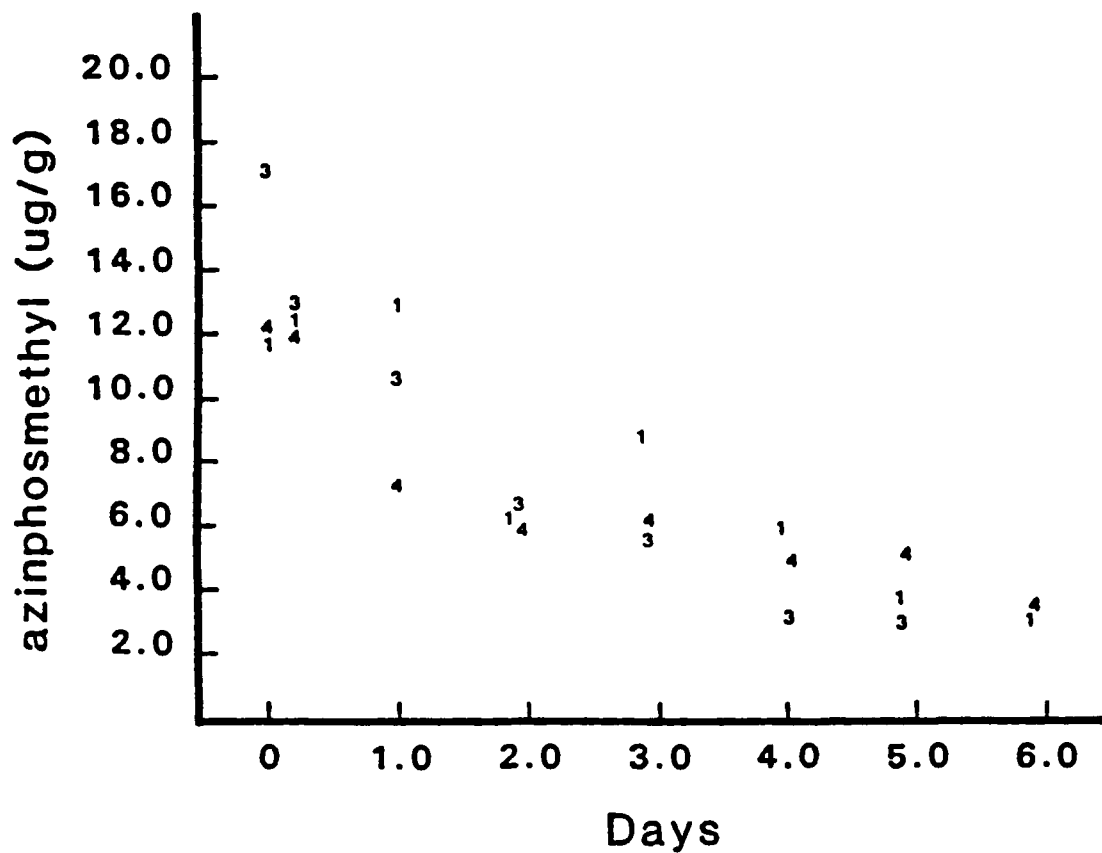
Fig. 5. Decline or loss of residue concentrations of azinphosmethyl from soil contained within pans in strips 1,3, and 4 of the squash subplot in field one. Numbers represent strips.
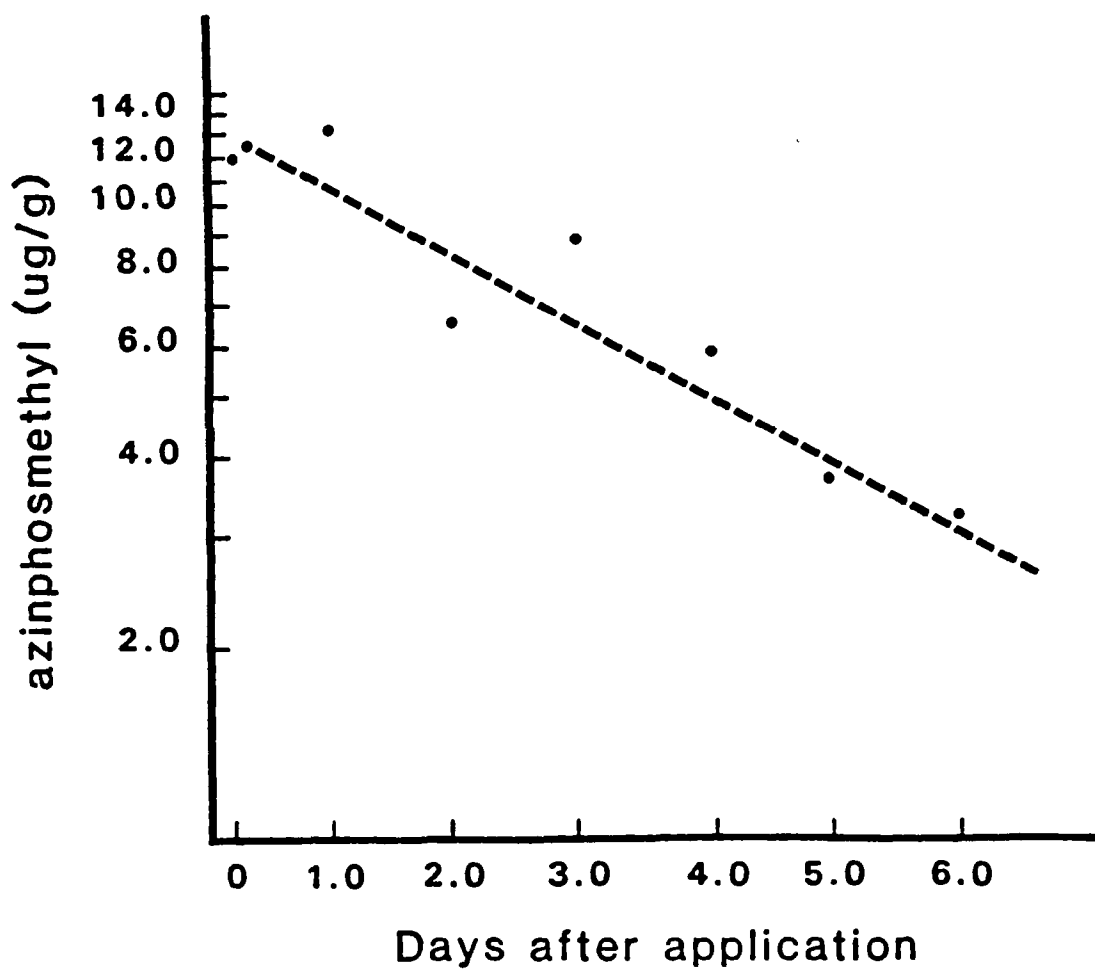
Fig. 6. Semilogarithmic display of residue concentrations of azinphosmethyl detected in soil obtained from pans in strip 1 of the squash subplot in field one.
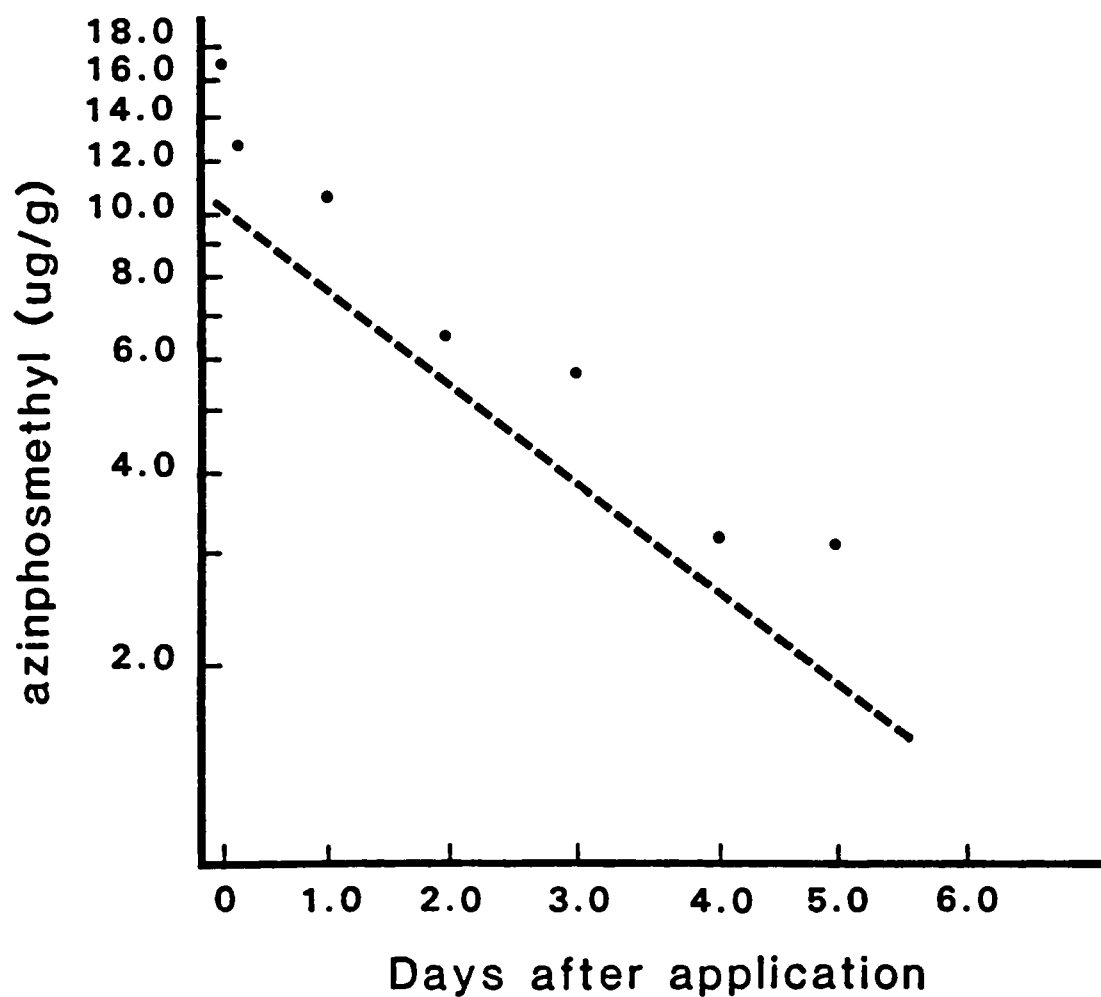
Fig. 7. Semilogarithmic display of residue concentrations of azinphosmethyl detected in soil obtained from pans in strip 3 of the squash subplot in field one.
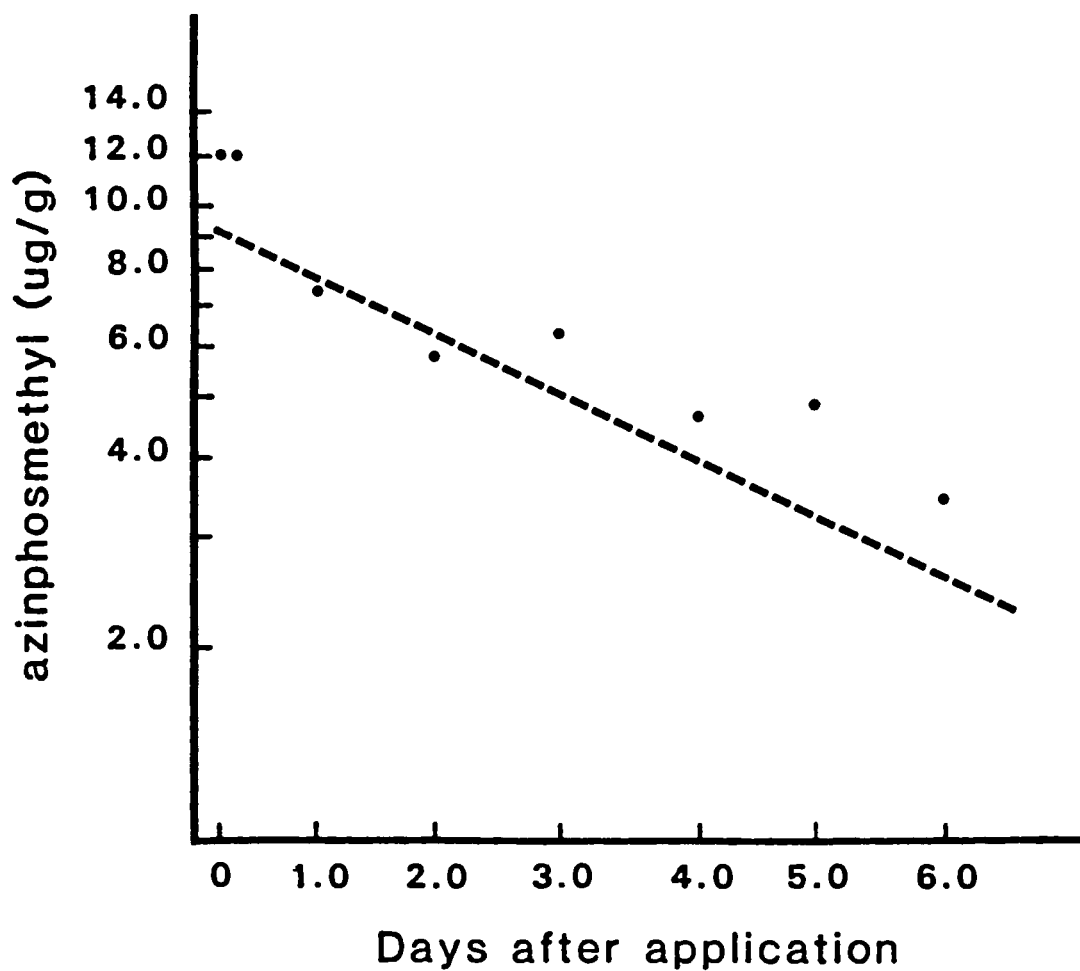
Fig. 8. Semilogarithmic display of residue concentrations of azinphosmethyl detected in soil obtained from pans in strip 4 of the squash subplot in field one.
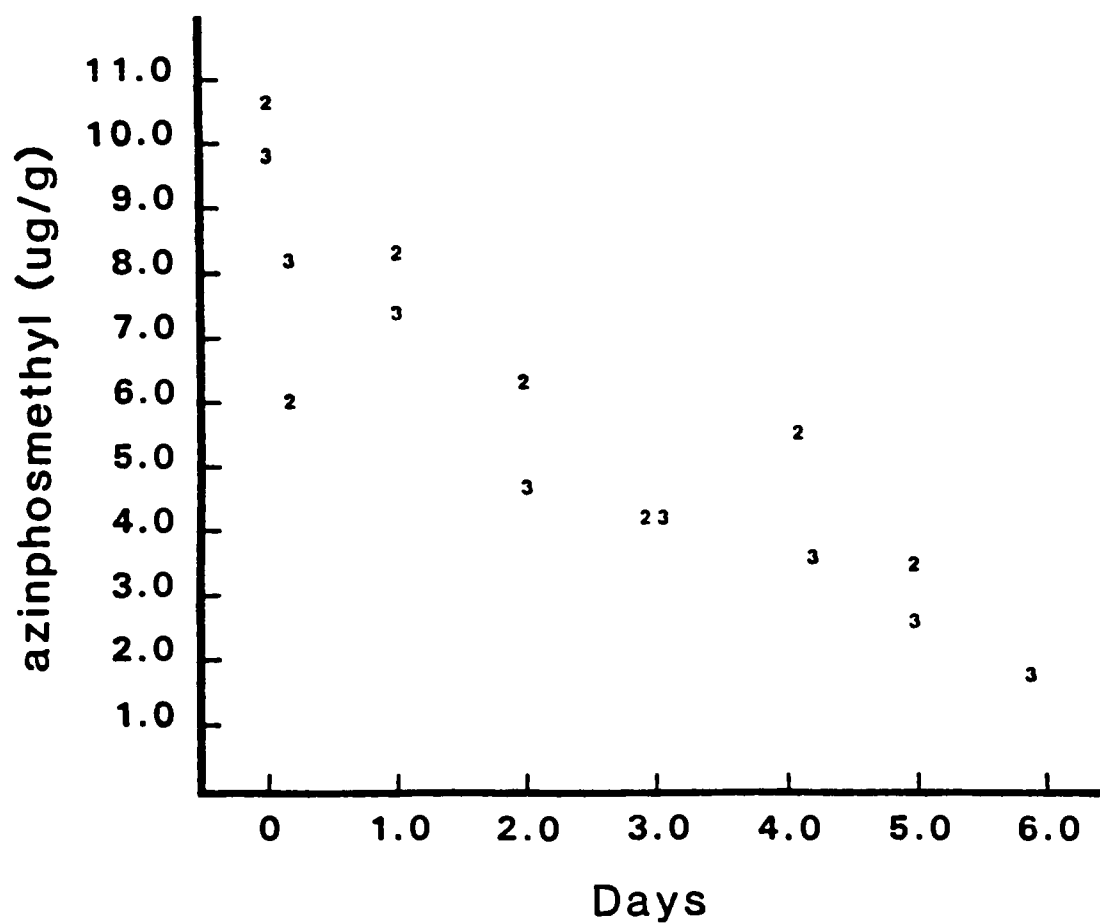
Fig. 9. Decline or loss of residue concentrations of azinphosmethyl from soil contained within pans in strips 2 and 3 of the cucumber subplot in field one. Numbers represent strips.
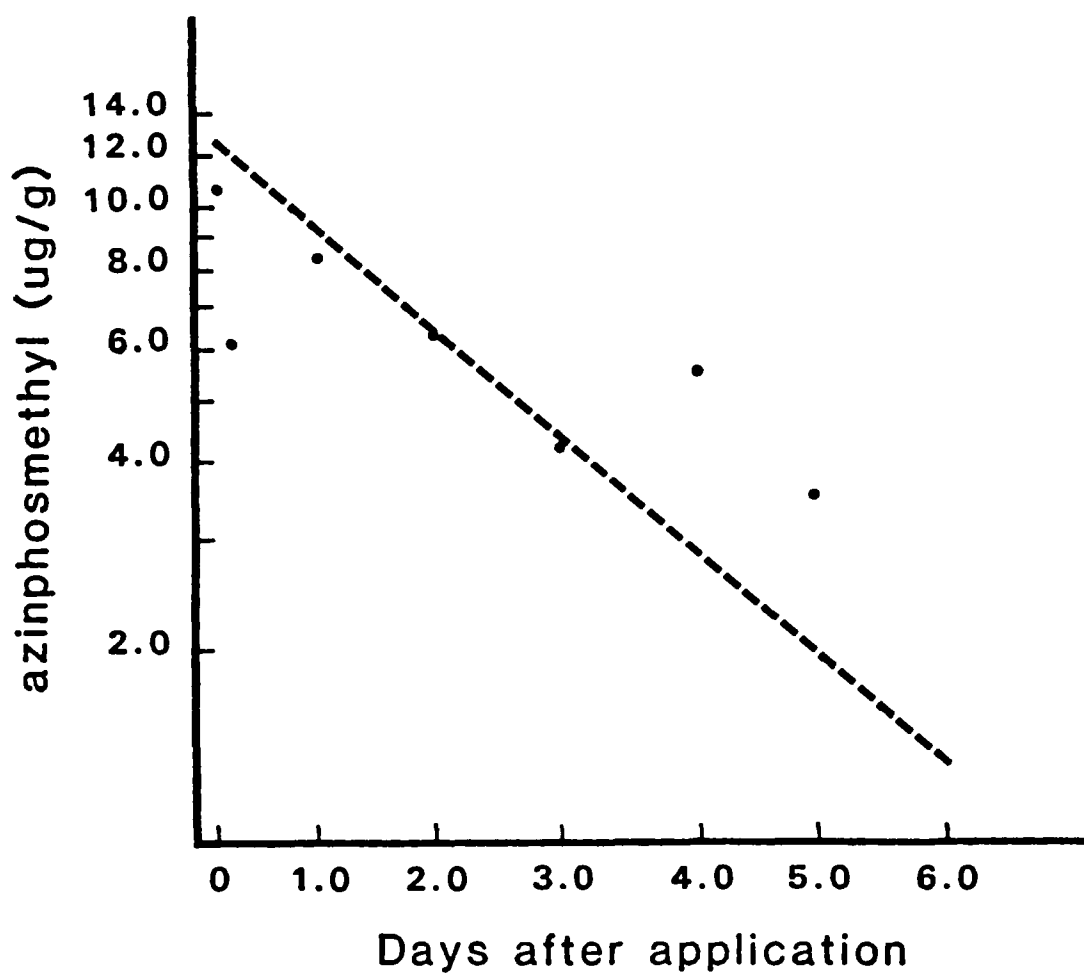
Fig. 10. Semilogarithmic display of residue concentrations of azinphosmethyl detected in soil obtained from pans in strip 2 of the cucumber subplot.
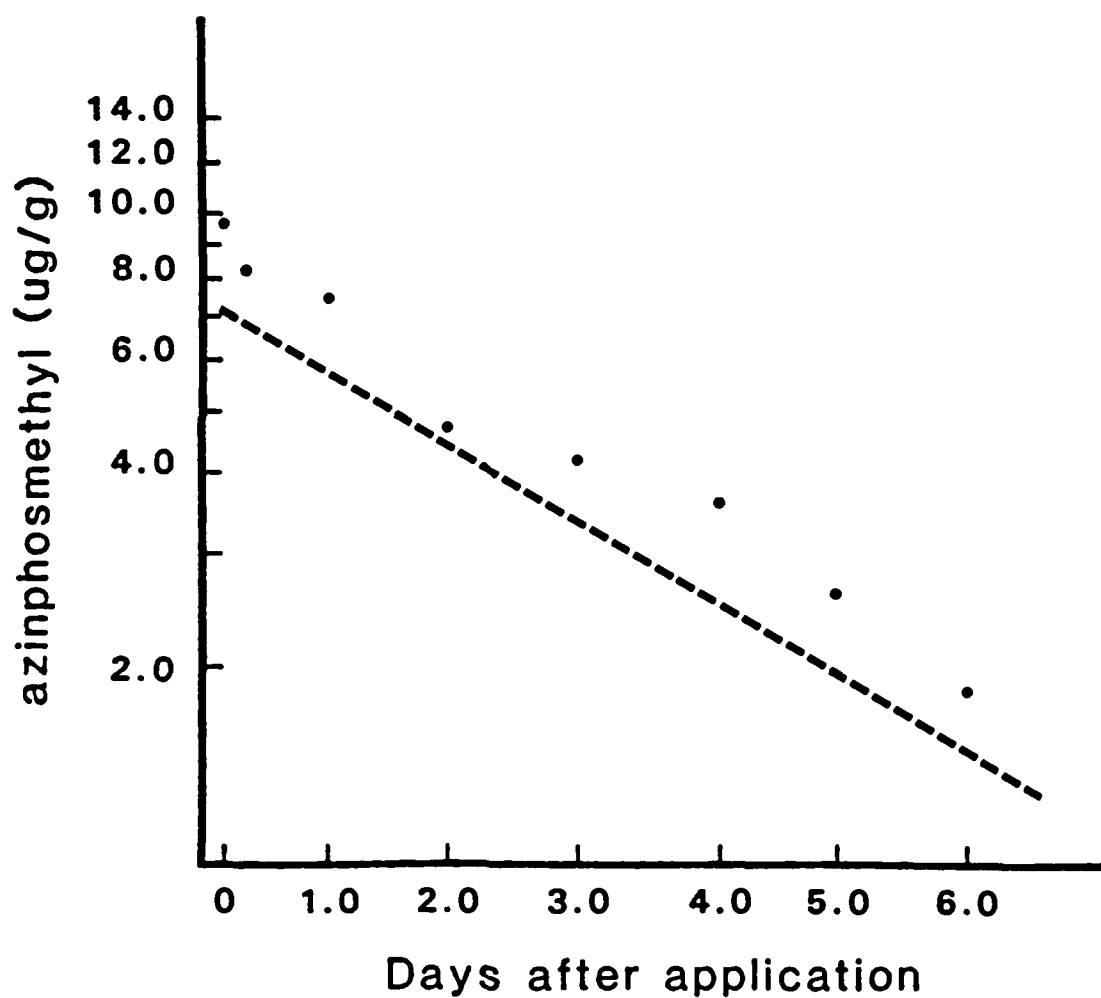
Fig. 11. Semilogarithmic display of residue concentrations of azinphosmethyl detected in soil obtained from pans in strip 3 of the cucumber subplot.
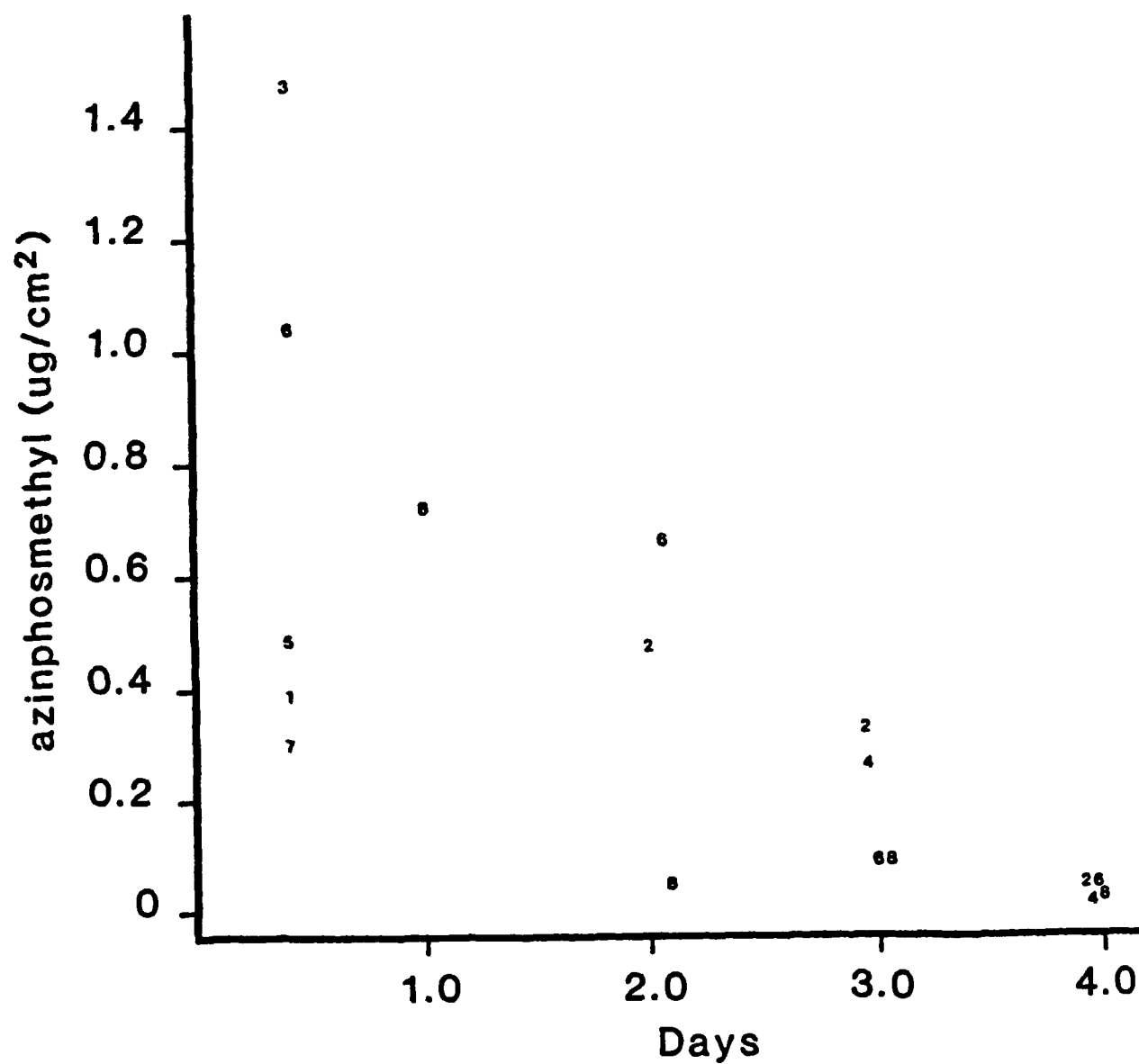
Fig. 12. Decline or loss of residue concentrations of azinphosmethyl on leaf punch samples taken from cucumber plants within strips of the second cucumber field. Numbers refer to strips.

Table 1. Cohort of six human female subjects exposed to dislodgable residues of a liquid formulation (Guthion 2L) of azinphosmethyl while harvesting cucumbers on a 21 acre field in the Lower Rio Grande Valley of Texas. A dash (-) indicates a missing value. Values in parentheses are heights in inches or weight in pounds. The buckets used during harvest are plastic and have a five gallon capacity. The mean value is accompanied by the standard deviation.

| Worker Number | Age | Physical Characteristics | | Buckets Harvested |
		Height(m)	Weight(kg)	
3	61	1.55 (61)	49 (108)	21
18	17	-	51 (112)	20
30	61	1.65 (65)	64 (142)	21
42	28	-	68 (150)	13
48	37	1.60 (63)	80 (177)	18
49	32	1.52 (60)	65 (145)	13
Mean	39.3 ± 18	1.58 ± 0.06	63 ± 12	17.7 ± 3.8

Table 2. Cohort of 22 human male subjects exposed to dislodgable residues of a liquid formulation (Guthion 2L) of azinphosmethyl while harvesting cucumbers on a 21 acre field in the Lower Rio Grande Valley of Texas. A dash (-) indicates a missing value. Values in parentheses are heights in inches or weight in pounds. The buckets used during harvest are plastic and have a five gallon capacity. The mean value is accompanied by the standard deviation.

| Worker Number | Age | Physical Characteristics | | Buckets Harvested |
		Height(m)	Weight(kg)	
1	38	1.65 (65)	70 (155)	20
26	42	1.83 (72)	96 (212)	-
31	24	1.68 (66)	60 (132)	21
33	53	1.68 (66)	77 (169)	18
34	47	1.70 (67)	57 (125)	26
35	38	1.70 (67)	82 (180)	13
36	19	1.62 (64)	52 (115)	17
37	22	1.62 (64)	64 (142)	16
38	39	1.75 (69)	60 (132)	18
39	36	1.70 (67)	54 (120)	13
43	34	1.68 (66)	54 (119)	33
45	28	1.75 (69)	72 (158)	20
46	52	1.57 (62)	54 (119)	-
47	25	1.70 (67)	53 (116)	13
50	70	1.60 (63)	68 (150)	18
51	85	-	66 (145)	14
52	61	1.70 (67)	65 (144)	11
53	65	1.65 (65)	73 (160)	20
54	34	1.62 (64)	54 (119)	25
55	65	1.65 (65)	67 (148)	-

Table 2. (Cont.)

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| Worker Number | Age | Physical Characteristics | | Buckets Harvested |
		Height(m)	Weight(kg)	
56	17	1.68 (66)	54 (118)	19
57	19	1.62 (64)	55 (122)	21
Mean	41.5 ± 18.8	1.68 ± 0.06	64 ± 11.2	18.7 ± 5.3

Table 3. Description of apparel worn by six female subjects exposed to dislodgable residues of a liquid formulation (Guthion 2L) of azinphosmethyl while harvesting cucumbers on a 21 acre field in the Lower Rio Grande Valley of Texas. Abbrebiations or keys used in the table are as follows: under Footwear, BT = Boots, SH = Street Shoes, SX = Stockings Only, TN = Tennis Shoes; Trouser Type, 1 = Other, 2 = Jeans; Shirt, 1 = Study, 2 = Non Study; Gloves, 1 = Gloved, 2 = Ungloved; Headwear, 1 = Cap, 2 = Hat, 3 = Bare, 4 = Handkerchief; Air Sampler, 1 = Yes, 2 = No.

| | | Articles of Clothing | | | | |
Worker Number	Footwear	Trouser Type	Shirt	Gloves	Headwear	Air Sampler
3	TN	1	1	1	4	2
18	SX	1	1	1	1	2
30	TN	1	1	1	2	2
42	TG	1	2	2	3	2
48	TN	1	2	1	1	1
49	SH	1	2	1	1	2

Table 4. Description of apparel worn by 22 male subjects exposed to dislodgable residues of a liquid formulation (Guthion 2L) of azinphosmethyl while harvesting cucumbers on a 21 acre field in the Lower Rio Grande Valley of Texas. Abbrebiatjons or keys used in the table are as follows: under Footwear, BT = Boots, SH = Street Shoes, SX = Stockings Only, TN = Tennis Shoes; Trouser Type, 1 = Other, 2 = Jeans; Shirt, 1 = Study, 2 = Non Study; Gloves, 1 = Gloved, 2 = Ungloved; Headwear, 1 = Cap, 2 = Hat, 3 = Bare, 4 = Handkerchief; Air Sampler, 1 = Yes, 2 = No.

	Articles of Clothing					
Worker Number	Footwear	Trouser Type	Shirt	Gloves	Headwear	Air Sampler
1	SH	1	1	1	1	2
26	BT	1	1	2	1	2
31	TN	2	1	1	1	2
33	SH	1	1	2	2	1
34	SH	1	1	1	1	2
35	SH	1	1	1	1	2
36	BT	1	2	1	3	2
37	BT	2	1	1	1	2
38	BT	2	1	2	1	1
39	BT	2	1	2	3	1
43	BT	1	2	1	1	2
45	BT	1	1	1	1	2
46	SH	1	2	2	3	2
47	SH	1	2	2	1	2
50	BT	1	1	1	1	2
51	BT	1	2	1	1	2
52	BT	1	2	1	1	2
53	SH	1	1	2	2	2

Table 4. (Cont.)

Worker Number	Articles of Clothing					
	Footwear	Trouser Type	Shirt	Gloves	Headwear	Air Sampler
54	BT	1	1	2	1	2
55	BT	1	2	2	1	1
56	BT	1	2	2	3	1
57	BT	1	1	1	1	1

Table 5. Concentrations of azinphosmethyl (ug/cm^2) detected in gauze patches (103.2 cm^2) from panels placed within strips of the squash and cucumber subplots in field one (Fig.) after ground application of Guthion 2L at 1205 hours on 7 April 1983.

Panel Location	Subplot	
Strips	Squash	Cucumber
2	-	0.19
3	-	0.15
1	0.27	-
3	0.21	-
4	0.41	-
	0.30 ± 0.10	0.17 ± 0.13

Table 6. Concentrations of azinphosmethyl (ug/cm^2) detected in panel patches from sampling sites along south to north and west to east coordinates in the second cucumber field following an aerial application of Guthion 2L at 0930 hours on 2 May 1983.

Distance from west edge of field	Distance (meters) from south edge of field					Total
	23	61	114	152	198	
11	0.18		1.75		0.41	2.34
34		0.40		0.33		0.73
57	0.95		0.84		1.63	3.42
80		0.31		0.50		0.81
103	1.26		1.19		0.85	3.30
126		1.08		0.77		1.85
149	0.25		0.37		MV[a]	0.62
171		0.52		0.57		1.09
195	0.68		0.50		MV[a]	1.18
Total	3.32	2.31	4.65	2.17	2.89	15.34

[a] Missing value

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Table 7. Subset 1, values and coordinates for estimation of homogeneity of deposition (ug/cm^2) of azinphosmethyl by two factor analysis of variance without replication.

Distance from West Edge of Field	Distance (meters) from South Edge of Field			
	23	114	198	Total
11	0.18	1.75	0.41	2.34
57	0.95	0.84	1.63	3.42
103	1.26	1.19	0.85	3.30
149	0.25	0.37	0.25[a]	0.87
195	0.68	0.50	0.54[a]	1.72
Total	3.32	4.65	3.68	11.65

[a] Values obtained by iteration

Table 8. Subset 2, values and coordinates for estimation of homogeneity deposition (ug/cm^2) of azinphosmethyl by two factor analysis of variance without replication.

Distance from west edge of field	Distance (meters) from south edge of field		Total
	61	152	
34	0.40	0.33	0.73
80	0.31	0.50	0.81
126	1.08	0.77	1.85
171	0.52	0.57	1.09
Total	2.31	2.17	4.48

Table 9. Deposition and loss of residues of azinphosmethyl from soil contained in aluminum cooking pans (522.6 cm^2) aligned in parallel lines of five pans within strips (16 rows) of the squash subplot in field one (Fig. 1).

Strip 1		Strip 3		Strip 4	
Day post applic.	Azinphosmethyl concentration (ug/g)	Day post applic.	Azinphosmethyl concentration (ug/g)	Day post applic.	Azinphosmethyl concentration (ug/g)
0	11.8	0	17.2	0	12.0
0.14	12.4	0.15	12.7	0.16	12.0
0.93	13.1	0.98	10.6	1.00	7.30
1.88	6.47	1.93	6.57	1.96	5.76
2.88	8.80	2.92	5.66	2.94	6.15
3.97	5.83	4.02	3.19	4.05	4.62
4.88	3.69	4.90	3.10	4.92	4.77
5.89	3.22			5.92	3.42

Table 10. Deposition and loss of residues of azinphosmethyl from soil contained in aluminum cooking pans (522.6 cm^2) aligned in parallel lines of five pans within strips (28 rows) of the cucumber subplot in field one (Fig. 1).

Strip 2		Strip 3	
Day post application	Azinphosmethyl concentration (ug/g)	Day post application	Azinphosmethyl concentration (ug/g)
0	10.6	0	9.82
0.16	6.12	0.17	8.24
1.02	8.29	1.02	7.43
1.98	6.25	2.01	4.68
2.97	4.24	3.01	4.15
4.14	5.47	4.16	3.59
4.96	3.30	4.97	2.55
		5.88	1.84

Table 11. Concentrations of azinphosmethyl detected in soil samples (10 g) taken from soil (100 g) contained in aluminum cooking pans (522.6 cm^2) placed within sections of 16 rows aligned in a south to north direction (Fig. 2).

Sample Collection		Location of Sample			
Date	Time		Distance From (m)		Azinphosmethyl
		Section			Concentration
May 1983	(hrs)	Section	West Edge	South Edge	(ug/g)
2	1000	3	57	23	4.60
2	1000	5	103	23	3.28
2	1000	5	103	134	3.62
2	1000	7	149	23	1.73
3	1115	5	103	114	0.92
3	1128	7	149	114	1.92
3	1118	5	103	114	2.37
4	0915	3	57	114	3.48
4	1055	5	103	114	1.65
4	1035	7	149	197	0.69
5	0835	3	57	197	0.77
5	0915	5	103	197	2.14

Median = 2.03 ug/g

Table 12. Concentrations of azinphosmethyl detected on leaf punch samples (n = 100) obtained from strips (16 rows) within the squash subplot (Fig. 1) at various times throughout the sampling period 7 April 1983 to 13 April 1983.

Sampling Date (April 1983)	Strip 1		Strip 2		Strip 3		Strip 4	
	Time (hrs)	ug/cm^2	Time (hrs)	ug/cm^2	Time (hrs)	ug/cm^2	Time (hrs)	ug/cm^2
7	1415	1.65	1430	1.46	1500	1.14	1520	1.91
7	1422	1.22	1445	1.67	1510	1.17	1530	1.52
8	1040	ND	1115	1.65	1145	2.74	1215	ND
8	1058	0.65	1127	0.41	1200	ND	1232	ND
9	0930	0.63	1003	ND	1040	ND	1120	0.82
9	0945	1.49	1016	0.71	1055	0.57	1130	0.87
10	0925	ND	1050	0.97	1025	0.60	1100	0.51
10	1050	0.97	1005	ND	1040	0.76	1115	ND
11	1135	ND	1215	ND	1245	ND	1320	ND
11	1155	ND	1230	0.54	1300	ND	1325	ND
12	0930	ND	1030	ND				
12	0940	ND	1010	ND				
13	0945	ND	1007	ND				
13	1000	ND	1030	ND				

Table 13. Concentrations of azinphosmethyl detected on leaf punch samples
(n = 100) obtained from strips (28 rows) within the cucumber
subplot (Fig. 1) at various times throughout the sampling period
7 April 1983 to 12 April 1983.

Sampling Date (April 1983)	Strip 1		Strip 2		Strip 3	
	Time (hrs)	ug/cm^2	Time (hrs)	ug/cm^2	Time (hrs)	ug/cm^2
7	1550	2.24	1620	4.64	1647	3.22
7	1600	0.93	1640	3.00	1657	7.22
8			1305	0.08	1355	0.05
8			1322	ND	1415	0.06
9			1200	ND	1230	0.11
9			1215	1.36	1250	1.20
10			1150	0.14	1235	0.58
10			1205	0.59	1255	ND
11			1535	0.08	1500	0.55
11			1600	0.67	1525	0.84
12			1120	ND		
12			1135	ND		

Table 14. Concentrations of azinphosmethyl (ug/cm^2) detected on leaf punch samples (n = 100) obtained from cucumber plants within strips (n = 8) of the second field (Fig. 2) sampled from 2 May 1983 to 6 May 1983.

Sampling Date (May 1983)	Time (hrs)	Day Post application	Strips in Field							
			1	2	3	4	5	6	7	8
2	1000	0.42	0.39		1.47		0.49	1.39	0.30	
3	1000	1.00								0.72
4	1035	2.01		0.47						
4	1150	2.06						0.66		
4	1210	2.09								0.05
5	0914	2.96		0.33						
5	0940	2.97				0.26				
5	1000	3.00						0.09		
5	1030	3.01								0.09
6	0825	3.93		0.05						
6	0900	3.96				0.01				
6	0933	3.97						0.05		
6	1005	4.00								0.04

Table 15. Concentrations of azinphosmethyl detected in sampling devices worn by farmworkers harvesting cucumbers in Field Two (Fig. 2). Harvesters entered the field 2 days after an aerial application of Guthion 2L on 2 May 1983. Exposure was monitored for 3 hours and 30 minutes (0800 to 1130 hours).

Worker Identification Number	Air Samplers (ug/m³)	Shirt Patches (ug/cm²)		Gloves (ug/cm²)	
		Outside	Inside	Right	Left
1		0.006	0.001	0.63	0.70
3		ND	ND	0.95	1.05
18		0.009	ND	0.68	0.85
26		ND	ND		
30		ND	ND	0.57	0.40
31		ND	ND	1.06	1.14
33	ND	0.021	ND		
34		ND	ND	0.83	2.15
35		0.003	ND	0.43	0.23
36		0.023	0.002	1.11	1.02
37		0.011	0.008	0.65	0.42
38	ND	ND	ND		
39	ND	0.033	ND		
42		0.006	ND		
43		ND	ND	2.07	1.86
45				0.92	0.71
46	ND	ND			
47	ND	ND			

(Cont.)

Table 15. (Cont.)

Worker Identification Number	Air Samplers (ug/m³)	Shirt Patches (ug/cm²)		Gloves (ug/cm²)	
		Outside	Inside	Right	Left
48	ND	0.001	0.004	0.66	0.70
49		0.067	ND	0.45	0.30
50				1.70	1.40
51		0.028	ND		
52		0.006	ND	0.69	0.67
53		0.005	0.001		
54		0.062	0.003		
55	ND	0.002	ND		
56	ND	ND	ND		
57	ND			1.44	1.21

Table 16. Urinary metabolites of organophosphorous insecticides detected in urine collected from six female agricultural workers harvesting cucumbers treated with a liquid formulation of azinphosmethyl, Guthion 2L, at the rate of one pint acre (0.25 lbs azinphosmethyl per acre). Abbreviations for urinary metabolites are as follows: DMP = Dimethylphosphate, DMTP = Dimethylthiophosphate. Samples with missing values are indicated by a dash (-). ND = Not detected

Worker Number	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolites (ug/ml)		Creatinine (mg/ml)
				DMP	DMTP	
3	1	1	0745	ND	ND	0.15
	2	1	0905	ND	ND	0.08
	3	1	1130	ND	ND	0.60
	4	2	0800	ND	ND	0.31
18	1	1	0800	ND	ND	0.09
	2	1	1135	-	-	-
30	1	1	0735	ND	ND	1.59
	2	1	1135	ND	ND	3.94
	3	2	0800	ND	0.23	1.18
42	1	1	0830	ND	ND	0.54
	2	1	1130	ND	ND	0.91
48	1	1	0750	ND	ND	0.78
	2	1	1135	ND	ND	0.83
	3	2	0800	ND	ND	2.02
49	1	1	0745	ND	ND	1.32
	2	1	0925	ND	ND	1.06
	3	2	0800	ND	ND	0.60

Table 17. Urinary metabolites of organophosphorous insecticides detected in urine collected from 22 male agricultural workers harvesting cucumbers treated with a liquid formulation of azinphosmethyl, Guthion 2L, at the rate of one pint per acre (0.25 lbs. azinphosmethyl per acre). Abbreviations for urinary metabolites are as follows: DMP = Dimethylphosphate, DMTP = Dimethylthiophosphate. Samples with missing values are indicated by a dash (-). ND = Not detected

Worker Number	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolites (ug/ml) DMP	DMTP	Creatinine (mg/ml)
1	1	1	0755	ND	ND	0.21
	2	1	1135	ND	ND	1.03
	3	2	0800	-	-	-
26	1	1	0740	ND	ND	0.89
	2	1	1140	ND	ND	1.14
	3	2	0800	ND	ND	1.18
31	1	1	0940	ND	ND	1.67
	2	1	1135	ND	ND	2.44
33	1	1	0755	ND	ND	1.07
	2	1	1130	ND	ND	2.42
	3	2	0800	ND	ND	2.86
34	1	1	0750	ND	ND	3.28
	2	1	1125	ND	ND	3.48
	3	2	0800	ND	ND	0.50
35	1	1	0750	ND	ND	2.90
	2	1	1135	ND	ND	2.82
	3	2	0800	ND	ND	0.98
36	1	1	0900	ND	ND	1.68
	2	1	1135	ND	ND	0.92
	3	2	0800	ND	0.10	1.81
37	1	1	0750	ND	ND	0.63
	2	1	1135	ND	ND	1.51
	3	2	0800	-	-	-
38	1	1	0750	ND	ND	0.60
	2	1	0905	ND	ND	0.46
	3	2	0800	ND	ND	0.60
39	1	1	0755	ND	ND	1.12
	2	1	1140	ND	ND	1.44

Table 17. (Cont.)   738

Worker Number	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolites (ug/ml) DMP	DMTP	Creatinine (mg/ml)
43	1	1	0800	ND	ND	0.46
	2	1	1135	ND	ND	1.25
	3	2	0800	ND	ND	1.29
45	1	1	0800	ND	ND	0.88
	2	1	1120	ND	ND	0.28
	3	2	0800	ND	ND	1.74
46	1	1	0755	ND	ND	0.28
	2	1	1145	ND	ND	0.83
	3	2	0800	ND	ND	0.76
47	1	1	1130	ND	ND	2.85
50	1	1	0750	ND	ND	1.71
	2	1	1130	ND	ND	1.24
	3	2	0800	ND	ND	2.32
51	1	1	1130	ND	ND	0.32
	2	2	0800	ND	ND	1.13
52	1	1	0755	ND	ND	0.67
	2	1	1130	ND	ND	1.95
53	1	1	0755	ND	ND	0.79
	2	1	1130	ND	ND	1.98
	3	2	0800	ND	ND	0.83
54	1	1	0755	ND	ND	0.99
	2	1	0900	ND	ND	3.81
	3	1	1125	ND	ND	4.21
	4	2	0800	ND	ND	2.11
55	1	1	0755	ND	ND	0.94
	2	1	1145	ND	ND	0.65
	3	2	0800	ND	ND	0.88
56	1	1	0800	ND	ND	0.65
	2	1	1140	ND	ND	2.11
	3	2	0800	ND	ND	0.74
57	1	1	0800	ND	ND	0.66
	2	1	1140	ND	ND	0.92
	3	2	0800	ND	ND	1.13

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LITERATURE CITED

Anonymous. 1968. Spectrometry nomenclature; Guide for measures of precision and accuracy. Anal. Chem 40(14):2271.

Conover, W. J. 1980. Practical nonparametric statistics, 2 ed. John Wiley & Sons, New York.

Daughton, C. G., A. M. Cook, and M. Alexander. 1979. Gas chromatographic determination of phosphorus-containing pesticide metabolites via benzylation. Anal. Chem. 51:1941-1953.

Davis, J. E., E. R. Stevens and D. C. Staiff. 1983. Potential exposure of apple thinners to azinphosmethyl and comparison of two methods for assessment of hand exposure. Bull. Environ. Contam. Toxicol. 31: 631-638.

Eto, M. 1979. Organophosphorus pesticides: Organic and biological chemistry. CRC Press, Inc., Boca Raton, FL.

Federal Working Group on Pest Management. 1974. Occupational exposure to pesticides. Report to the Federal Working Group on Pest Management from the Task Group on Occupational Exposure to Pesticides. 155 pp.

Gunther, F. A., J. H. Barkley, and W.E. Westlake. 1974. Worker Environment Research. II. Sampling and Processing Techniques for Determining Dislodgable Pesticide Residues on Leaf Surfaces. Bull. Env. Cont. Tox. 12(6):641-644.

Hansen, J. D., B. A. Schneider, B. M. Olive, and J. J. Bates. 1978. Personnel safety and foliage residue in an orchard spray program using azinphosmethyl and captan. Arch. Environm. Contam. Toxicol. 7:63-71.

Kirchmer, C. J. 1983. Quality control in water analyses. Environ. Sci. Technol. 17(4):174A-181A.

McFarren, E. F., R. J. Lishka, and J. H. Parker. Criterion for judging acceptability of analytical methods. Anal. Chem. 42(3):358-365.

Maddy, K. T., and S. C. Ediminston. 1982. Pesticide safety program of the California Department of Food and Agriculture based upon measurements of potential workplace exposure and the elimination of excess exposures. J. R. Plimmmer, ed. ACS Symposium Series No. 182, American Chemical Society, Washinton, D. C.

Menzie, C. M. 1978. Metabolism of pesticides, Update II. U.S. Department of the Interior Fish and Wildlife Service, Special Scientific Report-Wildlife No. 212, Washington, D. C.

Menzie, C. M. 1980. Metabolism of pesticieds, Update III. U.S. Department
of the Interior Fish and Wildlife Service, Special Scientific Report-
Wildlife No. 232, Washinton, D. C.

Mobay Chemical Company, Agricultural Chemicals Division. 1979. Material
Safety Data Sheet: Guthion Insecticide. Kansas City, MO.

Mobay Chemical Company, Agricultural Chemicals Division. 1982. Material
Safety Data Sheet: Guthion Insecticide. Kansas City, MO. 4 pp.

Munn, S., Lt. J. Keefe, and E. P. Savage. 1985. A comparative study of
pesticide exposures in adults and youth migrant field workers. Arch.
Environ. Health 40(4):215-220.

O'Brien, R. D. 1967. Mode of action of insecticides. Ann. Rev. Entomol. 11:
369-402.

Patel, C. P., and R. C. George. 1981. Liquid chromatographic determination
of creatinine in serum and urine. Anal. Chem. 53:734-735.

Pree, D. J., K. P. Butler, E. R. Kimball, and D. K. R. Stewart. 1976.
Persistence of foliar residues of dimethoate and azinphosmethyl and
their toxicity to the apple maggot. J. Econ. Entomol. 69(4): 473-478.

Reid, S. J., and R. R. Watts. 1981. A method for the determination of
dialkyl phosphate residues in urine. J. Anal. Tox. 5:126-132.

Sokal, R. R. and F. J. Rohlf. 1969. Biometry. W. H. Freeman and Company, 743
San Francisco, CA. 776 pp.

Snedecor, G. W. and W. G. Cochran. 1976. Statistical Methods. 6th Edition.
The Iowa State University Press, IA, U.S.A. 593 pp.

Takade, D. Y., J. M. Reynolds, and J. H. Nelson. 1979. 1-(4-nitrobenzyl)-3-
(4-tolyl) triazene as a derivatizing reagent for the analysis of urinary
dialkyl phosphate metabolites of organophosphorus pesticides by gas
chromatography. J. Agric. Food Chem. 27(4):746-753.

Texas Agricultural Extension Service. 1980. Texas guide for controlling
insects on commercial vegetable crops. Publ. No. B-1305. 28 pp.

U.S. Environmental Protection Agency. 1980. Manual of analytical methods for
the analysis of pesticides in humans and environmental samples. Health
Effects Research Laboratory, Research Triangle Park, NC. Publ. No. EPA-
600/8-80-038.

Wolfe, H. R., J. F. Armstrong and W. F. Durham. 1966. Pesticide exposure
from concentrate spraying. Arch. Environ. Health 13:340-344.

An Assessment of Exposure of Tomato
Harvesters to Chlorothalonil

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In behalf of the Texas PHAP the undersigned have reviewed and approved the report draft entitled "An Assessment of Exposure of Tomato Harvesters to Chlorothalonil."

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INTRODUCTION

Assessment of exposure of farmworkers to pesticide residues and the implied risk of adverse health effects associated with exposure has received considerable attention from federal regulatory agencies (Reinert and Severn, 1985). Farmworker exposure to pesticide residues as a result of reentry into fields to harvest fruits and vegetables has been observed at varyng levels for the past 25 years (Nigg and Stamper, 1982). The prediction of dermal exposure and prevention of injury has been of central interest to regulatory agencies and industry (Honeycutt et al., 1985). Although the knowledge about reentry exposure has advanced with respect to the adult farmworker, a good deal of information must be gathered to evaluate the extent of pesticide exposure to youth, 17 years of age and younger, and the potential adverse health effects of exposure.

Children of migrant farmworkers frequently enter the fields as harvesters or as dependents (Spear, 1982). Youths participating in the harvest may contact residues at the same rate as adults, but experience a higher absorbed dose because of lower body weights (Munn et al., 1985). A comparative study of pesticide exposure to youth and adult migrant farmworkers may be designed to compare relative contact with residues between adults and youths. The value of such a study is dependent on the detectability of the pesticide on environmental substrates and sampling devices worn by the workers and the harvest activities required for the crop. This study examined contact with residues on sampling devices: gloves, arm patches and leg patches worn by

farmworkers, youths and adults, harvesting tomatoes at two locations in the

Lower Rio Grande Valley of Texas on two separate dates - 17 May 1982 and

4 June 1982.

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ABSTRACT

Contact with residues of the fungicide chlorothalonil was examined in youth (age $\leq$ 17 years) and adult (age > 17 years) farmworkers during the harvest of tomatoes at two independent sites on 17 May 1982 (n = 25) and 4 June 1982 (n = 40). The accumulation of residues on sampling devices, gloves and arm and leg patches, worn by the harvesters was measured to assess areas of contact. The protective value of the gloves was estimated from paired comparisons of concentrations detected in gloves and in towels used to wash the hands. Both age classes, youths and adults, accumulated residues on the sampling devices at similar concentration levels. Gloves appeared to act as a protective barrier limiting further penetration of residues to the hands. Hand contact with residues could not, however, be explained by the performance of the harvesters. Contact with residues on arm and leg patches did not correlate with worker height or weight. The farmworkers at the first site, harvested 17 May 1982, 5 days after application of Bravo[R], contacted 16.2 $\pm$ 5.1 ng/Kg/hr^{-1} on arm and leg patches. The farmworkers harvesting tomatoes at the second site on 4 June 1982, 9 days after application of Bravo[R] contacted significantly less residue, 10.3 $\pm$ 5.7 ng/Kg/hr^{-1}. These results indicated that youths employed in the harvest of tomatoes may be expected to contact residues of the fungicide chlorothalonil at equal rates as adults.

BACKGROUND

Tomatoes are grown in Texas as fresh market and processing crops with an annual combined value of $10 million (Parsons et al., 1977). The greatest commercial production of tomatoes in Texas occurs in the Lower Rio Grande Valley with 39.3 percent of the total acreage (4,200 acres). Hidalgo County, where the study site was located, accounted for 72.7 percent of the three county area (1,650 acres) and 28.5 percent of the total (T.D.A., 1982).

Tomatoes are grown in the Lower Rio Grande Valley over 90 to 120 day periods during two seasons, from December to May and again from September to November (Parsons, et al., 1977). The temperatures during the two growing seasons range from 80°F to 85°F during the day and 60°F to 70°F in the evening. Harvest commences for green-wrap tomatoes when full size is achieved and the tomatoes are void of pink color. Vine-ripened tomatoes are picked when the stem changes from green to pink. Both harvests observed for this report were of green tomatoes only.

Harvesters pick according to the size of the tomato, entering the field as many as three times in accordance with grading practices of the grower. Labor associated with picking is sometimes divided between family members, with women and children picking the fruit, and the men carrying the loaded 5-gallon buckets through the rank foliage to the receiving crates. Because of this division of labor, women and children may come into contact with dislodgeable residues of pesticides more readily than men. Harvest of tomatoes requires close contact with foliage. Harvesters must stand knee deep

in foliage while separating leaves in order to pick. Exposure to dislodgeable residues of a pesticide may occur on the lower legs and from the elbows to the hands.

The Texas Department of Agriculture (Parsons et al., 1977) recommends repeated application of herbicides, insecticides and fungicides to tomatoes throughout the growing season. Parsons et al. (1977) did not list chlorothalonil (Bravo[R]) among the recommended fungicides. Bravo[R]-6F, a flowable formulation of chlorothalonil, was listed by Johnson and Amador (1975) for control of early blight, late blight, anthracnose, and gray spot leaf, as well as botrytis gray mold on tomatoes. Application of Bravo[R]-6F was recommended when disease threatens at the rate of 1-1/2 to 2 pints per acre for control of early blight and late blight with higher rates (2-3 pints/acre) required for control of anthracnose, gray leaf spot, and botrytis gray mold. Treatments were recommended every 7 to 10 days until harvest.

Chlorothalonil, 2,4,5,6-tetrachloroisophthalonitrile, is a broad spectrum fungicide registered under the trade names Clortosip, Daconil 2787, Exotherm, Termil and Bravo (Farm Chemicals Handbook, 1985). Chlorothalonil has a low vapor pressure (<0.01 @ 40°C) and water solubility (0.6 ppm) and may be expected to remain on the leaf surface to provide residual protection (Merck, 1976; Thomson, 1985; and Pimentel, 1981). The label for Bravo[R] 500 contains the signal word WARNING, while the labels for Clortosip and Exotherm are marked CAUTION (Farm Chemicals Handbook, 1985). Both Bravo[R] W-75 and Daconil[R] W-75 are labeled DANGER. In all cases, protective clothing is recommended when mixing, loading or applying chlorothalonil. Chlorothalonil has been found to cause dermatitis and eye irritation (Farm Chemicals Handbook, 1985 and Hallenbeck and Cunningham-Burns, 1985). The acute oral LD_{50} for male and female rats was reported in Farm Chemicals Handbook

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(1985) as 10 g/Kg. The dermal toxicity to albino rabbits was 10 g/Kg. The fungicidal activity of chlorothalonil has been attributed to the inactivation of thiol enzymes (Pimentel, 1981). Chlorothalonil has been observed (Pimentel, 1981) to bind to thiol groups of enzymes of the glycolytic pathway, e.g., glyceraldehyde-3-phosphate dehydrogenase. This action may be common to higher organisms and of considerable importance when assessing risk to non-target organisms.

The persistence of chlorothalonil on food crops (FAO, 1979; Hiramatsu and Furutani, 1979; Koseki et al., 1980; Soma et al., 1980; and Looney and Cochrane, 1981) and soil (Anon, 1979a,b and Soma et al., 1980) suggests the possibility of transfer of residues from foliage to non target animals. Residues of chlorothalonil have been detected on summer wheat (0.78 mg/Kg) 21 days after application and on winter barley (<0.01 mg/Kg) 47 days after application (FAO, 1979). A temporary maximum residue limit of 0.2 mg/Kg was recommended by the FAO (1979) on these commodities when chlorothalonil was used at the rate of 1 to 3 Kg AI/ha over a six week period following application. Similarly, wettable powder formulations of chlorothalonil were found by Hiramatsu and Furutani (1979) to persist on cucumbers in accordance with the growth rate of the vegetable. Other vegetables and fruit including tomatoes were found by Koseki et al. (1980) to contain residues from 0.001 to 1.35 ppm. Soma et al. (1980) observed chlorothalonil residues in tomatoes up to 0.32 ppm. These levels exceeded residue concentrations on many other vegetables but were dwarfed by extremely high levels (11.4 ppm) of chlorothalonil in soil taken from the same tomato field (Soma et al., 1980). Chlorothalonil is apparently used in large quantity in Japan for the control of Phytophthera infestans on tomatoes (Anon, 1979a). Disappearance of 50 percent of the residues in soil were observed to take 3 to 5 weeks with 80

percent disappearance in 10 weeks (Anon, 1979a). Residues appeared to remain on the soil surface (Anon, 1979a). Residues on tomatoes after standard application rates remained above threshold values of 1.0 ppm (Anon, 1979b).

Although application rates may differ substantially between Japan and the United States, the persistence of chlorothalonil on vegetables requires an investigation of the potential transfer of residues from foliage to harvesters picking tomatoes. This study was an attempt to estimate the potential for contact and accumulation of dislodgeable residues of chlorothalonil on sampling devices worn by farmworkers harvesting tomatoes. The aim of the study was to determine if underage farmworkers, ages 17 years and younger, contacted higher levels of residues than adults.

METHODS

Study Sites. Field one was a 22-acre field within the limits of the city of Mission, Hidalgo County, Texas. The field had two distinct sections, separated by a tree row. The northern-most section was an 8-acre square, while the southern-most was a 12-acre rectangle. A public thoroughfare provided the northern border of the field, and there were some dwellings across the street. Occupied homes were located at the northwest and northeast corners of the field. Tilled ground and citrus orchards bordered the rest of the field.

The soil of the entire field was classified as Hidalgo-Urban land complex. Soils of the Hidalgo series are deep, moderately permeable with a sandy clay loam surface layer (Jacobs, 1981). Irrigation of the field was along north-south trending furrows.

Field two was a 63-acre field in the Rio Grande River flood plain. It lies 4 Km northwest of the city of Hidalgo and 11 Km south-southwest of McAllen, Hidalgo County, Texas. The field is irregularly-shaped and is bordered on the west and south by resacas (oxbows), on the north by a levee, and on the east by a road. There were no dwellings adjacent to the field.

The soils at field two are deep, moderately well drained, somewhat permeable, silt loams and silty clay loams of the Rio Grande and Matamoros series (Jacobs, 1981). At its closest point, the field lies 0.6 Km from the Rio Grande River, at its farthest point, 2.1 Km. Irrigation of the field was along east-west trending furrows.

Crop and Pesticide Application. Both fields were planted with the Flora-Dade 908 variety of tomato, in 72 inch rows. By the time of harvest, the vines had spread to form a dense ground cover 12 to 26 inches deep.

Bravo[R] 500 and Pydrin[R] were applied by aircraft to field one on 12 May 1982 and the same chemicals were applied to field two on 26 May 1982. In both cases the application rates were one 1.5 pints (AI) of Bravo[R] 500 and 5.3 oz (AI) Pydrin[R] per acre.

The time between application and harvest for field one was five days and for field two was nine days. Leaf samples were collected from each field for each respective period. These samples were to be analyzed to establish the rate and degree of degradation of the pesticides before harvesters entered the fields. However, these samples decomposed in storage before the chlorothalonil methods could be perfected and validated. Thus an important part of the study was missing.

Weather. The weather conditions on the day of harvest (17 May 1982) at field one were: no wind; overcast skies with light, intermittent drizzle; high temperature was 80° F, low 75° F. Weather conditions at field two on the date of harvest (4 June 1982): no wind and clear skies; high temperature was 91° F, minimum was 76° F. In neither case was there precipitation between the date of application and the date of harvest.

Human Subjects. The populations studied consisted of crews of harvesters selected solely by the labor contractors. The workers did not have advanced notice of the study. The cohort in field one (17 May 1982) consisted of 25 farmworkers. The cohort in field two (4 June 1982) consisted of 40 farmworkers. In both cases the study participants numbered about half the harvesters actually working in the field. No attempt was made to determine the reasons some workers declined to participate. However, the notion of

being an experimental animal was clearly troublesome to a few persons, while others did not want to be encumbered by any of the sampling devices. Although volunteers were remunerated for their cooperation, to preclude any suggestion of human experimentation, no attempt was made to alter the level of participation by any worker.

The workers arrived at the fields in the period 1630 to 0715 hours. After an explanation of the work proposed, the volunteers proceeded through a series of study stations where they: (1) signed consent forms; (2) were briefly interviewed; (3) were weighed; and (4) were equipped with gloves and dermal patches. Workers were provided with the array of sampling devices on a voluntary basis. For easy identification, a group of participants were provided with long sleeved, twill work shirts bearing numbers on the front and back.

The workers entered the fields over the period 0730 hours to 0815 hours. While each worker was harvesting, a somewhat longer interview (15-20 minutes) was undertaken to obtain their work history as well as their perception of their own health and medical history. During the interview, notes were taken on individual picking practices (Appendix B). Harvest activities were completed for the first monitoring by 1431 hours and by 1320 hours for the second monitoring. No harvester was in the field longer than seven hours. The number of buckets of tomatoes picked by each worker was obtained from the labor contractor for possible correlation with residues detected in the substrates tested.

Both harvests reported upon were of the first picking of the field. Receiving crates were placed around the border of the fields and most of the workers started initially harvesting the crop in the vicinity of the crates. Periodically throughout the day, a collection of 10-20 workers was gathered to

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pick in front of a tractor pulling a disc harrow. This newly cultivated ground provided a new path for the placement of additional receiving crates, thereby shortening the distance required to carry loaded buckets. When a bucket was dumped into the receiving crate, the worker received a token which was later redeemed for pay.

Gloves, Towels, and Patches. The transfer of residues of chlorothalonil to workers harvesting tomatoes was examined by measuring the accumulation of residues on sampling devices worn by the workers. Hand contact with residues of chlorothalonil was estimated from an examination of residue concentrations in gloves and hand wash towels. The gloves were light weight 100% cotton twill work gloves with knit wristlets and seamless palms (Sears catalog number 51K25915). The glove surface area minus the knit wristlet was 549.7 cm^2. Exposure through the gloves was estimated from residues collected on towels used to clean both hands. The towels (84% cotton, 16% polyester, 890.3 cm^2, Leshner of St. Marys, Ohio 45885) were immersed in solvent (50:50 ethanol and water) and then used to wipe the hands clean.

To assess the potential for accumulation of residues on the arms and legs of workers, gauze patches (103.2 cm^2) were placed at near equal distances from the ankle on the outside legs and on the inner aspect of forearms equal distance from the wrist (Fig. 1). Following 3.5 hours of continuous exposure, the gloves, patches and soiled hand wash towels were sealed in plastic bags and placed on dry ice for transport to the laboratory. All samples were stored frozen until analysis.

Analytical Methods. The sampling devices were analyzed according to the methods outlined in Appendix A. The gloves and hand wash towels were cut into approximately 6.45 cm^2 pieces and extracted three times in 200 ml methanol for 15 minutes on a Burrell wrist-action shaker. The extracts were passed through

glass wool to obtain a combined sample. Sodium sulfate was added to the
sample to absorb excess water. The sample and five rinses were transferred to
a round bottom flask and reduced to near dryness on a Buchi Rotavapor R110.
The sample was reconstituted with 10.0 ml hexane and concentrated to 1.0 ml
with a gentle stream of nitrogen using a Meyer N-Evap. Following extraction,
the sample was passed through 2.0 g silica gel column deactivated with 400 ul
benzene extracted water. Fraction one (100% hexane) was used to elute the
sample. Fraction two (1% benzene/99% hexane) was discarded. Fractions three
(20% benzene/80% hexane) and four (60% benzene/40% hexane) were collected and
combined to obtain the final extract for GC analysis.

The arm and leg patches (103.2 cm^2) were extracted three times with 150
ml methanol in a 500 ml Erlenmeyer flask on a Burrell wrist-action shaker set
at 6. The extracts were collected and dried with sodium sulfate and
evaporated to 5.0 ml. The concentrate was adjusted to 10.0 ml and prepared
for analysis by GC.

Samples were analyzed for residues of chlorothalonil with a Tracor 220
gas chromatograph by electron capture (^3H) with two column confirmation (4.0%
SE30/3.0% OV210 and 1.5% OV17/1.95% OV210). The carrier gas (N_2) flow was 72
cc/min (isocratic) with an oven temperature of 200°C. Chlorothalonil
(Bravo$^{(R)}$) code 1640 was used as the reference standard. The standard was
obtained from the U.S. EPA Pesticides and Industrial Chemicals Repository,
U.S. EPA Environmental Research Center, Research Triangle Park, NC 27711. The
standard was prepared in methanol as 99.7% chlorothalonil.

Quality Assurance. Measurement of chlorothalonil residues on the
sampling devices worn by farmworkers harvesting tomatoes was complicated by
the large concentrations detected. Extracts of the samples required
considerable dilution to obtain resolvable peaks. Residue concentrations in

sample extracts were more readily detectable than companion check samples fortified at much lower concentrations. Minimum detection limits were established for each substrate from the check samples. Concentrations detected in gloves fortified with 0.27 ng/cm^2 were much greater than expected (Table 1) because of conflicting underlying peaks observed with each column (Fig. 2). Conflicting peaks were detected in blanks prepared with each check sample (Fig. 2). Dilution of blanks and check samples to conform with peak detection of test samples resulted in more stable baselines. However, conflicting peaks detected in check samples (0.91 ng/cm^2) on both columns made interpretation difficult (Fig. 3). An increase in the fortification level (18.2 ng/cm^2) produced easily resolvable peaks for chlorothalonil on both columns (Fig. 4). A series of check samples prepared to evaluate the quality of analysis revealed substantial improvement in recovery (109.3%) of chlorothalonil (18.2 ng/cm^2) on the SE30-OV210 column and 79.1 percent recovery on the confirmatory OV17-OV210 column (Table 2). The mean concentration of chlorothalonil (19.9 $\pm$ 1.5 ng/cm^2) detected in this series of check samples on the SE30-OV210 column were used to set control limits (C.V.=7.57%). Check samples prepared for each series of test samples were within control limits (Fig. 5). Control limits were exceeded for duplicate analysis on the OV17-OV210 column (Fig. 6). Minimum detection limits were established for chlorothalonil residues on gloves with the SE30-OV210 column at 18.2 ng/cm^2.

Determination of control limits for detection of chlorothalonil in hand wash towels was initiated at 0.56 ng/cm^2 (Table 3). A mean concentration of 0.60 $\pm$ 0.20 ng/cm^2 was recovered in the check samples with a recovery of 107.2 percent of expected (0.56 ng/cm^2). Recovery of chlorothalonil was quite variable (C.V. = 33.9%), however, necessitating reexamination of control limits

at higher fortification levels.

Check samples fortified with 11.2 ng/cm^2 were less variable (C.V. = 20.6%), although recovery was 81.1 percent of the expected. The mean recovery was 9.11 $\pm$ 1.88 ng/cm^2. Control limits were set with this series of check samples. Check samples within each sequence of test samples were found to be within control limits (Fig. 7). The mean recovery of chlorothalonil in hand wash towels was 10.6 $\pm$ 1.4 ng/cm^2 or 94.4 percent of the expected (11.2 ng/cm^2). Check samples within the sequences were less variable (C.V. = 13.0%) than the control check samples (C.V. = 20.6%).

Quality control samples for gauze patches worn on the shirt sleeves and trouser legs of harvesters were analyzed on two dates, shortly after sample collection on 1 December 1983, and much later with stored samples on 22 October 1985. A control series of check samples was not prepared prior to the analysis of samples tested on 1 December 1983. Recovery of a single check sample fortified with 96.9 ng/cm^2 was 96.0 ng/cm^2 or 99.1 percent. Additional check samples (n = 3) fortified with 48.4 ng/cm^2 yielded 55.5 $\pm$ 9.1 ng/cm^2, a recovery of 114.7 percent. The samples appeared to be within the control limits (C.V. = 16.5%) established for hand wash towels.

Recovery of chlorothalonil in gauze patches analyzed on 22 October 1985 was a good deal less (70.0%) than the 1 December 1983 analyses. A control series of check samples (n = 3) fortified with 96.9 ng/cm^2 yielded a mean recovery of 67.8 $\pm$ 6.5 ng/cm^2. Although some degree of accuracy may have been lost between dates of analysis as indicated by the different rates of recovery, a measure of precision was gained in the later analysis of the control series as indicated by the improvement in the coefficient of variation

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(9.63%). The check sample prepared with the test sample sequence was reflective of that level of precision (Fig. 8).

RESULTS

The transfer of residues of chlorothalonil to farm workers harvesting tomatoes was estimated from the concentration of chlorothalonil accumulated in sampling devices worn by the workers over the study periods in fields one and two. Comparisons between fields were not made because of differences in the individuals and their work habits between cohorts. Because of the lack of environmental data, e.g., residue concentrations on leaves and fruit, an effort was made to test the differences between the concentration of chlorothalonil in paired samples trapped in the sampling devices worn by the workers. Although direct inferences about transfer from environmental substrates to the workers could not be made, between sample differences in accumulation of chlorothalonil may provide an indication of anatomical areas of comparative contact with residues during harvest. Areas of contact, as reflected by the accumulation of chlorothalonil on the sampling devices, may vary between youths ($\leq$ 17 years) engaged in the harvest of tomatoes and their adult counterparts (> 17 years). A special effort was made to identify physical features which might be responsible for differences in contact with residues between youths and adults.

Of the 25 individuals engaged in the harvest of tomatoes in field one, three of the farmworkers were youths, 17 years and younger (Table 4). The average age of the cohort was 29.7 $\pm$ 9.9 years, the median age 28 years. Six members of the cohort were females. The three youths were males. The average height and weight of the youths was 64.7 $\pm$ 3.5 inches and 121 $\pm$ 13 pounds.

The average height of the entire cohort plus the youths was 65.7 ± 4.2 inches with a median height of 65 inches. The average weight was 151 ± 26 pounds. 763 The median weight was 147 pounds.

The three youths, worker numbers 5, 6, and 7, were grouped with five adults to measure the accumulation of chlorothalonil residues on gauze patches worn on the shirt sleeves and trouser legs of the harvesters (Table 5). The concentrations of chlorothalonil detected in arm patches (1.30 ± 0.80 ng/cm^2) were found to be not significantly different (t = -2.102, 7 d.f., P < 0.05) from the concentration found in leg patches (2.41 ± 0.84 ng/cm^2) according to the t-test on paired observations (Snedecor and Cochran, 1976). Contact with residues of chlorothalonil during harvest did not appear to differ between anatomical areas. In agreement with that observation, residue concentrations detected in arm patches worn by youths were not significantly different (t = 14, n = 3, P < 0.20) from adults. A similar result was obtained for leg patches (t = 13, n = 3, P < 0.20). The Mann-Whitney test for independent samples was used because of the size (n = 3, m = 5, N = 8) of the unbalanced data sets (Conover, 1980).

Youths appeared to come into contact with residues of chlorothalonil at the same level as adults, as indicated by the arm and leg patch data. Unfortunately, such a comparison could not be made with respect to the accumulation of residues on gloves and handwash towels; only adults were included in this cohort (Table 6). Comparisons were made, however, among sampling devices. A paired t-test of concentrations detected in right hand gloves and hand wash towels (Table 6) revealed a significantly greater (t = 3.706, d.f. = 12, P < 0.005) level of residues in gloves. The gloves appeared to trap the residues and not allow penetration to the hands. Any further interpretation of the protective quality of the gloves could not be made,

however, because of the lack of a companion cohort of ungloved individuals.

Hand contact, as indicated by the mean concentration of chlorothalonil detected in gloves (3.36 ± 3.11 ug/cm^2), was not significantly different from perceived contact with arm patches (t = 1.813, d.f. = 18, P < 0.10) and leg patches (t = 0.835, d.f. = 18, P < 0.50).

Results from the second field, studied on 4 June 1982, were not inconsistent with the first. The sample group was larger, composed of 24 males and 16 females ages 10 to 70 years (Table 7). The average age of the males was 30.9 ± 17.9 years, the females 35.3 ± 18.2 years. The median age of the entire cohort was 31 years, the average 32.9 ± 18.3 years. The study group was represented by 13 youths (≤ 17 years) and 26 adults (> 17 years). The age of one female subject was not recorded. The median height of the youths was 63 inches with the average height of 59.1 ± 8.4 inches. The average weight of the youths was 111.1 ± 32.3 pounds. The median weight was 110 pounds. These physical factors may be compared to those for the adults. The median and average height of the adult farmworkers were 64 inches and 61.2 ± 11.9 inches respectively. The median weight was 158 pounds and the average weight 164 ± 30 pounds.

A subset of workers composed of 5 youths and 7 adults was selected to examine the accumulation of chlorothalonil residues on arm and leg patches (Table 8). Unlike the results obtained for the previous field, the concentrations of chlorothalonil detected in leg patches were found to be significantly greater (t = 3.526, d.f. = 12, P < 0.005) than the concentrations detected in arm patches. The concentrations in leg patches worn by the youths were found to be not significantly different (t = 26, n = 5, m = 7, P < 0.20) from the adults according to the Mann-Whitney test for

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independent samples. A similar result was obtai

n = 5, m = 7, P < 0.20).

Hand contact with residues was examined with a second subset of
harvesters (Table 9). The accumulation of residues in gloves was compared to
the concentration of chlorothalonil found in hand wash towels. The
concentrations in gloves were found to be significantly greater (t = 3.679,
d.f. = 15, P < 0.005) than the concentrations detected in hand wash towels.
As observed in the previous study of field one, gloves appeared to accumulate
the residues with significantly lower concentrations reaching the hands. The
concentrations detected in gloves were not significantly different (t = 23, n
= 5, m = 9, P < 0.05) between youths and adults. A similar result was
obtained for hand wash towels (t = 29.5, n = 5, m = 9, P < 0.20). The age of
one female worker was not recorded and, as a result, residue values were not
included in the analysis. Unlike the results obtained in the study of field
one, hand contact with residues of chlorothalonil were significantly greater
than contact on forearms (t = 3.510, d.f. = 25, P < 0.005) and the lower legs
(t = 3.159, d.f. = 2.5, P < 0.005).

INTERPRETATION AND ANALYSIS

Farmworker contact with chlorothalonil residues while harvesting tomatoes appeared to be greater through the hands than coincident contact on the forearms or lower legs. Youths ($\leq$ 17 years) and adults appeared to contact residues at similar levels. As a result, an examination of physical factors which might be used to separate youths from adults, e.g., height and weight, was rendered academic.

Contact with residues might, however, be expected to increase with an increase in the size or performance of the harvester. Performance may be dependent on experience and health. In order to examine relationships between size and performance, rank correlations (Conover, 1980) were performed on paired values of height and weight against residue concentrations detected in arm and leg patches. Correlations based on ranks were performed because of the narrow spread and uncertainty about the distribution of the independent variables, height and weight.

Height and residue concentrations detected in arm patches from field one (Table 10) were found to be mutually independent (tau = 0.2381, n = 7, $P < 0.452$). The absence of trend was also observed for correlations on weight and residues in arm patches (tau = -0.1071, n = 8, $P < 0.356$), height and residues in leg patches (tau = -0.2381, n = 7, $P < 0.454$) and weight and residues in leg patches (tau = -0.0714, n = 8, $P < 0.403$). The lack of correlation between the physical parameters, height and weight, and residues in arm patches and leg patches in the first field was observed again for the

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second field (Table 11). The lack of correlation suggests the presence of unknown factors which might contribute to the prediction of causality. Further predictions of causality by multi-regression or factor analysis were deferred for more carefully controlled studies.

The accumulation of chlorothalonil residues in gloves was examined in relation to the performance of the harvesters as expressed in the amount of tomatoes harvested (Tables 10 and 11). Greater hand contact with the vegetables and foliage was expected to increase the concentrations of residues in the gloves worn by the harvesters. Correlations on ranks on the amount harvested and residue levels detected in gloves for fields one (tau = -0.4762, n = 7, P < 0.134) and two (tau = -0.0727, n = 11, P < 0.378) were found however to be disconcordant and independent. Hand contact with residues did not appear to be dependent on performance.

DISCUSSION AND CONCLUSIONS

Youths employed in the harvest of tomatoes were found to contact similar concentration levels of the fungicide chlorothalonil as adult harvesters. Although meaningful extrapolations about total body exposure could not be made, the youths in field one accumulated 69.6 ± 23.7 ng/Kg based on the summation of the concentrations detected in arm and leg patches. The ranked values, normalized to the individual weights (ng/Kg), were not significantly different from the adults ($t = 17$, $n = 3$, $m = 5$, $P < 0.20$). A similar result $t = 33$, $n = 5$, $m = 7$, $P < 0.20$) was observed for normalized values for youths and adults from field two. The youths accumulated 38.54 ± 24.7 ng/Kg during harvest in the second field.

As pooled samples, farmworkers from field one contacted 16.2 ± 5.1 ng/Kg hr^{-1} on arm patches and leg patches while harvesting tomatoes treated with chlorothalonil 5 days prior to reentry. Farmworkers in field two (treated 9 days prior to reentry) contacted 10.3 ± 5.7 ng/Kg hr^{-1} after a similar exposure period of 3.5 hours. The mean concentration for field one was found to be significantly greater ($t = 2.3489$, d.f. $= 18$, $P < 0.01$) than the mean concentration for field two. The relevance of such a comparison is questionable; environmental data, useful for a more direct comparison of decline in residues between fields, was not taken. In support of this supposition, significantly greater concentrations were detected in gloves taken from field two ($t = 2.3483$, d.f. $= 25$, $P < 0.025$) compared to field one. Clearly the conflict between greater residue levels in patches (between

fields one and two) and that observed in gloves (between fields) reflects on farmworker activities rather than differences in residue levels between reentry intervals for the fields.

The health implications of such exposure to chlorothalonil in both youths and adults is unclear. Chlorothalonil has been observed to cause dermatitis in the occupationally exposed (Hallenbeck and Cunningham-Burns, 1985 and Horiuchi et al., 1980). The mechanism of action may be related to the action of chlorothalonil on thiol enzymes (Pimentel, 1981) and the structural similarity of chlorothalonil to hexachlorobenzene and this compound's porphyrigenic activity (Hayes, 1982). Repeated exposure might influence iron distribution and the appearance of porphyria. Chronic exposure to chlorothalonil may be identified with the appearance of urinary coproporphyrin.

Future studies may be designed to investigate the subacute and chronic effects of chlorothalonil on agricultural workers. Environmental samples should be taken throughout the study period, from time of application to the completion of the harvest. Dermal exposure may be estimated from the accumulation of residues on sampling devices worn by the workers. Absorption of chlorothalonil may be examined in biliary excretions (Chin et al., 1980 and Chin et al., 1981) and compared to the appearance of porphyrins in urine after exposure.
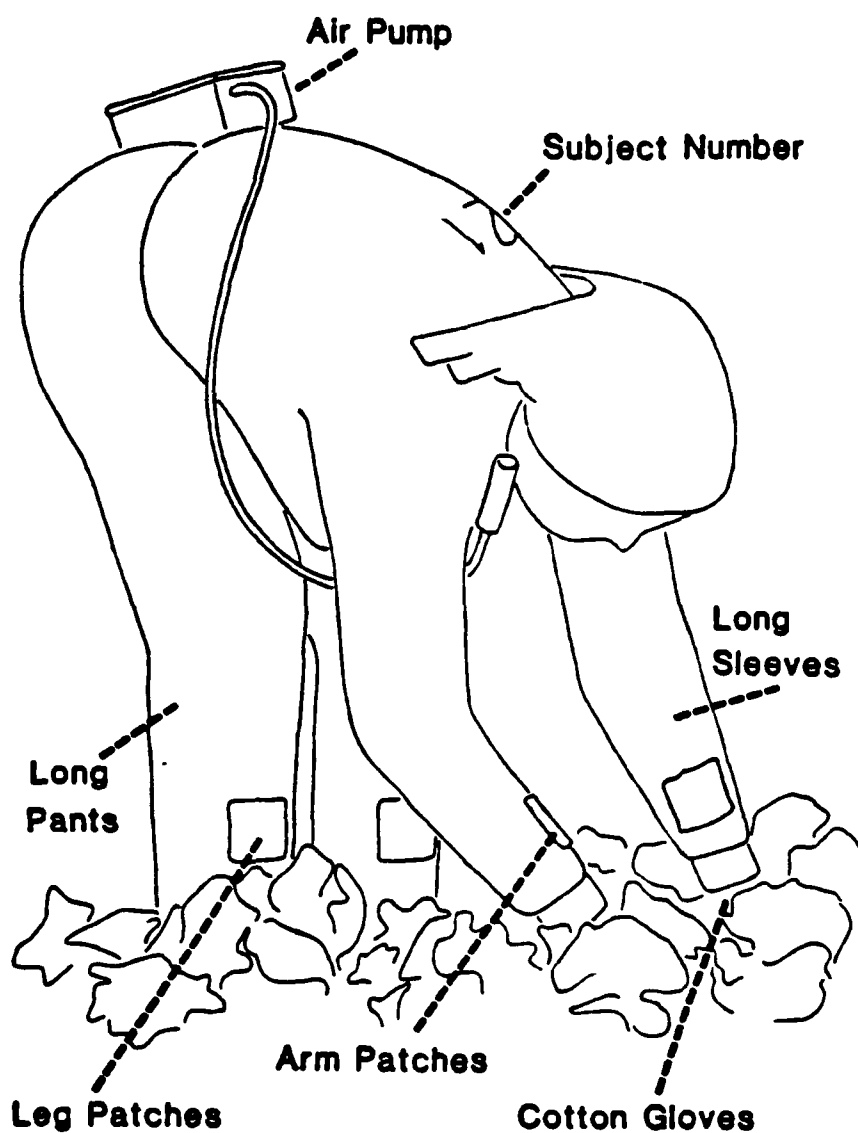
Fig. 1. Positions of sampling devices (body patches and gloves) worn by workers harvesting tomatoes treated with a formulation (Bravo$^{(R)}$ 500) of chlorothalonil.
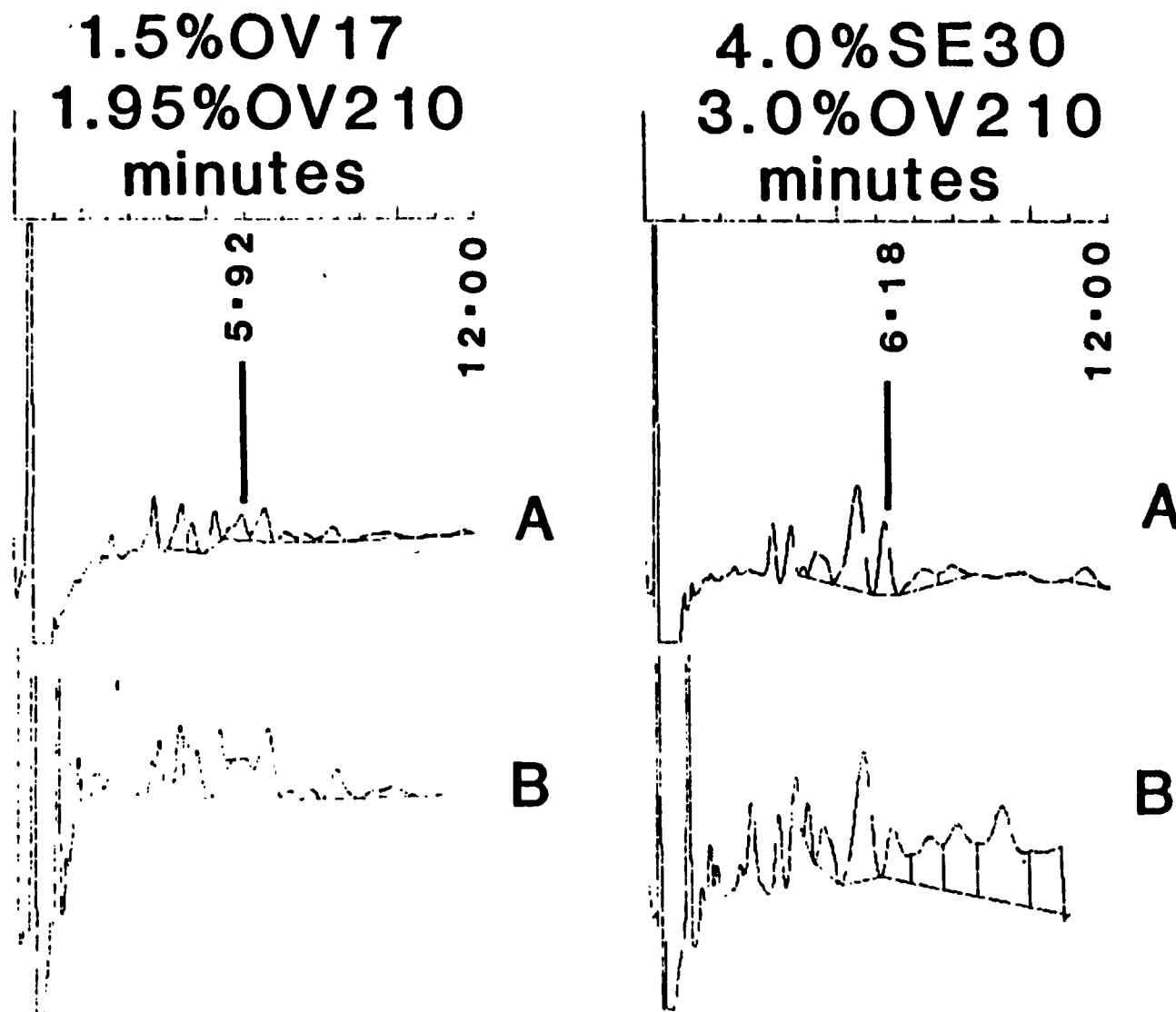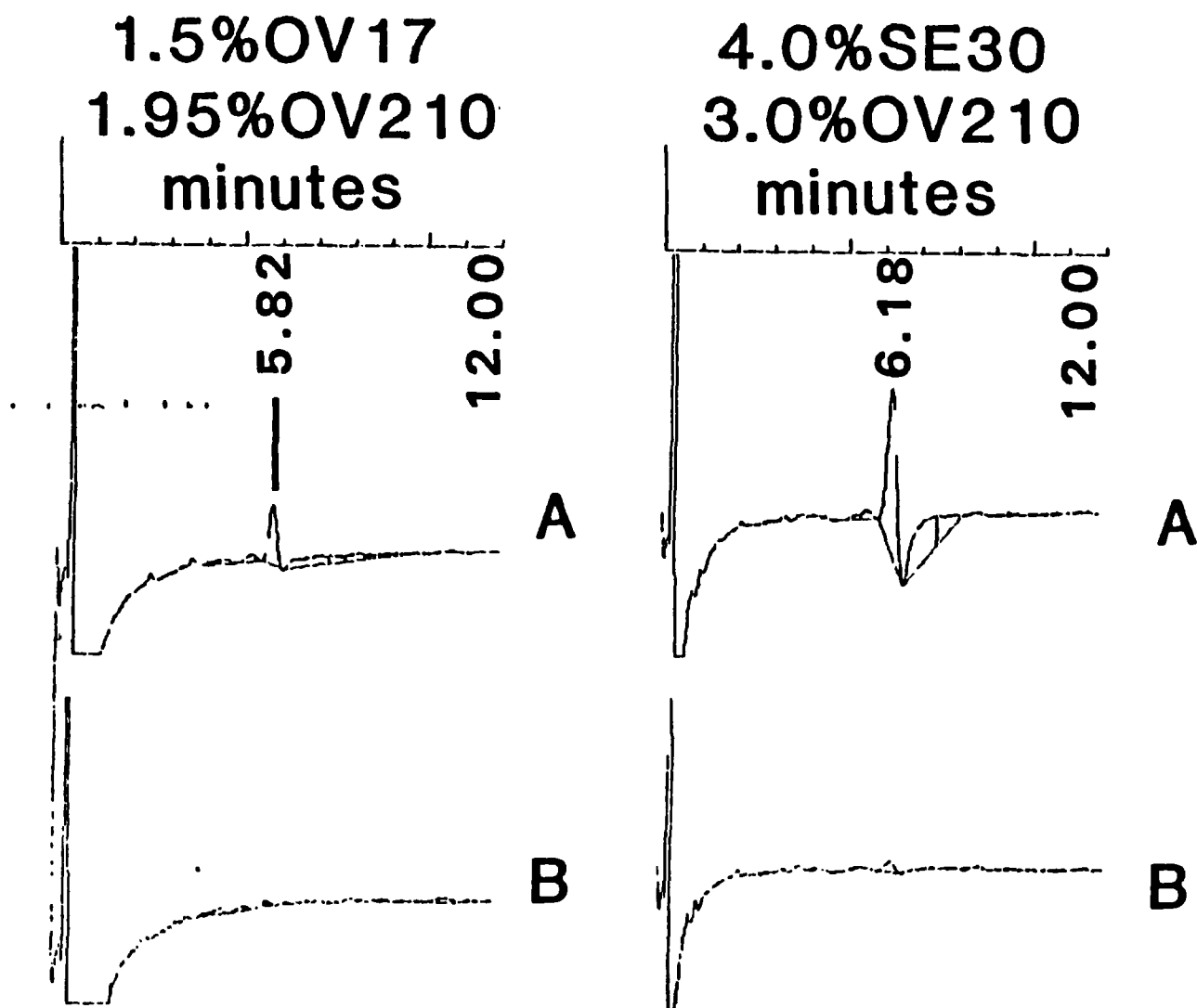
Fig. 2. Chromatographic display of the detection of chlorothalonil in fortified (0.27 ng/cm^2) check samples (A) and blanks (B) of glove extracts by two column confirmation (1.5% OV17/1.95% OV210 and 4.0% SE30/3.0% OV210) with electron capture {^{3}H} (Carrier gas (N$_2$) flow rate 57 cc/min at 200°C isocratic). Peak retention time is indicated for chlorothalonil.

1.5%OV17
1.95%OV210
minutes

4.0%SE30
3.0%OV210
minutes

6.05

12.00

6.22

12.00
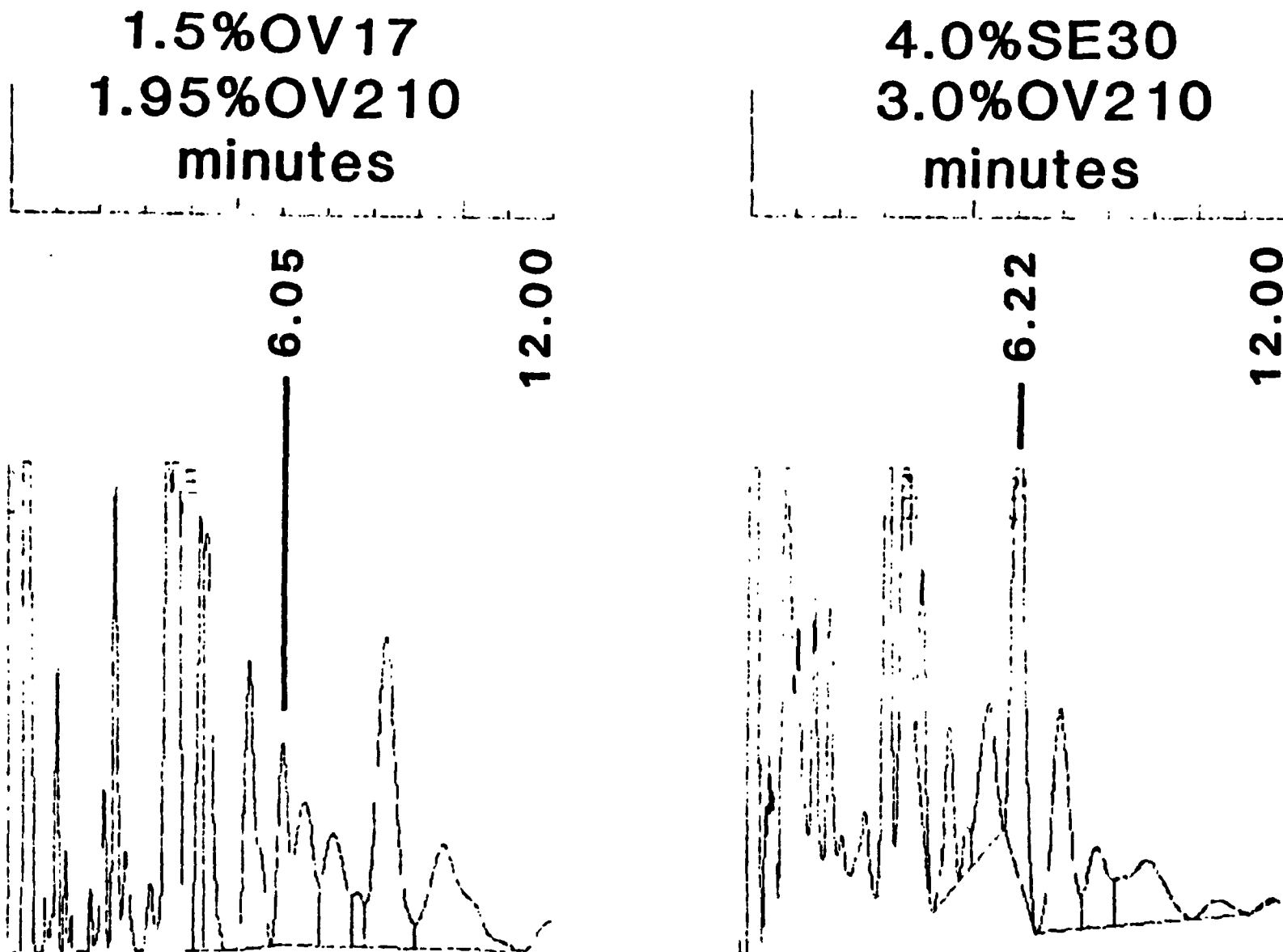
Fig. 3. Chromatographic display of the detection of chlorothalonil in fortified (0.91 ng/cm^2) check samples of glove extracts by two column confirmation (1.5% OV17/1.95% OV210 and 4.0% SE30/3.0% OV210) with electron capture [^{3}H] (Carrier gas (N$_2$) flow rate 57 cc/min at 200°C isocratic). Peak retention time is indicated for chlorothalonil.

1.5%OV17
1.95%OV210
minutes

4.0%SE30
3.0%OV210
minutes

Fig. 4. Chromatographic display of the detection of chlorothalonil
in fortified (18.2 ng/cm^2) check samples (A) and blanks (B) of glove
extracts by two column confirmation (1.5% OV17/1.95% OV210 and
4.0% SE30/3.0% OV210) with electron capture {^{3}H} (Carrier gas (N$_2$)
flow rate 57 cc/min at 200°C isocratic). Peak retention time is
indicated for chlorothalonil.
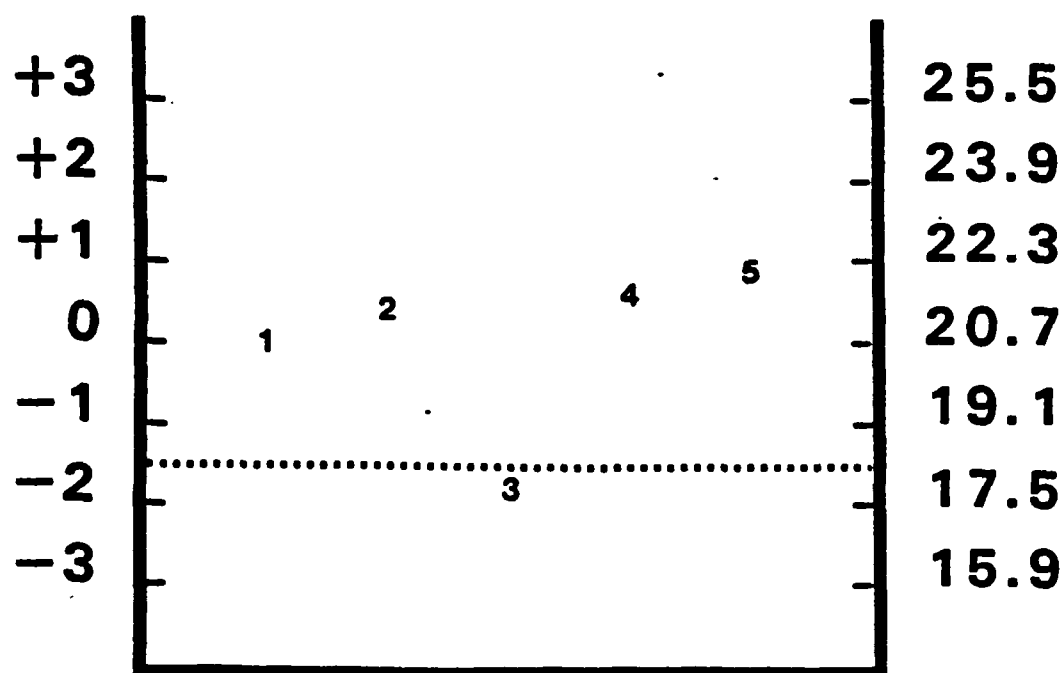
Fig. 5. Column SE30-OV210. Normal probability plot of glove samples ($\bar{x}$ = 20.7 ± 1.6 ng/cm^2) fortified with 18.2 ng/cm^2 chlorothalonil. Numbers represent individual samples. Dashed line represents expected recovery of fortified concentrations (18.2 ng/cm^2).
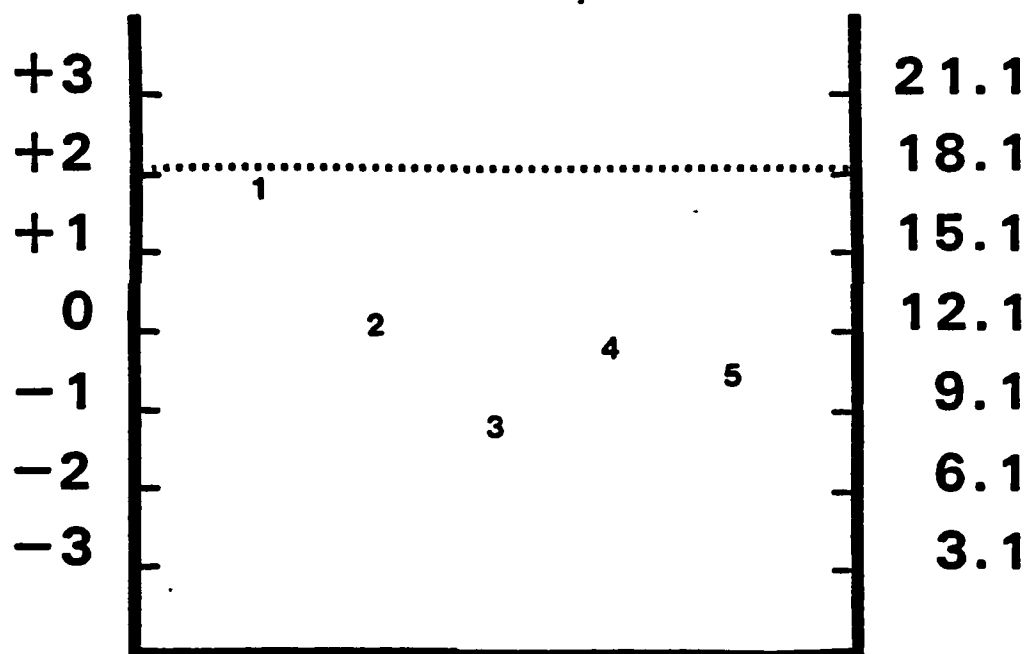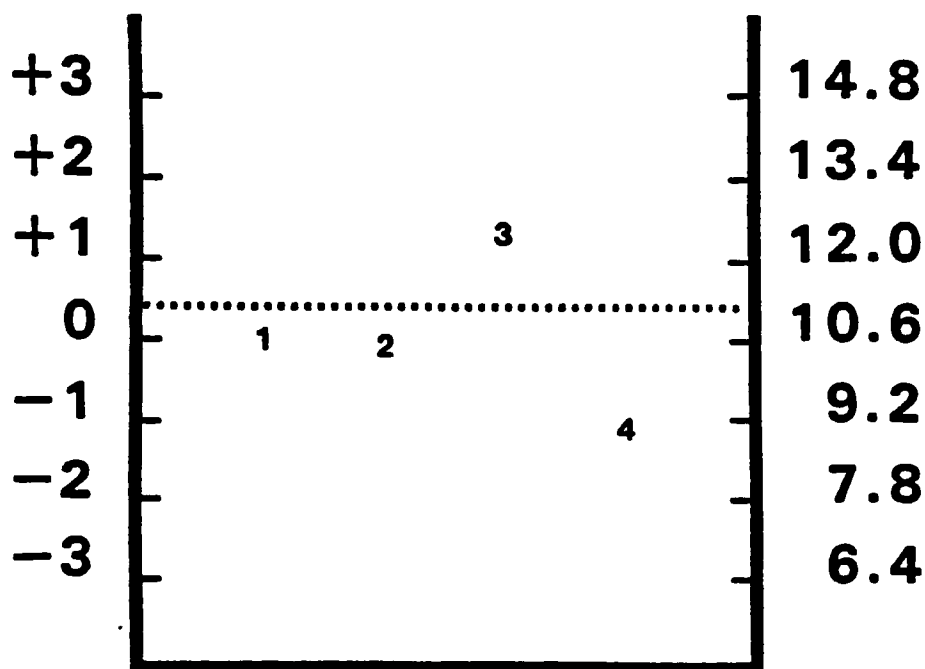
Fig. 6. Column OV17-OV210. Normal probability plot of glove samples ($\bar{x}$ = 12.1 ± 3.0 ng/cm²) fortified with 18.2 ng/cm² chlorothalonil. Numbers represent individual samples. Dashed line represents expected recovery of fortified concentrations (18.2 ng/cm²).

Fig. 7. Normal probability plot of hand wash towel samples ($\bar{x}$ = 10.6 + 1.4 ng/cm^2) fortified with 11.2 ng/cm^2 chlorothalonil. Numbers represent individual samples. Dashed line represents expected recovery of fortified concentrations (11.2 ng/cm^2).
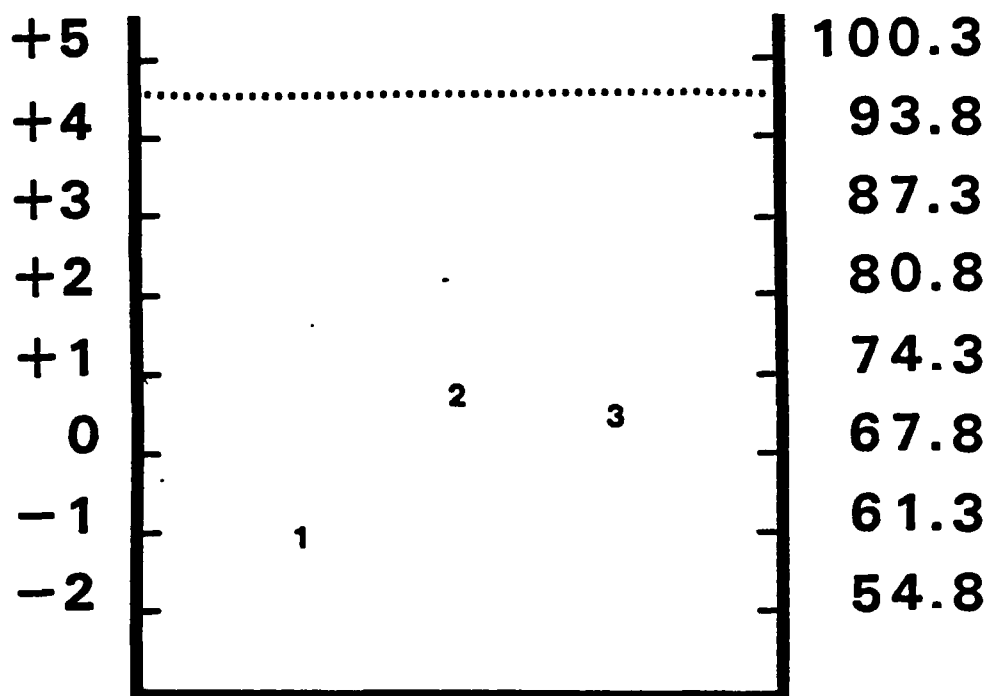
Fig. 8. Normal probability plot of patch samples
($\bar{x}$ = 67.8 $\pm$ 6.5 ng/cm^2) fortified with 96.9 ng/cm^2
chlorothalonil. Numbers represent individual samples.
Dashed line represents expected recovery of fortified
concentrations (96.9 ng/cm^2).

Table 1. Detection of chlorothalonil by two column confirmation analysis in glove check samples fortified with 0.27 ng/cm^2.

Sample	Chlorothalonil (ng/cm^2)[a]	
	4% SE30/3% OV210	1.5% OV17/1.95% OV210
Q. C. #1	0.50 (0.58)	0.66 (-)
Q. C. #2	4.33 (0.02)	6.14 (5.64)
Q. C. #3	0.01 (0.18)	0.27 (0.09)
Q. C. #4	2.91 (4.65)	3.90 (6.05)
Q. C. #5	2.71 (4.02)	3.49 (5.46)

[a] Values enclosed are from blanks prepared with each check sample.

Table 2. Detection of chlorothalonil by two column confirmation analysis in glove check samples fortified with 18.2 ng/cm^2.

Sample	Chlorothalonil (ng/cm^2)	
	4% SE30/3% OV210	1.5% OV17/1.95% OV210
Q. C. #1	19.1	14.9
Q. C. #2	18.9	13.6
Q. C. #3	21.6	14.6
Q.C. mean + S.D.	19.9 + 1.5	14.4 + 0.7
C.V.	0.0757	0.0474
Percent recovery	109.3 %	79.1 %

Table 3. Detection of chlorothalonil in hand wash towel check samples fortified with 0.56 ng/cm^2 on a 4% SE30/3% OV210 column.

Sample	Chlorothalonil (ng/cm^2)
Q. C. #1	0.72
Q. C. #2	0.37
Q. C. #3	0.72

Q.C. mean + S.D.	0.60 + 0.20
C.V.	0.339
Percent recovery	107.2 %

Table 4. Physical characteristics of human subjects involved in the harvest of tomatoes in field one (17 May 1982) treated with chlorothalonil. Performance of the harvesters is indicated by amount harvested (buckets).

| Worker Number | Physical Characteristics | | | | Amount Harvested |
	Sex	Age	Height (in)	Weight (lb)	
1	F	25	57	146	-
2	F	39	62	126	-
3	F	34	67	181	-
4	F	42	62	136	-
5	M	15	61	109	-
6	M	15	65	119	31
7	M	16	68	135	39
8	M	34	65	169	-
9	M	24	70	140	40
10	M	29	64	146	-
11	M	35	65	169	-
12	M	21	63	122	49
13	M	25	65	146	65
14	M	52	68	166	47
15	M	44	70	202	-
16	M	25	69	191	-
17	M	42	66	156	-
18	M	32	71	160	29
19	F	25	63	111	40
20	M	29	-	183	36

Worker Number	Physical Characteristics				Amount Harvested
	Sex	Age	Height (in)	Weight (lb)	
21	M	27	75	160	29
22	M	20	-	149	39
23	M	21	70	187	50
24	F	43	58	119	-
25	M	28	67	147	-

Table 5. Chlorothalonil residue concentrations on patches worn by human subjects while harvesting tomatoes in field one (17 May 1982).

Worker Number	Physical Characteristics				Chlorothalonil (ug/cm^2)a/		Amount Harvested
	Sex	Age	Height (in)	Weight (lb)	Arm Patch	Leg Patch	
5	M	15	61	109	1.90	2.84	-
6	M	15	65	119	0.83	2.75	31
7	M	16	68	135	1.06	1.85	39
8	M	34	65	169	0.57	2.10	-
14	M	52	68	166	3.00	0.74	47
16	M	25	69	191	1.14	3.18	-
17	M	42	66	156	0.69	3.33	-
22	M	20	-	149	1.21	2.47	39

a/ Patches for Worker Numbers 5-8 were analyzed on 6 December 1983.
 Patches for Worker Numbers 14-22 were analyzed on 22 October 1985.

Table 6. Chlorothalonil residue concentrations found on gloves and hand wash towels from human subjects harvesting tomatoes in field one (17 May 1982).

Worker Number	Physical Characteristics				Chlorothalonil (ug/cm^2)[a]		Amount Harvested
	Sex	Age	Height (in)	Weight (lb)	Right Glove	Hand Wash Towel	
4	F	42	62	136	0.92	0.01	-
9	M	24	70	140	1.66	0.03	40
13	M	25	65	146	2.02	0.09	65
15	M	44	70	202	1.54	0.02	-
17	M	42	66	156	4.60	0.02	-
18	M	32	71	160	4.52	0.01	29
19	F	25	63	111	2.43	0.02	40
20	M	29	-	183	11.69	0.02	36
21	M	27	75	160	6.27	0.04	29
23	M	21	70	187	0.65	0.02	50
24	F	43	58	119	1.71	0.00	-
25	M	28	67	147	2.28	0.01	-

[a] Gloves and hand wash towels were analyzed on 11-17 October 1985.

Table 7. Physical characteristics of human subjects involved in the harvest of tomatoes in field two (4 June 1982) treated with chlorothalonil.

Worker Number	Physical Characteristics				Amount Harvested
	Sex	Age	Height (in)	Weight (lb)	
1	M	17	68	154	-
2	M	13	58	85	-
3	M	12	57	80	15
4	M	10	48	82	-
5	M	19	68	140	21
6	M	19	68	151	53
7	M	19	65	139	60
8	F	49	60	159	-
9	M	17	63	128	20
10	M	17	68	125	-
11	M	15	65	131	38
12	M	17	68	139	39
13	F	12	48	71	10
14	F	16	65	110	-
15	F	15	65	171	3
16	F	10	48	80	13
17	F	16	48	90	16
18	F	-	-	160	40
19	F	58	60	143	19
20	F	52	65	153	16

Worker Number	Physical Characteristics				Amount Harvested
	Sex	Age	Height (in)	Weight (lb)	
21	F	40	61	210	20
22	F	60	62	170	-
23	F	50	58	129	-
24	F	41	60	165	33
25	F	52	62	195	23
26	F	23	61	157	23
27	F	36	61	125	30
28	M	33	59	150	-
29	M	22	61	264	20
30	M	29	64	136	28
31	M	56	68	205	29
32	M	60	66	150	39
33	M	58	63	175	33
34	M	31	-	173	56
35	M	34	64	185	46
36	M	48	65	170	46
37	M	56	66	150	-
38	M	32	67	165	30
39	M	38	66	136	-
40	M	70	65	175	20

Table 8. Chlorothalonil residue concentrations on patches worn by human
subjects while harvesting tomatoes in second field (4 June 1982).

| Worker Number | Physical Characteristics | | | | Chlorothalonil (ug/cm^2)[a] | | Amount Harvested |
	Sex	Age	Height (in)	Weight (lb)	Arm Patch	Leg Patch	
2	M	13	58	85	0.56	1.06	-
3	M	12	57	80	1.15	1.73	15
10	M	17	68	125	0.41	1.22	-
14	F	16	65	110	0.25	0.95	-
15	F	15	65	171	0.09	1.36	3
19	F	58	60	143	1.29	2.21	19
21	F	40	61	210	0.92	1.94	20
32	M	60	66	150	0.67	3.23	39
35	M	34	64	185	0.65	0.76	46
36	M	48	65	170	0.51	1.54	46
38	M	32	67	165	0.56	0.22	30
39	M	38	66	136	0.24	2.51	-

a/ Patches were analyzed on 19-21 September 1983.

Table 9. Chlorothalonil residue concentrations found on gloves and hand wash towels used as sampling devices by human subjects while harvesting tomatoes in second field (4 June 1982).

Worker Number	Physical Characteristics				Chlorothalonil (ug/cm^2)[a]		Amount Harvested
	Sex	Age	Height (in)	Weight (lb)	Right Glove	Hand Wash Towel	
1	M	17	68	154	0.14	4.96	-
4	M	10	48	82	0.12	0.26	-
7	M	19	65	139	1.57	2.64	60
11	M	15	65	131	15.60	0.00	38
12	M	17	68	139	0.12	0.04	39
16	F	10	48	80	7.71	0.02	13
18	F	-	-	160	10.42	2.83	40
23	F	50	58	129	10.50	1.32	-
24	F	41	60	165	0.82	0.23	33
25	F	52	62	195	18.14	1.08	23
26	F	23	61	157	11.38	0.04	23
28	M	33	59	150	13.53	0.52	-
30	M	29	64	136	27.58	0.01	28
33	M	58	63	175	9.04	1.68	33
34	M	31	-	173	28.63	2.73	56

a/ Gloves and hand wash towels were analyzed on 18-28 October 1985.

Table 10. Rank correlations (Kendalls-Tau) of paired values of the physical characteristics of the farmworkers and the amount of tomatoes harvested (buckets) against the concentrations of chlorothalonil detected in sampling devices (gloves, arm patches and leg patches) worn by harvesters working in field one.

==

Physical Characteristic	Correlation coefficients (P under $H_o = 0$) chlorothalonil concentration (ug/cm^2) Sampling device		
	Gloves	Arm Patches	Leg Patches
Height	-	0.2381 (P < 0.45)	-0.2381 (P < 0.45)
Weight	-	-0.1071 (P < 0.36)	-0.0714 (P < 0.40)
Amount Harvested	-0.4762 (P < 0.13)	-	-

Table 11. Rank correlations (Kendalls-Tau) of paired values of the physical characteristics of the farmworkers and the amount of tomatoes harvested (buckets) against the concentrations of chlorothalonil detected in sampling devices (gloves, arm patches and leg patches) worn by harvesters working in field two.

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Physical Characteristic	Correlation coefficients (P under $H_{o_2} = 0$) chlorothalonil concentration (ug/cm^2) Sampling device.		
	Gloves	Arm Patches	Leg Patches
Height	-	-0.4091 (P < 0.07)	-0.0606 (P < 0.39)
Weight	-	-0.0151 (P < 0.47)	0.0151 (P < 0.53)
Amount Harvested	-0.0727 (P < 0.38)	-	-

ACKNOWLEDGEMENTS

LITERATURE CITED

Anonymous. 1979a. Investigation of pesticide residues in soil. Annu. Rep. Hiroshima Pref. Agric. Exp. Stn. 1978:24.

Anonymous. 1979b. Investigation of the confirmation of the safety of pesticide residues. Annu. Rep. Hiroshima Pref. Agric. Exp. Stn. 1978:24.

Chin, B. H., R. D. Heilman, R. T. Bachand, G. Chernenko and J. Barrowman. 1980. Absorption and biliary excretion of chlorothalonil and its metabolites in the rat. Toxicol. Lett. 5(Sp 1):150.

Chin, B. H., J. B. McGloin, N. L. Spangler, and R. D. Heilman. 1981. Chlorothalonil equivalents in the blood and urine of rats following oral, endotracheal, and dermal administration of ^{14}C-chlorothalonil. Bull. Environ. Contam. Toxicol. 26(1):258-261.

Conover, W. J. 1980. Practical nonparametric statistics, 2ed. John Wiley & Sons, NY. 493 pp.

Farm Chemicals Handbook. 1985. Chlorothalonil. Meister Publishing Co., OH. 519 pp.

Food and Agriculture Organization. 1979. Chlorothalonil. FAO Plant Prod. 793
Prot. Paper 15 (Suppl):79-83.

Hallenbeck, W. H. and K. M. Cunningham-Burns. 1985. Pesticides and Human
Health. Springer-Verlag, NY. 166 pp.

Hayes, W. J., Jr. 1982. Pesticides Studied in Man. Williams & Wilkins,
Baltimore/London. 672 pp.

Hiramatsu, R. and F. Furutani. 1979. Persistence of sprayed captan and
chlorothalonil on cucumber grown in greenhouse. Effect of fruit growth
on reduction of concentration of pesticide residue. Yamaguchi-ken Nogyo
31:23-28.

Honeycutt, R. C., G. Zweig, N. N. Ragsdale. 1985. Dermal Exposure Related to
Pesticide Use. American Chemical Society, Washington, DC. 529 pp.

Horiuchi, N., S. Ando, and Y. Kambe. 1980. Dermatitis due to pesticides for
agricultural use. Jpn. J. Dermatol. 90(3):277.

Jacobs, J. L. 1981. Soil survey of Hidalgo County, Texas. United States
Dept. of Agriculture, Soil Conservation Service in cooperation with the
Texas Agricultural Experiment Station. 171 pp.

Johnson, J. D. and J. M. Amador. 1975. Texas guide for reducing vegetable
disease losses. Texas Agricultural Extension Service, the Texas A & M
University System. Publ. No. MP-902. 15 pp.

Koseki, M. Y. Shimamura, T. Maki, Y. Tamura, and Y. Naoi. 1980. Residues of
    chlorothalonil, captan, diazinon and guinomethionate in vegetables and
    and fruits. Annu. Rep. Tokyo Metrop. Res. Lab. Public Health 31(1):
    170-173.

Looney, N. E. and W. P. Cochrane. 1981. Relative effectiveness of, and
    residue declination values for, dichloroprop, fenoprop and naphthalene-
    acetic acid to control pre-harvest drop of McIntosh apples. Can. J.
    Plant. Sci. 61(1):87-91.

Merck Index. 1976. Ninth Ed. Merck & Co., Inc., Rahway, NJ. 1313 pp +
    4 Suppl.

Munn, S., T. J. Keefe, E. P. Savage. 1985. A comparative study of pesticide
    exposures in adults and youth migrant field workers. Arch. Environ.
    Hlth. 40(4):215-220.

Nigg, H. N. and J. H. Stamper. 1982. Regional considerations in worker
    reentry. Pages 59-73 in J. R. Plimmer, Ed., Pesticide Residues and
    Exposure. American Chemical Society, Washington, DC. 213 pp.

Parsons, J., R. Roberts, S. Cotner, T. Longbrake, P. Thompson, and W. Peavy.
    1977. Keys to profitable tomato production in South and West Texas.
    Texas Agricultural Extension Service, The Texas A & M University System.
    Publ. No. L-1045. Unnumbered pp.

Pimentel, D., Ed. 1981. CRC Handbook of Pest Management in Agriculture 795

   Vol. III. CRC Press, Inc., FL. 656 pp.

Reinert, J. C. and D. J. Severn. 1985. Dermal exposure to pesticides: the

   Environmental Protection Agency's viewpoint. Pages 357-368 in R. C.

   Honeycutt, G. Zweig, N.N. Ragsdale, Eds., Dermal Exposure Related to

   Pesticide Use. American Chemical Society, Washington, DC. 529 pp.

Snedecor, G. W. and W. G. Cochran. 1976. Statistical Methods.

   6th Edition. The Iowa State University Press, IA, U.S.A. 593 pp.

Soma, K., T. Mukai, T. Homma, M. Maho, K. Masuyama, and H. Arakawa. 1980.

   Investigation of the residue of chlorothalonil in crops and soils. Part

   2. Jpn. J. Public Health 27(10):643.

Spear, R. C. 1982. Farm worker exposure to pesticide residues: reflections

   on differential risk. Pages 67-76 in V. R. Hunt, M. K. Smith, D. Worth,

   Eds., Banbury Report II, Environmental Factors in Human Growth and

   Development, V. R. Hunt, M. K. Smith, D. Worth, Eds., Cold Spring Harbor

   Laboratory.

Texas Department of Agriculture. 1982. 1982 Texas Vegetable Statistics,

   Bulletin 212. 48 pp.

Thomson, W. T. 1985. Agricultural Chemicals Book IV, Fungicides. Thomson

   Publications, CA. 181 pp.

Appendix A

Methods

A1 Extraction of gloves, hand wash towels and patches for chlorothalonil.

A2 Gas chromatographic conditions for detection of chlorothalonil.

1. Cut sample into approximately 1 inch square pieces.

2. Place into 1000 (or 500) ml flasks.

3. Extract three times with methanol: first with 200 mls for 20 minutes, second and third time with 150 mls for 15 minutes using a Burrell wrist-action shaker.

4. Decant through glass wool in funnel into second 1000 ml Erlenmeyer flask. On last extraction be sure and wring sample out thoroughly and rinse glassware well.

5. Dry with Na_2SO_4 to absorb any moisture.

6. Transfer to round bottom flask and evaporate just to dryness.

7. Bring up to approximately 5-10 mls with hexane.

8. Evaporate with nitrogen to 1 ml.

9. Pass samples through columns, using 2 g of deactivated silica and the following fractions:

   Fraction I   100% hexane - use this to elute sample.
   Fraction II   1% benzene-hexane - discard.
   Fraction III 20% benzene-hexane - collect together with Fraction IV
   Fraction IV   60% benzene-hexane.

   Collect III and IV and bring down to desired level and give to chromatographer to be injected.

A1

Column I

Instrument - Tracor 220 gas chromatograph

Column - 4% SE30/3% OV210

Flow rate 72 cc/min., 200° C.

Detector - Electron capture (^{3}H)

Imput attenuation 10^3

Output attenuation 32

Bucking range 6

Detector flow control

O_2 85 ml/min.

H 100 ml/min.

Column 2

Instrument - Tracor 220 gas chromatograph

Column - 1.5% OV17/1.95% OV210

Flow rate 55 cc/min., 200° C.

Detector - Electron capture (^{3}H)

Imput attenuation 10^3

Output attenuation 64

Bucking range 6

Detector flow control

O_2 150 ml/min.

H 150 ml/min.

A2

APPENDIX B

Worker Interviews--17 May 1982

Worker Interviews-- 4 June 1982

An Assessment of Exposure of Cucumber
Harvesters to Methomyl

Research performed by

Texas Tech University
San Benito, TX   78586

February 28, 1986

In behalf of the Texas PHAP the undersigned have reviewed and approved the report draft entitled "An Assessment of Exposure of Cucumber Harvesters to Methomyl."

_____
Quality Assurance Officer

Feb 28 1986
_____
Date

_____
Project Director

2-28-86
_____
Date

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ABSTRACT

Transfer of dislodgable residues of methomyl (methyl N-[(methyl carbamoyl) oxy] trioacetimidate) to sampling devices worn by farm workers was examined to estimate the potential risk of exposure to a liquid formulation of Lannate[R] during the harvest of cucumbers grown in the Lower Rio Grande Valley of Texas on two sampling dates 4 May 1982 and 19 May 1982. The highest accumulation of methomyl residues were found on gloves on both study dates, 4 May 1982 (1.70 ± 0.97 ug/cm^2) and 19 May 1982 (0.88 ± 0.40 ug/cm^2). Residues did not penetrate through the gloves as indicated by the reduced concentrations detected in hand wash towels (0.067 ± 0.038 ug/cm^2). The concentrations of residues on gloves and arm and leg patches were compared with the physical characteristics of the workers which might influence their performance. Residue concentrations detected on the sampling devices were found to be independent of the amount harvested as well as the age, sex, height, and weight of the workers on both study dates.

harvesting cucumbers. Although methomyl is quite unstable and degrades rapidly, build up of methomyl after repeated applications has been observed (Kuhr and Dorough, 1977). The residual-persistence of methomyl may be short under certain environmental conditions (Kuhr and Dorough, 1977) with an expected half life of 1 week. The level of exposure to methomyl may be dependent on the capacity to transfer pesticide residues from leaf or fruit surfaces to a harvester. Cucumbers may represent a low-risk potential because of the low growth habit a property which restricts activities from the breathing zone and exposure to the torso and upper legs and arms. However, hands alone may account for perhaps the largest part of the residues accumulated by workers. The harvesting of cucumbers does require handling of considerable foliage. In addition, the picking of cucumbers in early morning when leaves are covered with dew may facilitate both the transfer and uptake of pesticide residues (Longbrake et al., 1980).

Measurement of residue concentrations transferred from the foliage to workers while harvesting may reflect the residual persistence of methomyl (Lannate[R] L). Lannate[R] L is a water soluble liquid formulation of 24 percent methomyl (DuPont, 1977). At the time of the study, Lannate[R] L was labeled for use on cucumbers (EPA Reg. No. 352-370) although the Texas Agricultural Extension Service (1980) did not recommend any formulation of methomyl for control of insects on cucumbers. The preharvest interval following applications at the rate of 2 to 4 pints per acre is one day while higher application rates require a three day preharvest interval (DuPont, 1977).

The purpose of this study was to examine the transfer of methomyl residues from the foliage to gauze patches located on the arms and legs, and gloves worn by juvenile (age < 17 years) and adult farmworkers.

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INTRODUCTION

Methomyl is a cholinesterase inhibiting insecticide with an oral LD 50s of 17.0 mg/kg for the male rat and 24 for the female rat (DuPont, 1980). The 24 percent liquid formulation has been observed to have an oral LD 50 of 130 in rats (DuPont, 1977) and a dermal LD 50 of 5,880 in rabbits (DuPont, 1980; A.C.G.I.H., 1984). Methomyl does not appear to significantly influence weight gain or growth of male or female rats (Hayes, 1982). Chronic feeding studies involving laying hens did not indicate any peripheral neurotoxic effect (Hayes, 1982). Methomyl does not have a cumulative action (Wagner, 1983). In addition, methomyl does not adversely effect reproduction or lactation (Hayes, 1982) and teratogenic and mutagenic effects have not been observed (Wagner, 1983).

Toxicity of methomyl to man has been observed from accidental poisoning (Ecobichon and Joy, 1982 and Hayes, 1982) with few reported incidents of occupational exposure (Wagner, 1983). Hayes (1982) reported 225 poisonings resulting from the use of dry formulations of methomyl. The continuation of problems associated with inhalation of a powdered formulation have been ruled out following reformulation and marketing of methomyl as a liquid concentrate (Hayes, 1982). Nevertheless, reentry may represent considerable hazard owing to the extreme toxicity of methomyl (Hayes, 1982). The risk of exposure can be reduced considerably by observing the reentry interval.

The potential exposure of migrant workers to methomyl may be estimatec from the detection of residues of methomyl on sampling devices worn by workers

METHODS AND MATERIALS

The chemical name of methomyl is methyl N-[(methylcarbamoyl)oxy] thioacetimidate; the structural formula is depicted below. This substance has a vapor pressure of 5×10^{-5} mm Hg at 25° C (A.C.G.I.H., 1984).

```
                O
                ‖
CH,-C=N -O- C  NH  CH
      |
      S--CH.
```

methyl N-((methylcarbamoyloxy)thioacetimidate
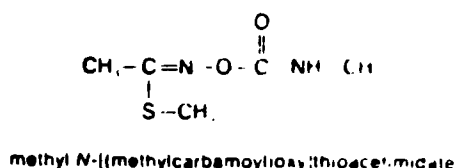
The Structure of Methomyl

Lannate[R] L is a water soluble liquid formulation of 24% methomyl produced by E. I. DuPont De Nemours (Wilmington, Delaware) and bears the EPA registration numbers 352-370-AA. The label restricts the use of this compound to certified applicators with the signal words DANGER - POISON.

Study Site. The study site was managed by a grower that raised a variety of crops, including citrus and several other vegetables. All the vegetables, including the cucumbers, were packed on the farm. An attempt was made to

grower was made only to remain informed of farm practices.

The site was an irrigated, single 20 acre block of cucumbers. The field was irregularly shaped, measuring approximately 799 m on the north side; 1,010 m on the east; 653 m on the south; and 653 m on the west. The topography was essentially flat, with furrows running north-south.

Application. Lannate[R] L was aerially applied at the rate of 2 pints per acre on two dates, 3 May 1982 and 18 May 1982. Both applications occurred before observers could reach the field, thus the exact times could not be established. But, in both instances the application occurred before 1600 hours. Reentry and harvest followed on consecutive dates after each application. There were no previous applications of any pesticides to this crop.

Weather. The weather on the first date of application (3 May 1982) was a morning low of 65° F and an afternoon high of 79° F. Scattered thundershowers were occurring and 0.1 inch of precipitation fell on the site in the morning. On the following day the temperature ranged from 65° F to 84° F. There was no precipitation at the site but scattered thundershowers remained in the area.

The temperatures on the second date of application ranged from 64° F to 85° F. Rainfall amounting to 3.32 inches had occurred overnight. There was no precipitation on the harvest date and tempertures ranged from 67° F to 90° F. Neither wind direction nor velocity were recorded for any of the dates.

Human Subjects. The population studied consisted of a crew of harvesters selected solely by the labor contractor. The workers did not have advanced notice of the study. The cohort on the day following the first application (4 May 1982) consisted of 10 female and 23 males (Tables 1,2). The cohort following the second application (19 May 1982) consisted of 9 females and 27 males (Tables 3,4).

Details of the actual harvest of cucumbers may vary from region to region, and often from grower to grower, but the most common practices in South Texas are those observed in this study. Individual workers are assigned rows of vines to facilitate crediting the vegetables picked to the appropiate worker. A worker may chose to pick one or two or sometimes more rows depending upon their speed. Each harvester is equipped with a 5 gallon plastic pail and a supply of burlap bags. The bags are either tied around the waist or thrown ahead as the harvest proceeds down the row. Mature cucumbers are placed into the plastic pail until it is full. The contents of the pail are then dumped into a burlap sack and the sack is left behind to be later picked by a loading crew with a truck.

Depending upon market conditions, the crop may be harvested three or more times. At first picking vines do not cover the ground. Thus contact with foliage, possibly bearing residues, is confined almost exclusively to the hands. As the season progresses there is more contact between the foliage and the feet, ankles, and forearms. Although the growth habit of the crop is low and would appear to pose minimal risk, the leaves are very large and the vegetable lies on the ground. Thus there is considerable contact with the foliage.

The workers arrived at the field at 0630. After an explanation of the work proposed, the volunteers proceeded through a series of study stations where they: (1) signed consent forms; (2) were briefly interviewed; (3) were weighed; and (4) were equipped with gloves and dermal patches. For easy identification, all participants had numbered tags pinned to their clothing. None of the workers were provided with any clothing or protective devices beyond what they brought to the field.

On the dates of study all the workers had entered the field at 0800.

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While they were harvesting, a somewhat longer interview (15-20 minutes) of each worker was undertaken to obtain their work history as well as their perception of their own health and medical history. During the interview, notes were taken on individual picking practices (Tables 1, 2). On both dates harvest activities were completed by 1145; no harvesters were in the field longer than four hours. On the first harvest date the number of buckets of cucumbers picked by each worker was obtained from the labor contractor for possible correlation with residues detected in the several substrates tested. The contractor declined to provide the same information on the second harvest date.

Gloves and Patches. Harvesters were equipped with sampling devices, gloves and 103.2 cm^2 gauze patches on both arms and legs (Fig. 1). Gauze patches were placed at near equal distances from the ankle on the outside legs and on the inner aspect of the forearms equal distance from the wrist. Light weight twill work gloves of 100 per cent cotton (Sears catalog number 51 K 259151) were worn by workers to measure the amount of contact with residues through the hands. The average surface area of the gloves minus the knit wristlet was 549.7 cm^2.

Following a period of exposure, gloves and patches were collected, sealed in plastic bags, and placed on dry ice. The gloves were cut into 2 to 3 cm^2 pieces (the knit wristlets were not tested) and placed in a 1.0 l Erlenmeyer flask and extracted three times with 350 ml methanol on a Burrell wrist-action shaker at setting 8. The pieces were transferred to a Buchner funnel and washed. The extracts were combined, filtered, and concentrated to 1.0 ml with a Buchi Rotavapor R110. The concentrate was transferred to a 13 ml centrifuge tube and adjusted to 10 ml. The mixture was centrifuged at 1,000 RPM for 1

minute to obtain the final extract and prepared for high performance liquid chromatography (HPLC).

The right and left leg patches (206.4 cm²) were extracted together as were the right and left forearm patches. The patches were extracted three times with 150 ml methanol in a 500 ml Erlenmeyer flask on a Burrell wrist-action shaker on setting 6. The extracts were collected and dried with sodium sulfate and evaporated to 5.0 ml. The concentrate was adjusted to 10.0 ml and prepared for analysis by HPLC.

Hand Washes. Exposure to the hands was estimated from residues collected on hand towels used by the workers after they completed their work. The towels (84 % cotton, 16 % polyester, 890.3 cm², from Leshner, St. Marys, OH) were saturated with a 50:50 ethanol and water mixture then wrung out just prior to use by the workers. Each worker was given a single towel and instructed to thoroughly wipe between the fingers and the fronts and backs of the hands only as high as the wrist. Once the washing was completed, the worker dropped the hand towel directly into a resealable plastic bag held open by a technician. These bags were placed on dry ice for transport to the laboratory, where they were kept frozen until analysis. The procedure for extracting and testing for residues was the same as that described for gloves and patches above.

Other Substrates. No samples of soil, urine, or deposition panels were collected or used in this study. Eight workers had been equipped with personal air samplers on both study dates with the expectation that a suitable method could be developed to extract methomyl from the entrapment medium. This could not be done. Foliage samples were collected on both dates just prior to the workers entering the fields. However all specimens

decomposed before testing could be initiated.

Instrumentation. Measurements of methomyl residues in the extracts from the sampling devices were determined by HPLC according to the method of Cramer et al. (1982). Analysis was performed on a Waters HPLC equipped with two Model 6000A solvent delivery systems and a Model 440 absorbance detector set a 254 nm for the detection of methomyl. The column utilized was a C-18 by Waters Associates. Reverse phase was used with 25 % acetonitrile and 75 % water at a flow rate of 1 ml per minute.

Recoveries. Recovery of 100 ug methomyl in patches was 97.46 ± 2.84 % of expected concentrations. The recoveries were well clustered about the mean (CV = 2.92 %). Methomyl recovered from gloves fortified with 1000 ng of the compound averaged 1055 ± 203 (CV = 19.2). The recovery of 200 ug of methomyl fortified to wash towels averaged 54.9 ± 9.4 % and was also somewhat variable (CV = 17.0).

Analytical Standards. The analytical standards used for fortification and comparison were obtained from the U.S. Environmental Protection Agency's Health Effects Research Laboratory at Research Triangle Park, NC, 27711. The standard used was methomyl, code number 4520, with a documented purity of 99+ %. The concentrated standard prepared for fortification purposes was a 1 mg/ml concentration. The working standard was at a 500 ng/ml concentration.

RESULTS AND DISCUSSION

The transfer of dislodgable residues of Lannate$^{(R)}$ L from the foliage to workers harvesting cucumbers was examined by measuring concentrations of methomyl on sampling devices, gauze patches on arms and legs and gloves worn by farmworkers. Concentrations of methomyl on right and left hand gloves were examined to determine if harvesters were demonstrating right or left hand preferences. Residue levels might be expected to be greater in right hand gloves if workers were biased to use the right hand while picking. A paired t-test of the difference between residue concentrations of methomyl detected in right and left hand gloves did not indicate a significant difference (t = 0.6367, d.f. = 17, P > 0.50) between residue levels on the first sampling (Table 5). Similarly, on the second sampling an hour later, no significant difference (t = -0.0684, d.f. = 13, P > 0.50) was observed between residue levels in right and left hand gloves (Table 6). The harvesters did not appear to prefer either hand while harvesting. The gloves were regarded as a single population and pooled to compare differences between residue concentrations at each sampling period.

The differences in methomyl concentrations between sampling periods were compared by worker. The paired test revealed a significant difference (t = 7.9125, d.f. = 21, P < 0.001) in methomyl concentrations between sampling periods. Significantly greater residues of methomyl (1.67 $\pm$ 0.97 ug/cm^2, n = 36) were found in the first sample period. The difference observed in residue

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concentrations in gloves between periods was attributed to loss of methomyl from the foliage; the performance of the workers did not change.

The concentrations of methomyl detected in arm patches for the two sampling periods (Tables 7,8) appeared to reflect the difference observed for gloves. Greater concentrations of methomyl were detected in arm patches from the first sampling period (0.54 $\pm$ 0.35 ug/cm^2, n = 15) compared to the second (0.38 $\pm$ 0.57 ug/cm^2, n = 3). However, the ranks of the unequal samples were found to be not significantly different (T = 22, n = 3, m = 15, P > 0.44) by the Mann-Whitney test for independent samples. This result was challenged by a paired test of samples obtained from workers entering the field on the two sampling periods. The Wilcoxon signed ranks test of matched pairs revealed no significant difference (T = 0.4286, d = 3, P > 0.344) between samples from the two periods. Concentrations of methomyl on arm patches did not appear to reflect loss of residues from foliage between periods. The residue levels on arm patches appeared to represent reduced contact between foliage and arm patches.

Mean residue concentrations in arm patches (0.54 $\pm$ 0.35 ug/cm^2, n = 15) and leg patches (0.40 $\pm$ 0.38 ug/cm^2, n = 12) collected on the first sampling period were found to be significantly different (F = 30.485, d.f. 2,60, P < 0.001) from gloves (1.67 $\pm$ 0.97 ug/cm^2). Duncans multiple range test revealed no significant difference between mean concentrations of methomyl residues in arm (Table 7) and leg patches (Table 9) at the 5.0% level of confidence. Exposure appeared to occur predominately through the hands.

The protective value of the gloves was examined on the second date of application (19 May 1982). As observed in the previous study (4 May 1982), the mean concentration of methomyl detected in right hand gloves (0.86 $\pm$ 0.48 ug/cm^2, n = 22) was not significantly different (t = -0.2442, d.f. = 41, P >

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0.50) from left hand gloves (0.90 $\pm$ 0.43 ug/cm^2, d.f. = 21, P > 0.50). However, the means of the pooled samples for both studies were found to be significantly different (t = 4.7183, d.f. = 77, P < 0.001). The studies were regarded as independent.

Inferences about the protective value of gloves were gained from comparisons of mean residues detected in gloves and concentrations found in hand washes in study 2 (Table 10). Using the surface area of the gloves to produce similar units (ug/cm^2), the pooled mean concentration of methomyl in gloves (0.88 $\pm$ 0.40 ug/cm^2, n = 43) was significantly greater (t = 8.5442, d.f. = 65, P < 0.001) than that recovered in hand washes (0.067 $\pm$ 0.038, n = 24). Gloves appeared to afford protection from accumulating residues of methomyl on the hands. Assigning protective value to the gloves did not appear to be appropriate given the adjustment necessary to normalize units to the size of gloves. Clearly, however, the predominant area of exposure appeared to occur through the hands. As in the first sample, concentrations in the gloves were significantly greater (F = 14.279, d.f. = 2,67, P < 0.001) than in either arm patches (0.24 $\pm$ 0.22 ug/cm^2, n = 14) or leg patches (0.49 $\pm$ 0.41 ug/cm^2, n = 13 (Table 10). However, in contrast to the first sample, the Duncans multiple range test revealed a significant difference (P < 0.05) between mean concentrations in arm and leg patches.

Concentrations of methomyl detected in the sampling devices were examined in relation to worker performance and physical characteristics, such as height and weight, to expose biases which might influence worker exposure. The performance of a worker was believed to be dependent on sex, age, height, and weight. The physical condition of the subjects, relative to habits which might effect health (Tables 1,2,3,4), may attenuate effects of sex, age, height and weight on performance.

Although many of the same workers were involved in harvesting on both dates, the worker groups were considered independent. Ranks of the age of female workers (Table 1) were found to be not significantly different (t = 178.5, n = 10, m = 23, P > 0.369) from males (Table 2) according to the Mann-Whitney test for independent samples. The mean age of female workers was 43.3 ± 12.8 years. The mean age of male workers was 37.0 ± 19.0 years. The lack of an age difference between males and females was attributed to the composition of the work unit as a group of families.

As might be expected the ranks of heights of male workers (Table 2) were significantly different (t = 55, n = 8, m = 22, P < 0.001) from females (Table 1). However, the ranks of weights of males (Table 2) and females (Table 1) were not significantly different (t = 149.5, n = 10, m = 23, P > 0.211). The mean height of males was 1.67 ± 0.12 m while the mean height of females was 1.59 ± 0.07 m. The mean weight of females was 68.4 ± 22.2 Kg. The mean weight of males was 69.3 ± 14.0 Kg.

The performance of the workers in terms of cucumbers picked was compared to the physical factors of age, height, and weight. Correlations on ranks of amount harvested (Tables 1,2) and the physical factors for females were found to be independent by age (Tau = 0.3928, P > 0.10) and height (Tau = -0.0667, P > 0.20). The correlation on weight was found to be more ambiguous (Tau = 0.5357, P > 0.05); weight of female workers appeared to influence performance.

The correlations of amount harvested with the physical factors for males were found to be independent for age (Tau = 0.1324, P > 0.20), height (Tau = 0.3167, P > 0.05), and weight (Tau = 0.3162, P > 0.05). The combined effects of these factors was not examined.

Exposure of harvesters to methomyl residues on cucumber leaves was examined in relation to the physical factors of age, height, and weight.

Contact with cucumber foliage was expected to depend on performance. Rank correlations were performed between residue concentrations detected on gloves, arm patches and leg patches and amount harvested. Residue concentrations on gloves were found to be independent (Tau = 0.1304, P > 0.62, n = 12) of amount harvested. A similar result was obtained between concentrations found in arm patches and amount harvested (Tau = 0.1970, P > 0.50). Concentrations detected in gloves was also found to be independent of amount harvested (Tau = 0.2333, P > 0.20, n = 9). Clearly, the accumulation of residues of methomyl on these sampling devices was not influenced by the ability to harvest.

Relationships sought between the physical factors, age, height and weight, and residue concentrations in the various substrates were found to be independent as well. The correlations between the concentrations of methomyl detected in the sampling devices and the physical factors for the workers involved in the first sampling period on day 1 (Table 11) and day 2 (Table 12) were uniformly independent. These results suggest that accumulation of residues of methomyl on the clothing of farmworkers is independent of physical characteristics of the workers and their ability to harvest cucumbers.
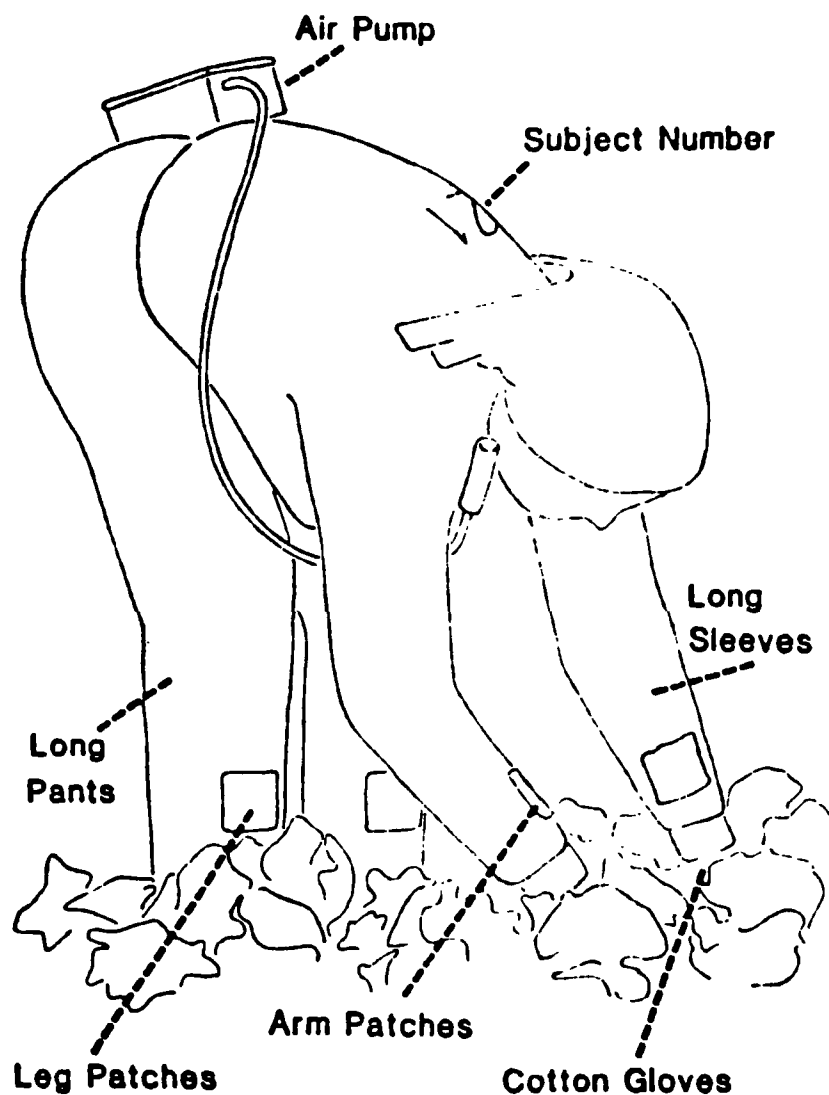
Fig. 1. Positions of sampling devices (air pumps, body patches and gloves) worn by workers harvesting cucumbers treated with a formulation (Lannate$^{(R)}$ L) of methomyl.

Table 1. Physical characteristics and health habits of female workers involved in harvesting cucumbers treated with Lannate$^{(R)}$ L on first day (4 May 1982) after first application.

===

Worker Number	Physical Characteristics [a]			Health Habits			Amount Harvested
	Age	Height(m)	Weight(kg)	Smoker	Alcohol Consumer	Under Medication	
1	36	1.62 (64)	81 (179)	Yes	Yes	No	-
3	30	1.60 (63)	71 (156)	No	No	No	44
5	33	1.55 (61)	58 (128)	Yes	Yes	No	-
7	34	1.68 (66)	51 (113)	No	Yes	No	23
8	30	1.52 (60)	54 (118)	Yes	No	No	30
9	70	-	46 (102)	No	No	No	20
11	54	-	64 (140)	Yes	Yes	No	25
21	48	1.57 (62)	123 (270)	No	No	Yes	30
32	40	1.50 (59)	59 (129)	No	Yes	No	31
33	48	1.68 (66)	77 (169)	No	No	No	33

===

[a] Height in meters and weight in kilograms. Values enclosed are inches and pounds respectively.

Table 2. Physical characteristics and health habits of male workers involved in harvesting cucumbers treated with Lannate[R] L on first day (4 May 1982) after first application.

| Worker Number | Physical Characteristics[a] | | | Health Habits | | | |
	Age	Height(m)	Weight(kg)	Smoker	Alcohol Consumer	Under Medication	Amount Harvested
2	41	1.83 (72)	94 (206)	No	No	Yes	-
4	51	1.70 (67)	82 (180)	No	Yes	No	-
6	18	1.72 (68)	61 (134)	Yes	Yes	No	-
10	64	-	67 (147)	Yes	Yes	No	36
12	39	1.65 (65)	70 (155)	Yes	Yes	No	24
13	25	1.65 (65)	61 (135)	No	No	No	25
14	58	1.65 (65)	70 (155)	Yes	Yes	No	24
16	25	1.70 (67)	64 (140)	Yes	Yes	No	-
17	65	1.60 (63)	69 (152)	No	Yes	No	22
19	57	1.75 (69)	57 (126)	Yes	No	Yes	27

Table 2 (Cont.).

| Worker Number | Physical Characteristics[a] | | | Health Habits | | | Amount Harvested |
	Age	Height(m)	Weight(kg)	Smoker	Alcohol Consumer	Under Medication	
20	43	1.65 (65)	65 (144)	Yes	Yes	No	23
22	15	1.19 (47)	59 (130)	Yes	Yes	No	-
23	52	1.72 (68)	86 (190)	No	Yes	No	22
24	15	1.68 (66)	59 (130)	No	No	No	21
25	35	1.72 (68)	110 (242)	No	No	No	28
26	71	1.62 (64)	75 (165)	No	Yes	No	22
27	62	1.78 (70)	61 (134)	Yes	Yes	No	33
28	47	1.78 (70)	86 (189)	Yes	No	No	30
29	46	1.70 (67)	59 (130)	Yes	Yes	No	42
30	15	1.68 (66)	55 (122)	No	No	No	31
31	14	1.68 (66)	59 (130)	No	No	No	31
34	33	1.65 (65)	54 (120)	Yes	Yes	No	40
35	23	1.68 (66)	71 (156)	Yes	Yes	No	-

==

[a] Height in meters and weight in kilograms. Values enclosed are inches and pounds respectively.

Table 3. Physical characteristics and health habits of female workers involved in harvesting cucumbers treated with Lannate[R] L on second application (19 May 1982).

Worker Number	Physical Characteristics[a]			Health Habits		
	Age	Height(m)	Weight(kg)	Smoker	Alcohol Consumer	Under Medication
10	60	1.52 (60)	50 (111)	No	No	No
11	34	1.70 (67)	60 (132)	No	Yes	No
12	20	1.57 (62)	54 (120)	Yes	Yes	Yes
13	54	1.52 (60)	66 (145)	Yes	Yes	No
14	53	1.52 (60)	95 (210)	No	No	No
15	34	1.60 (63)	48 (106)	Yes	No	No
16	50	-	76 (168)	No	No	No
17	36	1.65 (65)	62 (137)	No	No	No
18	40	1.57 (62)	59 (130)	No	No	No

[a] Height in meters and weight in kilograms. Values enclosed are inches and pounds respectively.

Table 4. Physical characteristics and health habits of male workers involved in harvesting cucumbers treated with Lannate[R] L on second application (19 May 1982).

| Worker Number | Physical Characteristics\a | | | Health Habits | | |
	Age	Height(m)	Weight(kg)	Smoker	Alcohol Consumer	Under Medication
1	39	1.65 (65)	68 (150)	Yes	Yes	No
2	25	1.68 (66)	60 (132)	No	No	Yes
3	27	1.60 (63)	68 (150)	Yes	Yes	No
4	18	1.72 (68)	57 (126)	Yes	Yes	No
5	33	1.65 (65)	54 (120)	Yes	Yes	No
6	51	-	57 (125)	Yes	Yes	No
7	15	-	-	-	-	-
8	15	1.70 (67)	56 (124)	No	No	No
9	14	1.60 (63)	60 (131)	No	No	No
19	54	1.78 (70)	86 (190)	No	No	Yes
20	57	1.75 (69)	59 (129)	Yes	No	Yes
21	36	1.68 (66)	111 (244)	No	No	No
22	27	1.55 (61)	58 (127)	Yes	Yes	No
23	41	1.83 (72)	94 (207)	-	-	-
24	23	1.57 (62)	59 (130)	Yes	Yes	No

Table 4 (Cont.).

Worker Number	Physical Characteristics[a]			Health Habits		
	Age	Height(m)	Weight(kg)	Smoker	Alcohol Consumer	Under Medication
25	22	1.60 (63)	63 (139)	Yes	Yes	No
26	21	1.62 (64)	81 (178)	No	No	Yes
27	20	-	69 (152)	Yes	Yes	No
28	22	1.70 (67)	74 (162)	No	No	No
29	68	-	74 (163)	Yes	Yes	Yes
30	64	1.72 (68)	69 (151)	Yes	Yes	No
31	67	1.72 (68)	70 (153)	No	No	No
32	64	1.65 (65)	71 (157)	No	Yes	No
33	60	1.78 (70)	73 (161)	No	Yes	No
34	46	1.70 (67)	61 (134)	Yes	Yes	No
35	74	1.62 (64)	68 (150)	No	No	No
36	62	1.78 (70)	60 (131)	Yes	Yes	No

===

[a] Height in meters and weight in kilograms. Values enclosed are inches and pounds respectively.

Table 5. Methomyl residue concentrations on gloves worn by human subjects while harvesting cucumbers during the first sampling period after first day of application (4 May 1982). F = Females, M = Males. Values with - are missing.

Worker Number	Sex	Methomyl (ug/cm^2)	
		Left Glove	Right Glove
1	F	2.82	2.39
2	M	0.24	0.27
3	F	0.22	0.27
4	M	1.58	4.56
5	F	3.15	2.77
6	M	3.43	3.57
7	F	0.90	0.73
9	F	1.28	1.46
10	M	1.49	1.50
15	M	1.70	2.49
18	M	1.38	1.51
19	M	1.33	1.35
20	M	1.86	1.94
21	F	1.43	1.47
24	F	1.38	0.72
25	M	1.46	-
28	M	1.10	-
29	M	1.55	1.84
33	F	2.01	1.09
		1.59 ± 0.83	1.76 ± 1.13

Table 6. Methomyl residue concentrations on gloves worn by human subjects while harvesting cucumbers during the second sampling period after first day of application (4 May 1982). F = Females, M = Males.

Worker Number	Sex	Methomyl (ug/cm^2)	
		Left Glove	Right Glove
4	M	0.00	0.00
7	F	0.00	0.00
9	F	0.01	0.00
10	M	0.10	0.12
12	M	1.44	1.49
14	M	1.10	1.10
19	M	0.05	0.04
20	M	0.04	0.09
21	F	0.12	0.13
24	M	0.00	0.07
25	M	0.04	0.00
28	M	0.00	0.03
29	M	0.00	0.00
33	F	0.05	0.02
		0.21 ± 0.46	0.22 ± 0.46

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Table 7. Methomyl residue concentrations on arm patches worn by human subjects while harvesting cucumbers during the first sampling period after first day of application (4 May 1982). F = Females, M = Males.

Worker Number	Sex	Methomyl (ug/cm^2) Arm Patch
8	F	0.68
13	M	1.38
14	M	0.38
16	M	0.06
17	M	0.69
22	M	0.68
23	M	0.33
26	M	0.19
27	M	0.28
30	M	0.95
31	M	0.77
32	F	0.46
34	M	0.72
35	M	0.59

0.58 ± 0.34

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Table 8. Methomyl residue concentrations on patches worn by human subjects while harvesting cucumbers during the second sampling period after first day of application (4 May 1982). F = Females, M = Males.

Worker Number	Sex	Methomyl (ug/cm^2)	
		Arm Patch	Leg Patch
13	M	1.04	0.00
23	M	0.00	0.00
30	M	0.04	0.00
		0.36 $\pm$ 0.59	0.00

Table 9. Methomyl residue concentrations on leg patches worn by human subjects while harvesting cucumbers during the first sampling period after first day of application (4 May 1982). F = Females, M = Males.

Worker Number	Sex	Methomyl (ug/cm^2) Leg Patch
8	F	0.41
11	F	0.47
14	M	0.25
17	M	0.26
22	M	0.78
23	M	0.05
26	M	0.10
27	M	0.23
30	M	0.22
31	M	0.18
34	M	0.41
35	M	1.42

0.40 ± 0.38

Table 10. Methomyl residue concentrations found on substrates from human subjects while harvesting cucumbers on second application (19 May 1982). Value for hand wash = ug methomyl/glove surface area. F = Females, M = Males. Values with - are missing.

Worker Number	Sex	Methomyl (ug/cm^2)
		Left Glove	Right Glove	Hand Wash	Arm Patch	Leg Patch
1	M	0.24	0.28	0.04	-	-
3	M	-	-	0.00	0.13	0.26
4	M	0.26	0.28	0.07	-	-
5	M	-	-	-	0.11	0.06
6	M	0.57	0.63	0.05	-	-
7	M	0.20	0.09	-	-	-
8	M	-	-	0.13	0.11	0.10
9	M	1.05	1.20	-	-	-
10	F	-	-	0.06	0.02	1.21
11	F	1.64	1.15	0.05	-	-
12	F	0.95	0.61	0.07	-	-
13	F	-	-	-	0.42	0.59
14	F	0.59	0.71	0.04	-	-
15	F	0.98	0.97	0.09	-	-
16	F	1.10	0.94	0.05	-	-
17	F	-	-	-	0.03	0.08

Table 10. Cont.

Worker Number	Sex	Methomyl (ug/cm^2)				
		Left Glove	Right Glove	Hand Wash	Arm Patch	Leg Patch
18	F	-	-	-	0.41	0.76
19	M	0.80	0.59	0.03	-	-
20	M	0.76	0.86	0.03	-	-
21	M	1.27	1.37	-	-	-
22	M	0.86	1.08	0.00	-	-
23	M	0.03	0.00	-	-	-
24	M	1.06	1.03	0.10	-	-
25	M	1.04	1.00	0.13	-	-
26	M	-	-	0.13	0.03	0.43
27	M	1.38	1.58	0.10	-	-
28	M	-	-	0.11	0.71	0.95
29	M	0.81	0.81	0.03	-	-
30	M	-	-	0.06	0.35	1.12
31	M	-	-	-	0.00	0.02
32	M	1.82	2.10	0.08	-	-
33	M	0.67	0.65	0.07	-	-
34	M	1.03	1.08	0.09	-	-
35	M	-	-	-	0.38	0.22
36	M	-	-	-	0.18	0.53
============		0.87+0.45	0.86+0.48	0.067+0.038	0.22+0.21	0.49+0.41

Table 11. Rank correlations (Kendalls-Tau) of concentrations of methomyl detected in sampling devices collected from farm workers during the first sampling period first sample day (4 May 1982).

===

Substrate	Correlation coefficients (P under $H_0 = 0$) Methomyl Concentration		
	Age	Height	Weight
Left glove	-0.0812 (P< 0.65)	-0.2732 (P< 0.16)	0.0074 (P< 0.96)
Right glove	0.3828 (P< 0.85)	-0.0790 (P< 0.71)	0.0383 (P< 0.84)
Arm patch	-0.4000 (P< 0.07)	-0.1907 (P< 0.40)	-0.4122 (P< 0.06)
Leg patch	-0.1679 (P< 0.45)	-0.3587 (P< 0.13)	-0.1985 (P< 0.37)

===

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Table 12. Rank correlations (Kendalls-Tau) of concentrations of methomyl detected in sampling devices collected from farm workers on the second date (19 May 1982).

==

Substrate	Correlation coefficients (P under H_O = 0) Methomyl Concentration		
	Age	Height	Weight
Left glove	-0.1148 (P< 0.08)	-0.1585 (P< 0.38)	0.0286 (P< 0.86)
Right glove	-0.0339 (P< 0.80)	-0.2340 (P< 0.20)	0.0190 (P< 0.90)
Hand wash	-0.3303 (P< 0.02)	-0.0055 (P< 0.97)	-0.0582 (P< 0.68)
Arm patch	-0.1326 (P< 0.51)	-0.0928 (P< 0.67)	-0.1677 (P< 0.43)
Leg patch	0.0513 (P< 0.81)	-0.2518 (P< 0.24)	0.0129 (P< 0.95)

==

ACKNOWLEDGEMENTS

A number of persons contributed materially to the work described above, in either the planning of the project, doing fieldwork, analyzing samples, testing the data, or preparation of the report. These are: V. F. Cox, C. C. Dary, M. A. Garcia, M. E. Garcia, R. L. Garcia, A. Guillen, Jr., K. J. Huxford, N. J. Magouirk, A. Martinez, T. R. Mollhagen, A. G. Navarro, J. L. Valdez.

LITERATURE CITED

American Conference of Government Industrial Hygienists. 1984. Documentation of the threshold limit values for chemical substances in the environment A.C.G.I.H., Inc., Cincinnati, OH. 504 pp.

Bondy, M. K., R. H. Lebow, M. O'Malley, T. Reilly. 1976. Occupational health and safety for agricultural workers. DHEW (NIOSH) Publ. No. 77-150. Washington, D.C.

Cramer, P. H., A. D. Drinkwine, J. E. Going, and A. E. Carey. 1982. Determination of carbofuran and its metabolites by high-performance liquid chromatography using on-line trace enrichment. J. Chromatog. 235:489-500.

E. I. Dupont de Nemours & Co. 1977. Material safety data sheet for Lannate$^{(R)}$ L insecticide. Biochemical Dept., Wilmington, DE. 3 pp.

E. I. Dupont de Nemours & Co. 1980. Methomyl technical data sheet. Biochemical Dept., Wilmington, DE. 6 pp.

Ecobichon, D. J. and R. M. Joy. 1982. Pesticides and neurological diseases. CRC Press, Inc. Boca Raton, FL. 219 pp.

Federal Working Group on Pest Management. 1974. Occupational exposure to pesticides. Report to the Federal Working Group on Pest Management from the Task Group on Occupation Exposure to Pesticides. 155 pp.

Hayes, W. J., Jr. 1982. Pesticides studied in man. Williams & Wilkins, Baltimore/London. 455 pp.

Kuhr, R. J., and H. W. Dorough. 1977. Carbamate insecticides: chemistry, biochemistry and toxicology. CRC Press, Inc., Cleveland, OH. 301 pp.

Longbrake, T., R. Roberts, and S. Cotner. 1980. Keys to fresh markert cucumber production. Texas Agric. Ext. Serv., Publ. No. L-1556. 4 unnumbered pp.

Texas Agricultural Extension Service. 1980. Texas guide for controlling insects on commercial vegetable crops. Publ. No. B-1305. 28 pp.

Wagner, S. L. 1983. Clinical toxicology of agricultural chemicals. Noyes Data Corporation, Park Ridge, NJ. 253 pp.

Zavaleta, A. N. 1981. Introduction - Mexican American health status: selected topics from the borderlands. Borderlands J. 4(1): 1-6.

Appendix C

Intralaboratory Quality Control

The tables and figures that follow in this section are summaries of the recovery of methomyl from quality control samples for each substrate.
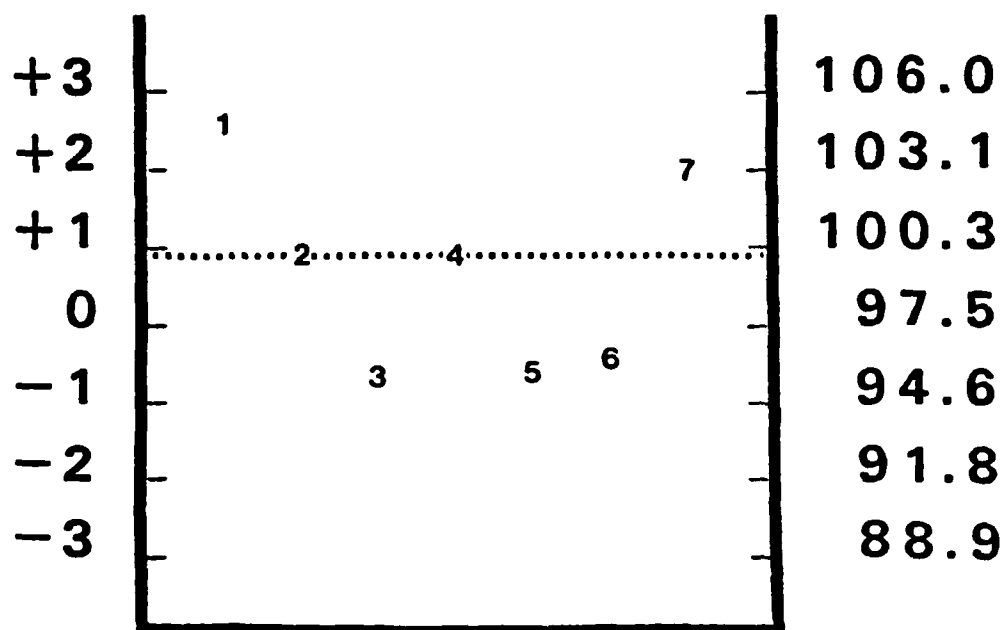
Fig. 1. Normal probability plot of patch samples
($\bar{x}$ = 97.46 + 2.84) fortified with 100 ug methomyl.
Numbers represent individual samples. Dashed line
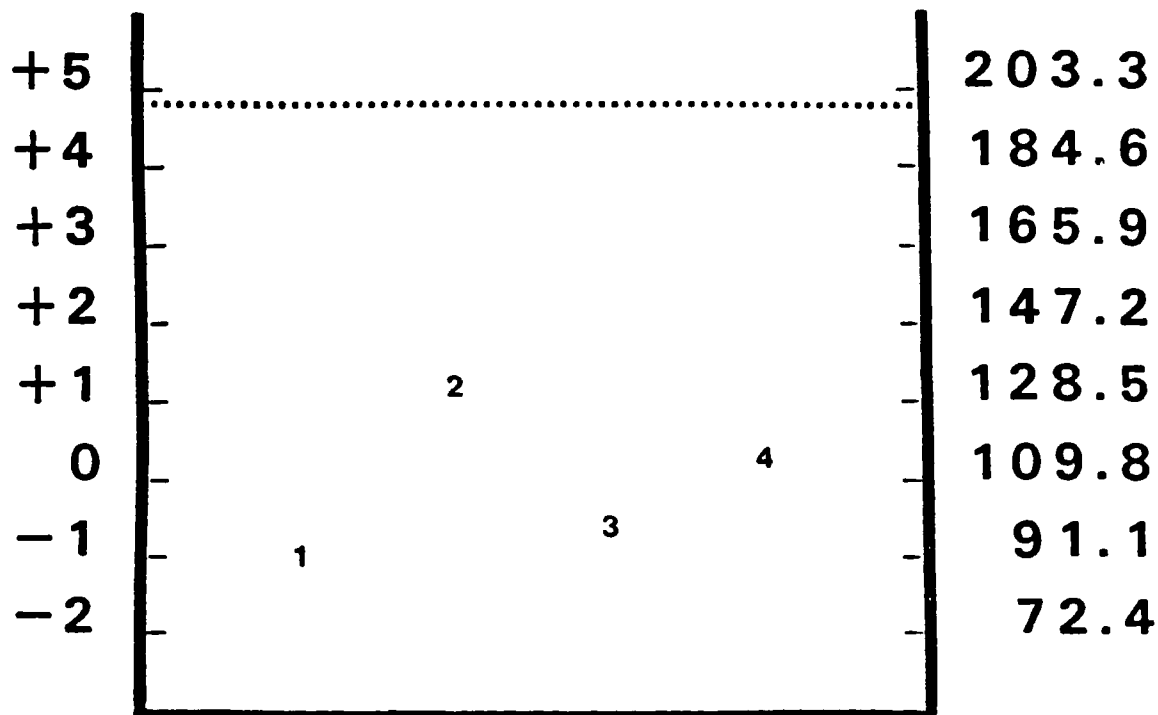represents expected recovery of fortified
concentrations (100 ug).
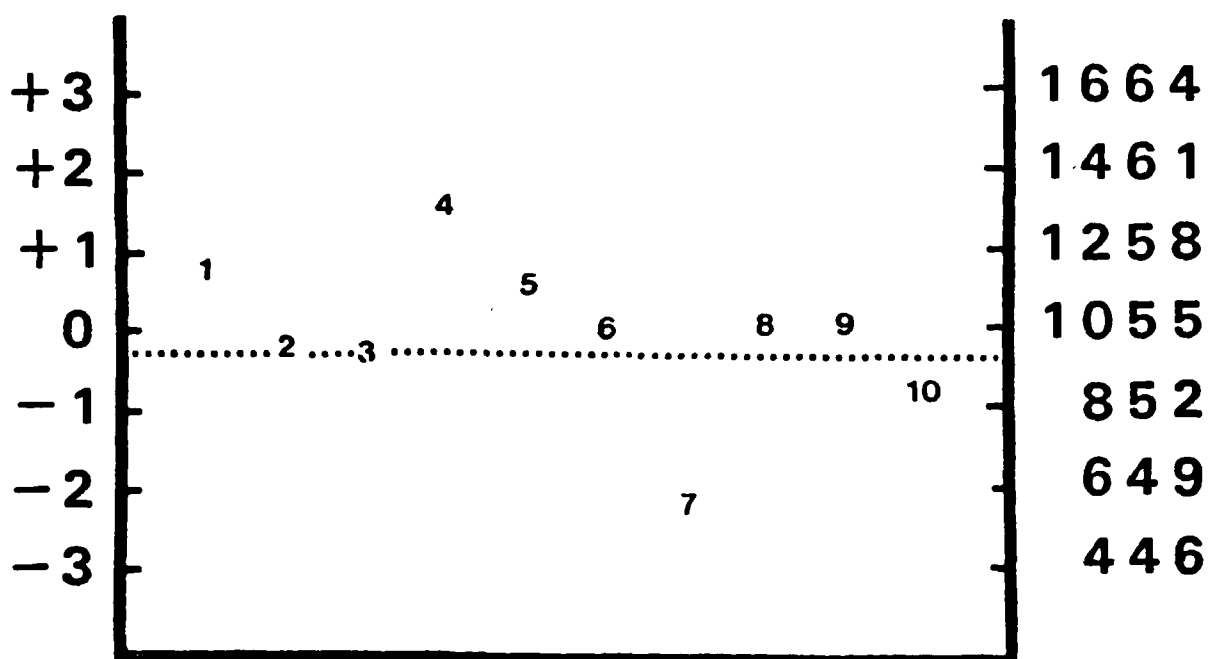
Fig. 2. Normal probability plot of glove samples
($\bar{x}$ = 1055 $\pm$ 203) fortified with 1000 ng methomyl.
Numbers represent individual samples. Dashed line
represents expected recovery of fortified
concentrations (1000 ng)

Fig. 3. Normal probability plot of hand wash towel samples ($\bar{x}$ = 109.78 ± 18.71) fortified with 200 ug methomyl. Numbers represent individual samples. Dashed line represents expected recovery of fortified concentrations (200 ug).

Table C1. Recovery of methomyl in patches from quality control samples
fortified with 100 ug methomyl.

===

Sequence	Sample Type	Observed Recovery (ug)	Percent Recovery
1	Q.C.	100.0	100.0
2	Q.C.	98.1	98.1
3	Q.C.	100.0	100.0
4	Q.C.	98.3	98.3
5	Q.C.	98.8	98.8
6	Q.C.	94.3	94.3
7	Q.C.	92.7	92.7

===

Table C2. Chromatographic summary of injection sequence for recovery of methomyl from gloves fortified with 1000 ng methomyl.

Sequence	Sample[a] Type	Observed Recovery (ng)	Peak Area	Peak Retention Time	Percent Recovery
0	Standard	1010	2273592	4.81	-
1	Q.C.	1205	2710154	4.83	120.5
2	Q.C.	1014	2280542	4.83	101.4
3	Q.C.	1003	2256749	4.83	100.3
4	Q.C.	1382	3107739	4.83	138.2
5	Q.C.	1194	2686269	4.78	119.4
6	Q.C.	1069	2403023	4.76	106.9
7	Q.C.	615	1382731	4.76	61.5
8	Q.C.	1076	2418742	4.76	107.6
9	Q.C.	1084	2438002	4.76	108.4
10	Q.C.	906	2036845	4.76	90.6

[a] Sequence for recovery of 1000 ng standard and quality control samples fortified with 1000 ng methomyl.

Table C3. Recovery of methomyl in hand wash towels from quality control samples fortified with 200 ug methomyl.

Sequence	Sample Type	Observed Recovery (ug)	Percent Recovery
1	Q.C.	90.7	45.4
2	Q.C.	133.0	66.5
3	Q.C.	99.4	49.7
4	Q.C.	116.0	58.0

Appendix D

Methods

D1 Extraction of gauze patches for pesticides

D2 Extraction of gloves and hand wash towels for pesticides

D3 High performance liquid chromatographic conditions for detection of methomyl

Extraction of Gauze Patches

1. Place one 4" X 4" gauze patch in a 500 ml Erlenmeyer flask and add 150 mls of methanol.

2. Extract twice using a Burrell Wrist-Action Shaker set at #6.

3. Collect to extracts and dry using Na_2SO_4 and evaporate to 5 mls.

4. Take to chemist for the addition of the internal standard.

1. Cut gloves into approximately 1 inch square pieces.

2. Place sample into 1000 ml Erlenmeyer flask and extract with methanol (350 ml portions) three times on wrist-action shaker for 20, 15, and 15 minutes.

3. Decant through glasswool in funnel into second 1000 ml Erlenmeyer flask. Place sufficient sodium sulfate to absorb any moisture in the extract. Transfer to round bottom evaporating flask.

4. During second wrist-action extraction evaporate samples down so second extraction will fit into round bottom evaporating flask.

5. Repeat for third extraction.

6. Bring up to approximately 10 ml.

7. Take to GC lab.

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High Performance Liquid Chromatographic Conditions
for Detection of Methomyl

Instrument - Waters Liquid Chromatograph

Detector - Model 440 at 254 nm

Column - C^{18} Silica Gel - Waters

Mobil Phase - 25% Acetonitrile
              75% H_2O

Flow Rate - 1.0 ml/min

An Assessment of Exposure of Turnip and
Mustard Green Harvesters to Phosdrin

Research performed by

Texas Tech University
San Benito, TX 78586

April 1, 1986

In behalf of the Texas PHAP the undersigned has reviewed and approved the report draft entitled "An Assessment of Exposure of Turnip Green Harvesters to Mevinphos."

_____
Project Director

_____
4 - 1 - 86
Date

TABLE OF CONTENTS

AN ASSESSMENT OF EXPOSURE OF TURNIP GREEN HARVESTERS TO MEVINPHOS

ABSTRACT

Exposure of farmworkers to Phosdrin$^{(R)}$ 4EC while harvesting turnips was examined after an extended 10 day reentry period in December of 1982. Dermal exposure was assessed through the measurement of residues of Phosdrin$^{(R)}$ detected as cis-mevinphos on sampling devices, gloves, gauze shirt patches, and air sampling cartridges worn by the harvesters. Residue levels detected in sampling devices were to be compared to the concentrations of cis-mevinphos detected in soil and foliage throughout the 10 day period prior to reentry. The half-life of Phosdrin$^{(R)}$ on leaves and soil was estimated to be 0.53 to 1.10 days, respectively. Loss of Phosdrin$^{(R)}$ from soil and leaves was relatively rapid, reaching non-detectable levels at the time of reentry. No residues were detected in sampling devices worn by the workers. This was consistent with the loss of residues from leaves and soil. Exposure of the harvesters was negligible after the 10 day period as indicated by the detection of only trace levels of dimethylphosphate (DMP) in post harvest voids. The absence of residues in sampling devices associated with workers precluded any statistical comparison of age or sex subsets of workers.

AN ASSESSMENT OF EXPOSURE OF TURNIP GREEN HARVESTERS TO MEVINPHOS

INTRODUCTION

A series of studies on the effects of pesticides on youths employed in
agriculture was conducted by the National Pesticide Hazard Assessment Projects
with the cooperation of the U.S. Environmental Protection Agency (EPA) and the
U.S. Department of Labor. The studies were intended to provide an assessment
of the exposure of harvesters to one or more pesticides used to protect crops
from damage by pests and disease. The accumulated data might be of value in
predicting the level of risk assumed by adult and juvenile farmworkers while
harvesting crops treated with the studied pesticides.

The migrant streams of the western United States are comprised mainly of
Spanish-speaking peoples. Because of the predominantly Hispanic culture, the
Lower Rio Grande Valley (LRGV) of south Texas is home to one of the largest
migrant farmworker populations in the United States. During the period
September through May of most years, the region provides intermittent work
harvesting a wide variety of fruits and vegetables. In the Spring, as the
local harvests near completion, the workers will gradually depart to follow
harvests of many of the same crops at progressively more northern latitudes.
Workers of the LRGV are the chief component of the central migrant stream that
works the Great Plains and the Midwest. However, many migrant workers will
travel directly to Florida or California to work the coastal streams northward.

The migrant worker may become exposed to pesticides throughout the year while engaged in agricultural activities. The effects on health posed by exposure to agricultural chemicals is compounded by the health problems associated with the migrant hispanic population (Zavaleta, 1981 and Bondy et al., 1976). The health status of the migrant laborer might require special attention when addressing occupational exposure to pesticides. Reentry intervals may require accommodation to the health considerations associated with the migrant worker population. Because pesticides are applied to virtually all crops grown in the LRGV, residues of the pesticides may represent a health hazard to field workers either through prolonged dermal contact with leaves and fruit or through inhalation or ingestion of dislodgable residues.

The commodities grown in this four-county region are annually treated with perhaps as much as five million pounds of pesticide products, or 25 to 35 percent of all the pesticides used in Texas. Hidalgo County alone, probably the most intensively farmed county in the state, may receive as much as the other three Valley counties combined. Cotton and grains account for possibly the greatest portion of this usage. However, these crops require little human contact during growth or harvest. On the other hand, citrus, many vegetables, and some specialty crops do require hand labor and also require considerable pesticide usage, occasionally during harvest.

The climate of the Lower Rio Grande Valley (LRGV) has been classified as humid desert. Mid-day relative humidities average 61 percent at Brownsville and decline to about 45-50 percent in Starr County to the west, while mean annual rainfall ranges from 27 to 19 inches in the same direction (U.S. Weather Service, Brownsville, pers. comm.). Summer temperatures frequently exceed 100°F. This climate could influence the formation of oxons from

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organophosphate insecticides. Oxons are frequently noted as having some importance in poisoning incidents involving harvesters in arid parts in California (Maddy and Edmiston, 1982). The combination of both high temperature and high humidity has been observed to promote degradation (Eto, 1979). Most farmworkers in the region are employed in the Fall and Spring. During this period humidity remains relatively high and temperatures are much lower. The rate of degradation of certain pesticides may be subsequently lower than during the summer.

Turnips are grown sparingly in the LRGV. Turnips are a dual purpose crop grown for greens and vegetable roots (McCraw, 1979). Planting should be made in the early spring or late fall. Harvest is usually performed by hand, before the weather gets hot. The plants are low-growing with leaves attaining heights of 14 to 16 inches at harvest. Most workers harvest the crop on their knees. The foliage is manually cut off at ground level. After blemished leaves are removed, bundles of leaves are usually held against the chest and tied together with string or light wire. The cutting, sorting, and binding procedures require a level of dexterity that prohibits most workkers from wearing any kind of gloves, except on the coldest of days. This exposure plus the extensive contact with foliage by the chest and forearms during binding represent the greatest potential for the transfer and penetration of residues.

Insect pressure on turnips may require treatment with malathion for aphids, Sevin[R] for flea beetles, a formulation of <u>Bacillus thuringiensis</u> for control of loopers and a pre-plant treatment of Diazinon[R] for control of root maggots (McCraw, 1979). Phosdrin[R] was not listed by the Texas Agricultural Extension Service (McCraw, 1979) for control of insect pests on turnips. However, commercial production of turnips may require treatment with Phosdrin[R].

Phosdrin(R) 4EC is labeled for use on turnips grown as field or vegetable crops at the rate of 1/4 to 1/2 pint per acre for control of aphids and 1/2 to 1 pint per acre for control of cabbage worms, false chinch bugs, leaf miners (Diptera), grasshoppers, leafhoppers and mites (Shell Chemical Company, 1982). The harvest interval between last treatment and reentry to harvest is 3 days (Shell Chemical Company, 1982).

Phosdrin(R) 4EC is an emulsible liquid concentrate of 28.3% mevinphos (Shell Chemical Compay, 1982) consisting of at least 60% of the alpha or cis isomeric form (Hayes, 1982). According to the nomenclature of Eto (1979) the cis-isomer is beta mevinphos and the trans-isomer alpha mevinphos. The geometry of mevinphos previously reported by Fukuto et al. (1961) was viewed by Eto (1979) as reversed. The geometrical isomers will be referred to as cis or trans in this document. The cis-isomer has been observed (Eto, 1979) to be 10-20 times more inhibitory to acetylcholinesterase (AChE) than the trans-isomer. The cis-isomer is about 100 fold more toxic to insects.

Similar differences in activity between isomers can be addressed to degradation and metabolism of mevinphos. The half-life for alkaline hydrolysis of cis-mevinphos was reported by Eto (1979) as 4.5 hours (70° C, pH 6.0). The trans-isomer was more rapidly hydrolized (3.7 hours, 70° C, pH 6.0). Hydrolysis of mevinphos in aqueous solution appears to be pH dependent (Hayes, 1982). The half-life of hydrolysis of cis-mevinphos and trans-mevinphos at pH 11.0 (28° C) was 3.0 hours and 1.8 hours, respectively. Hydrolysis of trans-mevinphos yields only dimethylphosphate (Eto, 1979). Two hydrolysis products may be produced from cis-mevinphos, dimethylphosphate and trans-phosdrin acid (Eto, 1979). Under environmental conditions, light energy (UV-irradiation) causes photo isomerization of either isomer to a mixture of 30 percent cis and 70 percent trans isomers (Eto, 1979). Residues of

Phosdrin[R] (60% cis-mevinphos) on foliage may be expected to be converted to disproportionate concentrations of trans-mevinphos.

Metabolism of cis-mevinphos occurs through microsomal induction in mammalian hepatic systems to yield glutathione sulfur conjugates (Eto, 1979) and cis-desmethyl phosdrin (Morello et al., 1968a). The trans-isomer is degraded by esterases at the vinyl ester linkage (Hutson et al., 1972, Eto, 1979) to yield dimethylphosphate (Morello et al., 1968b). Mouse liver homogenates were able to degrade trans-phosdrin more rapidly than cis-phosdrin (Morello et al., 1968c). The metabolites of both isomers are excreted in feces and urine (Casida et al., 1958, Haley et al., 1978).

Mevinphos is an organophosphorous compound of high oral (3.7 - 6.1 mg/kg) and dermal (4.5 mg/kg) mammalian toxicity (Merck Index, 1976). The Department of Labor and EPA (Federal Working Group on Pest Management, 1974) placed mevinphos in category I, compounds with dermal LD_{50} less than 200 mg/kg. Mevinphos acts as an irreversible inhibitor of red blood cell (RBC) cholinesterase (Hayes, 1982). RBC cholinesterase activity may be depressed 25% with 0.036 mg/kg/day without symptoms or reduction in plasma cholinesterase activity (Hayes, 1982). The primary symptom resulting from exposure to mevinphos was impairment in judgment (Hayes, 1982). Blurred vision might be demonstrated as a consequence of contracted pupils (Hayes, 1982). Symptoms, high fever and abdominal cramps, may be observed up to 48 hours after contact (Hayes, 1982). Numerous human poisoning cases have been reported which describe the signs of acute intoxication (Abbadie et al., 1980, Haley et al., 1978, and Hayes, 1982). Mass poisoning of humans from consumption of greens contaminated with residues of mevinphos has been reported (Murphy, 1975).

Because of the small difference between oral and dermal toxicity, mevinphos represents a compound of high risk to the occupationally exposed (Federal Working Group on Pest Management, 1974). This study examined the exposure of farmworkers harvesting turnips to a liquid formulation of mevinphos, Phosdrin[R] 4EC. The objective of the study was to compare the concentrations of residues of mevinphos on turnip foliage and soil to the accumulation of residues on sampling devices worn by farmworkers while harvesting. The aim of the study was to relate the transfer of residues from soil and foliage to exposure of farmworkers to Phosdrin[R] 4EC based on concentrations of urinary metabolites.

METHODS AND MATERIALS

The two isomeric forms of mevinphos (2-carbomethoxy-1-methylvinyl dimethyl phosphate) are depicted below:

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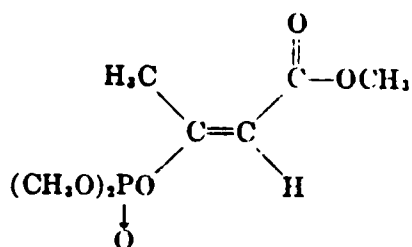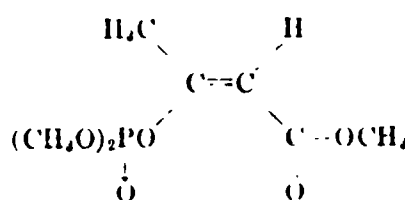
cis-mevinphos   trans-mevinphos

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The NMR spectra melting point and stability of the isomers differ greatly (Eto, 1979, Hayes, 1982). The melting point of cis-mevinphos is 21° C while the melting point of the trans-isomer is 6.9° C (Hayes, 1982). Phosdrin[R] 4EC, a restricted-use product of Shell Chemical Company bearing the EPA Registration Number 201-289 (28.3% cis-mevinphos, 18.8% related compounds, 47.9% petroleum hydrocarbons and 5% inert ingredients), was the formulation studied.

Study Site. The study site was managed by a grower that raised a variety of crops, including citrus and several other vegetables. All the vegetables, including the turnips, were packed on the farm. An attempt was made to minimize interference with ordinary growing practices. Contact with the grower was made only to remain informed of farm practices.

The site was an irrigated, single 18 acre block of turnips. The field measured approximately 110 m on the north side; 653 m on the east; 110 m on the south; and 653 m on the west (Fig. 1). The topography was essentially flat, with furrows running north-south. The soil is largely a Willacy fine sandy loam with a somewhat saline Racombes sandy clay loam portion on the eastern margin.

Application. No previous pesticide use history for the site was obtained. Phosdrin[R] 4EC was applied aerially at the rate of 1/2 pint per acre on 17 December 1982 (1500 hours). The aircraft was equipped to cover a 20 row swath and deliver three gallons per acre of spray volume through 8000-6 nozzles (at 35-40 psi).

Weather. The wind direction at the time of application was not recorded. The low temperature for the day was 48°F in the morning and the high temperature of 75°F was reached shortly after the time of application. The prevailing weather for the next nine intervening days to harvest was unremarkable. High temperatures never exceeded 84°F, lows never fell below 50°F, nor was there any precipitation (Table 18). However, on the evening of 26 December a notherly cold front passed through the area, carried by winds gusting to 20 mph. These conditions remained through the date of harvest. The cool temperature of the day of 47°F occurred as the workers were arriving at the field. The high of 59°F was recorded in the afternoon, about four hours after harvesting had ceased.

Deposition. Deposition of Phosdrin[R] 4EC was measured on turnip leaves and soil after application. Soil samples were taken from five locations within the field (Fig. 1). Soil was scraped from the surface of the field to a depth of 0.5 inches. The first samples (approximately 100 g of soil) were collected approximately 200 minutes after the application.

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Subsequent samples were collected over an eight day period. The samples were placed in 120 cc polyethylene urine sample cups and put on dry ice for transport to the laboratory. On arrival at the laboratory, the samples were catalogued and stored frozen for later analysis.

A ten gram soil sample was placed in a narrow-mouthed Erlenmeyer flask and extracted with acetone three times for 15 minutes with a Burrell wrist-action shaker set on number six. The three extracts were combined, dried with sodium sulfate, filtered through Whatman No. 1 paper on a Buchner funnel, and concentrated to 5 ml using a Buchi Rotovapor R110. Adjustments were made to the volume prior to analysis by GC.

Foliage. Deposition of mevinphos on foliage was measured by obtaining 20 leaf punches (100 cm^2) from plants along selected rows (Fig. 2). Samples were collected prior to the entry of harvesters into the field. Leaf punches were obtained with a Birkstrand punch equipped to cut a 2.5 cm^2 circle. The punches were collected in resealable plastic bags and stored on dry ice for transport to the laboratory. On arrival, the samples were catalogued and stored frozen until analysis.

Samples were extracted using the method of Gunter et al. (1974) for measurement of dislodgable residues. A 50 cm^2 sample (10 punches x 2 sides x 2.5 cm^2) was placed in a 120 cc polyethylene urine specimen container to which 3 drops of a 0.5 % dilution of Witconol NP-100 surfactant and 75 ml of distilled water were added. The samples were extracted three times for 15 minutes on a Burrell wrist action shaker set at speed six. These extracts were combined and transferred to a 1 liter separatory funnel and extracted again three times with 400 ml hexane and 150 ml methylene chloride. A saturated 2 % solution of sodium sulfate in water was used to break up emulsion. Hexane was dried with anhydrous sodium sulfate and concentrated

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with a Buchi Rotavapor R110 to 5 ml. Final evaporation to 0.5 ml was done on a Meyer N-Evap. This volume was adjusted to 5 ml with methanol. Additional volume adjustments were made prior to analysis by GC.

Human Subjects. The transfer of residues on foliage and soil to workers harvesting turnips was studied on a population of hispanic farmworkers. These workers were selected solely by the labor contractor. The workers did not have advanced notice of the study. The workers arrived at the field at approximately 0700. After an explanation of the work proposed, the volunteers proceeded through a series of stations where they signed consent forms, received their numbered shirts, received their sampling devices, and were briefly interviewed. Owing to the disagreeable weather, all subjects were wearing shoes, caps, jackets, and long pants, in addition to the numbered shirt provided. The sampling devices worn was on a voluntary basis. All workers entered the field within a few minutes of 0800; all workers completed their harvest activities between 1045 and 1120. The amount of work performed was not obtained from the labor contractor. Drinking water and washing facilities were provided but not utilized.

Study subjects were also required to contribute urine specimens to measure the concentration of pesticide metabolites which might result from exposure while harvesting the crop. Specimens were obtained from each subject. Portable restrooms for both males and females were provided. Samples were collected before the subject started to work and as they retired from the field. They were also asked to contribute their first void the following morning. Urine samples were collected in standard, plastic, four-ounce urine specimen containers, and were placed directly on dry ice for immediate transport to the laboratory.

The cohort consisted of 6 females and 11 males (Tables 1,2). The average age of the females was 20.5 $\pm$ 12.0 years. The youngest female was 11 years; the oldest 40 years. The ranks of the ages of the females were found to be not significantly different (T = 49.5, P > 0.20, n = 6, m = 11) from the males according to the Mann-Whitney test for two independent samples (Conover, 1980). The average age of the males was 26.9 $\pm$ 16.9 years. The youngest male was 8 years, the oldest 55 years. The closeness of age of the males and females was determined to be related to the make up of the population as a group of families (Mollhagen et al., 1985). The uniformity of the age of the population may be used to explain the lack of a significant difference (T = 25, P > 0.20, n = 4, m = 10) between the ranks of the weights of the males and the females. The average weight of the females was 51.0 $\pm$ 8.2 Kg; the average weight of the males was 62.6 $\pm$ 27.2 Kg. The transfer of residues may be examined in relation to the pooled ages and weights of the workers with effects partitioned by sex.

Gloves. Transfer of residues onto the workers was measured on sampling devices (gloves, arm patches and air samplers) worn by the workers (Fig. 3). To estimate the amount of contact with pesticide residues through the hands, 9 subjects were recruited to wear a pair of lightweight 100% cotton twill work gloves with knit wristlets and seamless palms (Sears catalog number 51 K 25915). The average surface area of three gloves (minus the knit wristlet) was 85.2 in^2 $\pm$ 1.29 (549.7 cm^2). After the exposure period, the gloves were sealed in a plastic bag and placed on dry ice. The samples were catalogued and stored in a freezer until analysis was started.

The gloves were cut into 1 to 2 cm^2 pieces (the knit wristlets were not tested) and placed in a 1.0 liter Erlenmeyer flask and extracted three times with methanol on a Burrell wrist-action shaker at setting 8. The pieces were

transferred to a Buchner funnel and washed. The extracts were combined, filtered, and concentrated to 5 ml with a Buchi Rotavapor R110. The volume was adjusted as needed for analysis by GC.

Gauze Patches. To assess the potential for pesticide contact and absorption through the arms, gauze exposure patches with surface area 103.2 cm^2 per patch were placed on 6 subjects, one on each forearm outside the shirt (Fig. 3). Workers performed their normal work activity for 3.5 hours. At the end of the day the patches were collected from the workers. The samples were catalogued and stored in a freezer until analysis. Gauze patches were extracted intact three times in a 500 ml Erlenmeyer flask containing 75 ml methanol using a Burrell wrist-action shaker at setting 6. The three extracts were combined, filtered through Whatman No. 1 paper on a Buchner funnel, dried with anhydrous sodium sulfate, and concentrated to 5 ml on a Buchi Rotavapor R110. Final volume adjustment was made as needed prior to analysis by GC.

Air Samples. Five of the subjects were fitted with a DuPont P-4000 Personal Air Sampling Pump equipped with an air cartridge. This was done to assess the potential for inhalation of airborne residues. In every case the pumps were clipped to a military web belt and the pump positioned to ride at the waist in the small of the back (Fig. 3). This location caused very little interference with worker movement. The pumps were set to draw 1 liter per minute. Calibration was done just prior to sampling and immediately upon returning from the field. The time that the workers wore the pumps was documented in two ways. First, each pump had a device to report running time. Second, these values were compared with the notes on the times the pumps were checked out and checked in.

The pumps were connected to the cartridges through a 90 cm length of quarter inch (inside diameter) tygon tubing. The tubing was adapted to the 4 mm cartridge nipple. The tubing from the pump passed between an arm and the torso and the cartridge was clipped to the shirt collar. The trapping cartridge was constructed of the barrel section of a 20 cc plastipack disposable syringe packed with 1.5 g Sepralyte Octadecyl C-18 100 um silica gel and closed with 0.5 square inches of polyurethane.

The exposed cartridges were sealed inside a plastic bag and stored on dry ice until transport to the laboratory where they were catalogued and placed in a freezer until analysis. Extraction of the residues from the entrapment medium was accomplished by eluting 150 ml of acetone through the cartridge at approximately 5 ml/min. This solution was dried with anhydrous sodium sulfate and evaporated to 1 ml with a Buchi Rotovapor R110 and prepared for GC analysis.

Analytical Methods. Samples were analyzed for residues of mevinphos by gas-liquid chromatography with a Tracor 222 gas chromatograph equipped with a 4.0% SE 30/6% OV 210 column (flow rate 20 cc/min, 200° C) and flame photometric detector (FPD) in phosphorous mode. Detection of mevinphos was confirmed by two column analysis (10% DC 200, flow rate 50 cc/min, 165° C). Mevinphos (Phosdrin[R]) code 4640 as cis-mevinphos was used as the reference standard. The standard was obtained from the U.S. EPA Pesticides and Industrial Chemicals Repository, U.S. EPA Environmental Research Center, Research Triangle Park, NC 27711. The standard was prepared in methanol as 100% cis-mevinphos.

Recoveries. Recovery of added concentrations of mevinphos in the substrates was examined to estimate precision, accuracy and reproducibility of methods of extraction and analysis. The substrates were fortified with

concentrations of mevinphos to reflect recovery of minimally detectable levels. A series (n = 10) of 10 gram soil samples were fortified with 150 ng of mevinphos and compared to 150 ng/ml standards. The mean recovery of the 10 samples was 112.4 ± 11.3 ng with a coefficient of variation of 10.0%. Although recovery was less than expected (75%), observed values were within control. Observed values were not greater than two standard deviations (Fig. 4). The chromatographic summary is provided in Appendix A.

Recovery of mevinphos from fortified (300 ng) gauze patches was improved (86.7%) over recovery in soil (75.0%). The mean recovery of 10 samples was 260.2 ± 30.2 ng with a coefficient of variation of 11.6%. The improved recovery of mevinphos from the patches was reflected in the more uniform distribution of values about the expected line of recovery (Fig. 5). This level of precision was attributed to the ease of extraction and the level of fortification (300 ng). The chromatographic summary is provided in Appendix A.

The mean recovery of mevinphos from leaves fortified with 300 ng was 266.7 ± 27.1 ng. Values were well clustered about the mean (Fig. 6) as indicated by the coefficient of variation (10.1%). The coefficient of variation was consistent among substrates. Greater percent recovery was realized for leaves (89.0%) than for soils (75.0%) or gauze patches (86.7%). A summary of the chromatographic sequence for leaves may be reviewed in Appendix A.

Recovery of fortified concentrations of cis-mevinphos in gloves was 99.0 percent of expected (300 ng). The mean recovery of cis-mevinphos was 297.0 ± 51.2 ng. The coefficient of variation (C.V. = 17.2%) was greater than the C.V. obtained for the other substrates. However, individual sample values

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were within control (Fig. 7). The chromatographic summary is provided in Appendix A.

The average recovery of the urinary metabolite of Phosdrin[R] dimethylphosphate (DMP) in urine samples fortified with 0.25 ug/ml DMP was 0.22 $\pm$ 0.02 ug/ml or 88 percent. Values were within control (Fig. 8) with a coefficient of variation of 8.93 percent. The chromatographic summary of the injection sequence may be reviewed in Appendix A.

RESULTS AND DISCUSSION

The disposition of Phosdrin$^{(R)}$ detected as <u>cis</u>-mevinphos was measured on soil and foliage. Deposition was determined from soil and leaf samples acquired immediately after application. Decline or loss of residues was estimated from samples obtained over an extended period, six days for leaves and eight days for soil.

Deposition of <u>cis</u>-mevinphos detected in soil samples obtained from five sites within the field was extremely variable (Fig. 1). Concentrations ranged from 44.0 ng/g at site 1 to non-detectable or zero levels at site 3. Loss of <u>cis</u>-mevinphos from soil at site 1 was rapid over the eight day sampling period (Table). However, the decline in residue level did not follow a time dependent trend. The two-tailed test for trend using Kendalls-tau (Conover, 1980) was not significant (Hotelling-Pabst T = 125, n = 8, P > 0.20). A similar result, as expected, was obtained for site 3 (Hotelling-Pabst T = 135, n = 8, P > 0.10). The greater value for Hotelling-Pabst statistic was associated with the number of zero ties (Table 4). A lack of significant trend (Hotelling-Pabst T = 113, n = 8, P > 0.20) was also observed for site 5 (Table 5).

Time dependent trends were observed for sites 2 (Table 6) and 4 (Table 7). A highly significant trend (Hotelling-Pabst T = 162, n = 8, P = 0.001) was observed for site 4. The decline in residue concentrations in soil from site 2 appeared to be time dependent (Hotelling-Pabst T = 147, n = 8, P < 0.05). A plot of concentrations of <u>cis</u>-mevinphos detected in soil from sites 2 and 4

against time (Fig. 9) appeared to follow first-order kinetics. The combined samples revealed a significant time dependent trend (Hotelling-Pabst T = 1205, n = 16, P < 0.001).

The data for each site were transformed (log scale) to obtain estimates of the half-life of Phosdrin$^{(R)}$ residues in soil over the interval 0.1 to 8 days post application. A significant correlation (t = 3.582, P > 0.025) was obtained between the log cis-mevinphos concentration and time (days) for site 4 (Fig. 10). A half-life of 1.01 days was obtained from the slope of the equation (log (ng/g) = -0.2966 [log (ng/g) day $^{-1}$] + 1.51 days, r = -0.8483, r^2 = 0.7196). The mean residue level was 0.653 $\pm$ 0.723 ng/g with the mean time of sampling 2.88 $\pm$ 2.07 days.

Although the correlation was significant, the half-life and the linear estimates of mean residue concentration and mean time were obtained from an equation with 28.04 percent of the variability unaccounted for by the regression. Zweig et al. (1985) obtained linear estimates and calculated half-life from equations with approximately 15.36 percent of the variability unaccounted for by the regression. Estimates of half-life must be evaluated according to the variability in the regression. The correlation on log cis-mevinphos concentrations and time (days) for site 2 was found to be not significant (t = -1.196, dif.= 4, P > 0.20). Approximately 58.28 percent of the variability in the equation log (ng/cm^2) = -0.1095 [log (ng/cm^2) days $^{-1}$] + 0.822 days, r = -0.6459, r^2 = 0.4172 was unaccounted for by the regression. A half-life could not be estimated with confidence from the equation.

Deposition and loss of Phosdrin$^{(R)}$ from foliage was observed on the day of application and on six subsequent days. Leaf punches were collected along rows at different times over the six day period. The deposition of Phosdrin$^{(R)}$ detected as cis-mevinphos appeared to vary among rows (Fig. 2).

The lack of replicate values did not allow for statistical evaluation of deposition among rows. The highest concentration of cis-mevinphos (0.37 ng/cm^2) was detected in leaf punches from row A, 19 meters from the west edge of the field. Except for a slight rise in concentration (0.35 ng/cm^2) in leaf punches from row C, the deposition of Phosdrin[R] appeared to decline from west to east (Fig. 2). A test of trend between residue concentration and distance from the west edge of the field using Kendalls-tau (Conover, 1980) indicated a lack of trend (Hotelling-Pabst T = 38, n = 5, P > 0.05). The test for trend was complicated by the differences in the time of sample collection among rows (Table 8). Leaf punches from row A were collected 206 minutes after application while leaf punches from row D were collected 20 minutes later. The time of sample collections may have contributed to the concentration differences among rows and represent a time dependent loss of residue. However, the test of trend between residue concentrations and the time of sample collection was less ambiguous (Hotelling-Pabst T = 36, n = 5, P > 0.05) than the test for directional trend.

The loss or decline of residues on leaves was examined more directly by row in relation to time of sample collection. Concentrations declined rapidly after the first day in row A (Table 9). A time dependent trend was not indicated (Hotelling-Pabst T =31, n = 5, P > 0.20). Further analysis for trend for the additional 4 rows was equally negative (Tables 10-13). Although residue levels declined rapidly to non-detectable levels, the detection of concentrations greater than zero altered the apparent trend to zero levels for most rows.

Treatment of the data as a single population revealed a significant trend (Hotelling-Pabst T = 5265, n = 26, P < 0.001) as evidence for a decline of mevinphos concentrations. A plot of positive values (Fig. 11) appeared to

follow a first-order decay curve. A test of trend for the positive values was significant (Hotelling-Pabst T = 288, n = 10, P < 0.02). An estimate of the rate of decline of phosdrin (k_t = 1.33 ng/cm^2 . day $^{-1}$) was obtained from the integral of the first-order decay curve over the period of positive values. The half-life was estimated to be 0.53 days. A regression on the log transformed data, although significant (t = -2.653, P < 0.025), left only 46.81 percent of the variability attributable to the equation log (ng/cm^2) = - 0.0831 [log (ng/cm^2) days^{-1}] - 0.92 days. An estimate of half-life based on the regression was considered inappropriate.

Transfer of residues from soil and foliage to sampling devices, gloves, arm patches, and air cartridges worn by workers harvesting turnips was examined to estimate the level of exposure to Phosdrin[R] 4EC. Concentrations of cis-mevinphos detected on the sampling devices was compared to residues of the metabolite dimethylphosphate (DMP) detected in urine samples provided by the workers during harvest.

Farmworkers entered the field 10 days after application and collection of the last field samples. Residue levels on sampling devices were expected to reflect the concentrations detected in soil and foliage on the final day of field sampling. Consistent with this supposition, cis-mevinphos was not detected in gloves, or air sample cartridges (Tables 14,15). The detection of 130 ng or 1.26 ng/cm^2 in arm patches worn by worker 20 (Table 15) was regarded as a spurious anomaly. The apparent detection of cis-mevinphos in air cartridges was ruled out by two column confirmation (see Appendix B1). Cis-mevinphos detected by the SE 30/OV210 column could not be confirmed on DC-200. Transfer of residues to sampling devices appeared to reflect zero exposure in accordance with the loss of residues from soil and foliage.

The lack of transfer was substantiated by the detection of trace levels
of dimethylphosphate (DMP) in urine samples of the harvesters (Tables 16,17).
These concentrations were lower than clinically important levels of DMP, 0.4
ppm in cases of moderate poisoning with mevinphos and 2.0 ppm in a more severe
case (Hayes, 1982). The formation of DMP occurs as a result of esterase
activity on the p-o-vinyl bond of trans-mevinphos (Eto, 1979, Hutson et al.,
1972). The cis-isomer may be degraded to cis-desmethyl phosdrin and S-methyl
glutathione (Morello et al., 1968c, Beynon et al., 1973). Assessments of
exposure to phosdrin based strictly on the measurement of DMP in urine may
underestimate the extent of exposure. Moreover, DMP is a metabolite of a
variety of organophosphorous compounds (Eto, 1979). Detection of low levels
of DMP may be a consequence of incidental exposure to organophosphorous
compounds used outside the workplace. The trace levels of DMP detected in the
urine of the workers after harvest (Tables 16,17) may have occurred from
incidental exposure rather than from occupational exposure to phosdrin.
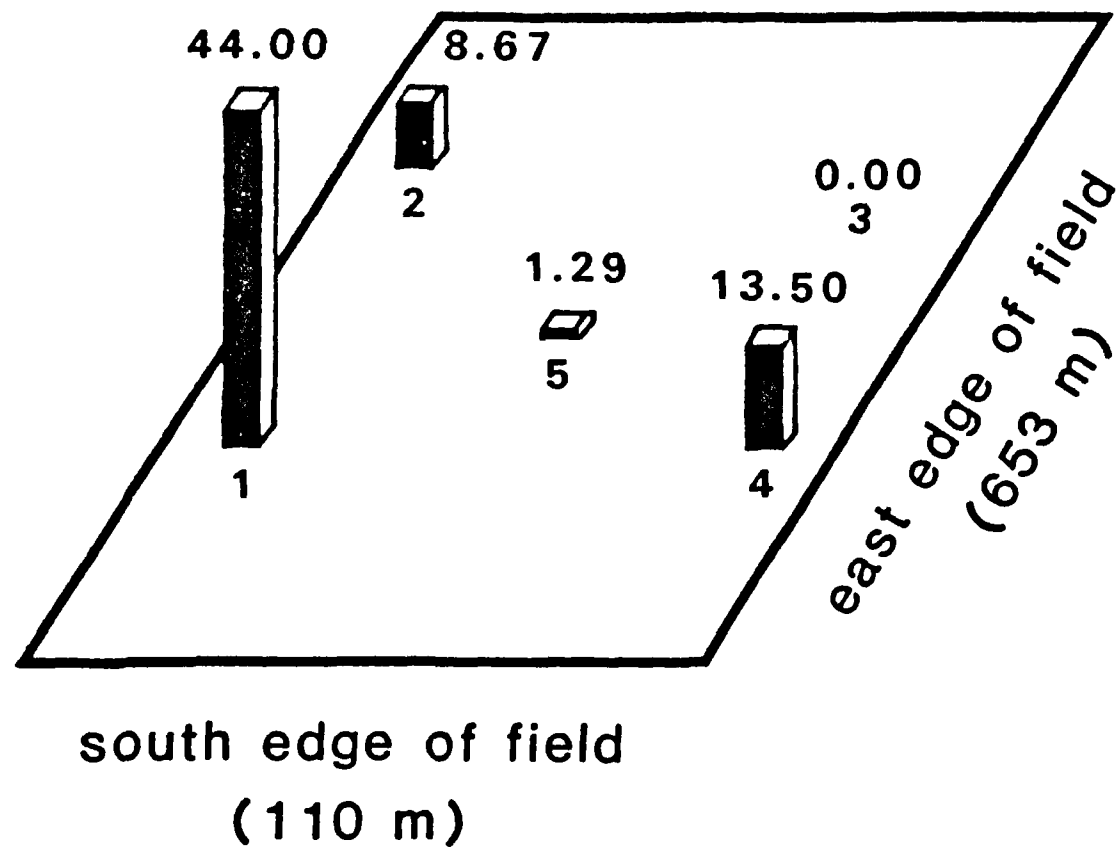
Fig. 1. Deposition of Phosdrin(R) 4EC detected as cis-mevinphos (ng/g) in soil samples collected from sites within a turnip field following aerial application of Phosdrin(R) 4EC (0.5 pint per acre) on 17 December 1982 at 1500 hours.
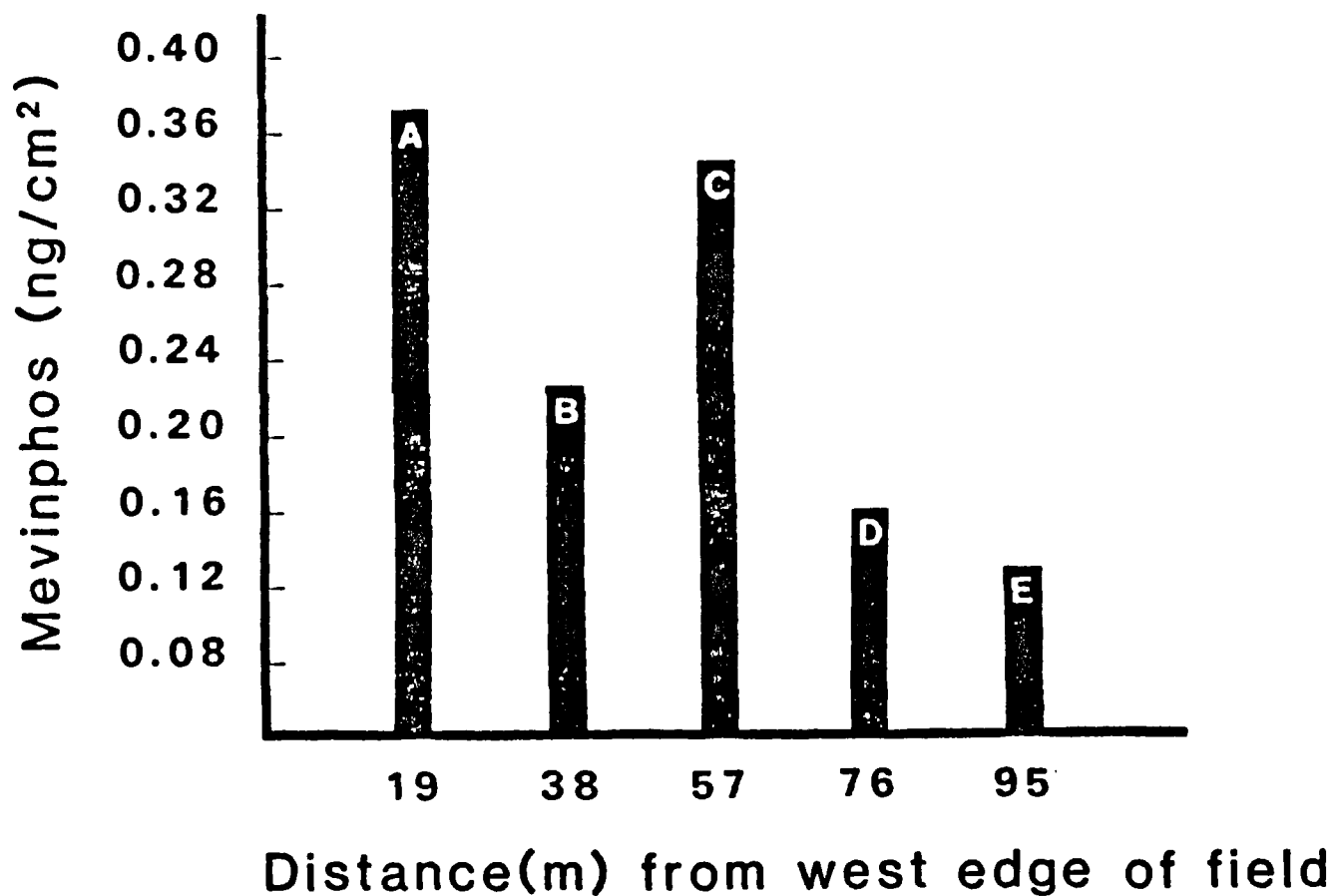
Fig. 2. Deposition of Phosdrin[R] detected as cis-mevinphos in leaf punches collected from turnip foliage along rows from the west edge of the field immediately after an aerial application of Phosdrin[R] 4EC (0.5 pint per acre) on 17 December 1982 at 1500 hours. Letters refer to rows in field.
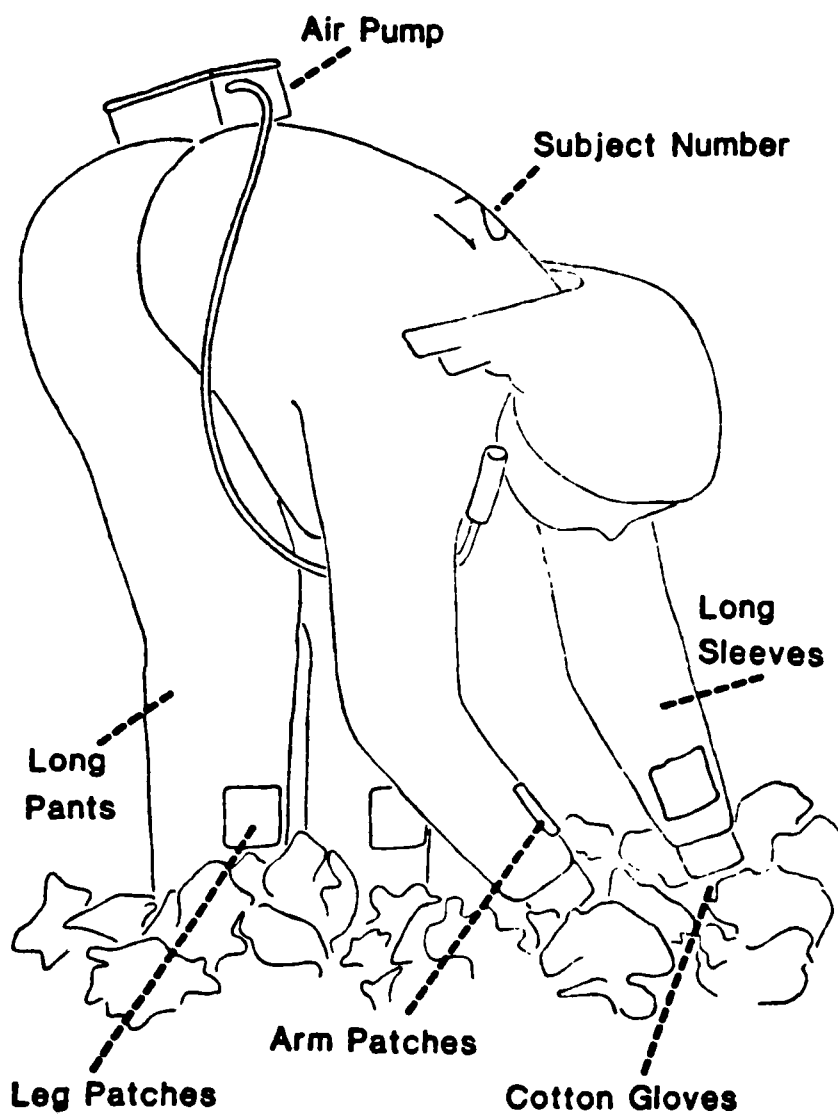
Fig. 3. Positions of sampling devices (air pumps, body patches and gloves) worn by workers harvesting turnips treated with a formulation (Phosdrin$^{(R)}$ 4EC) of mevinphos.
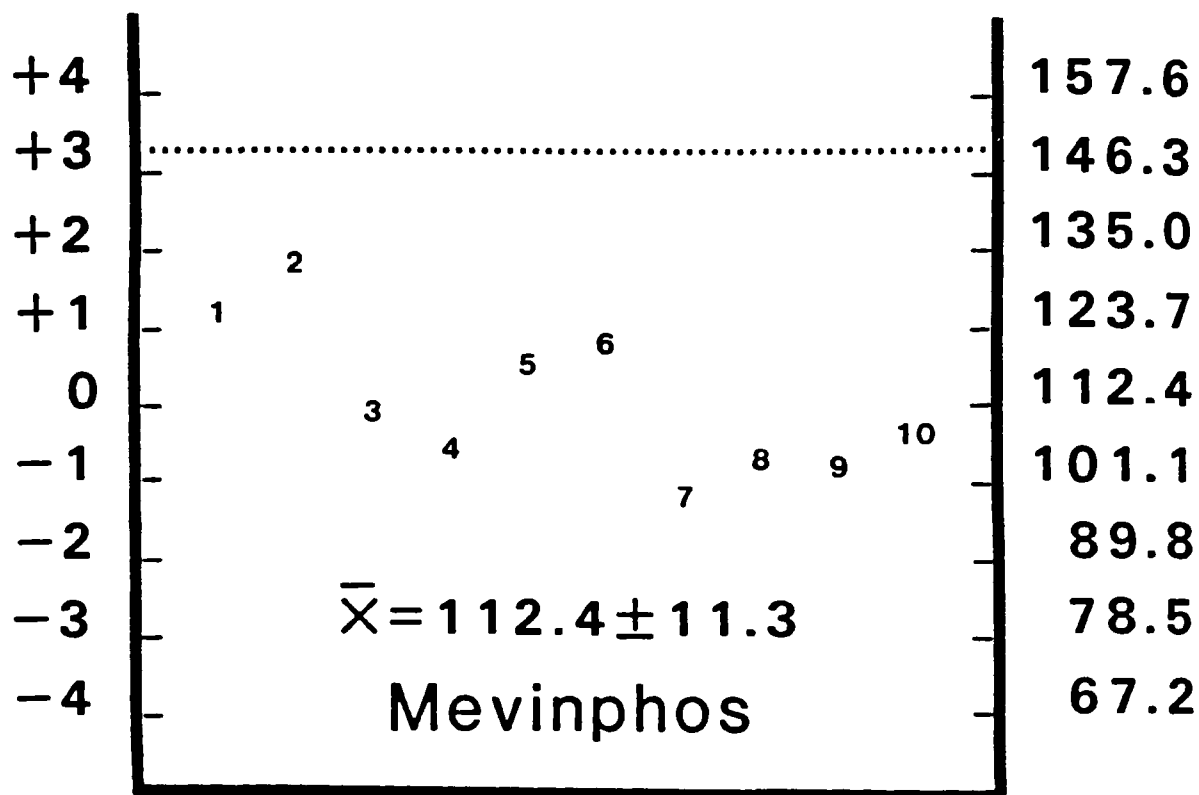
Fig. 4. Normal probability plot of soil samples fortified
with 150 ng mevinphos. Numbers represent individual samples.
Dashed line represents expected recovery of fortified
concentrations (150 ng).
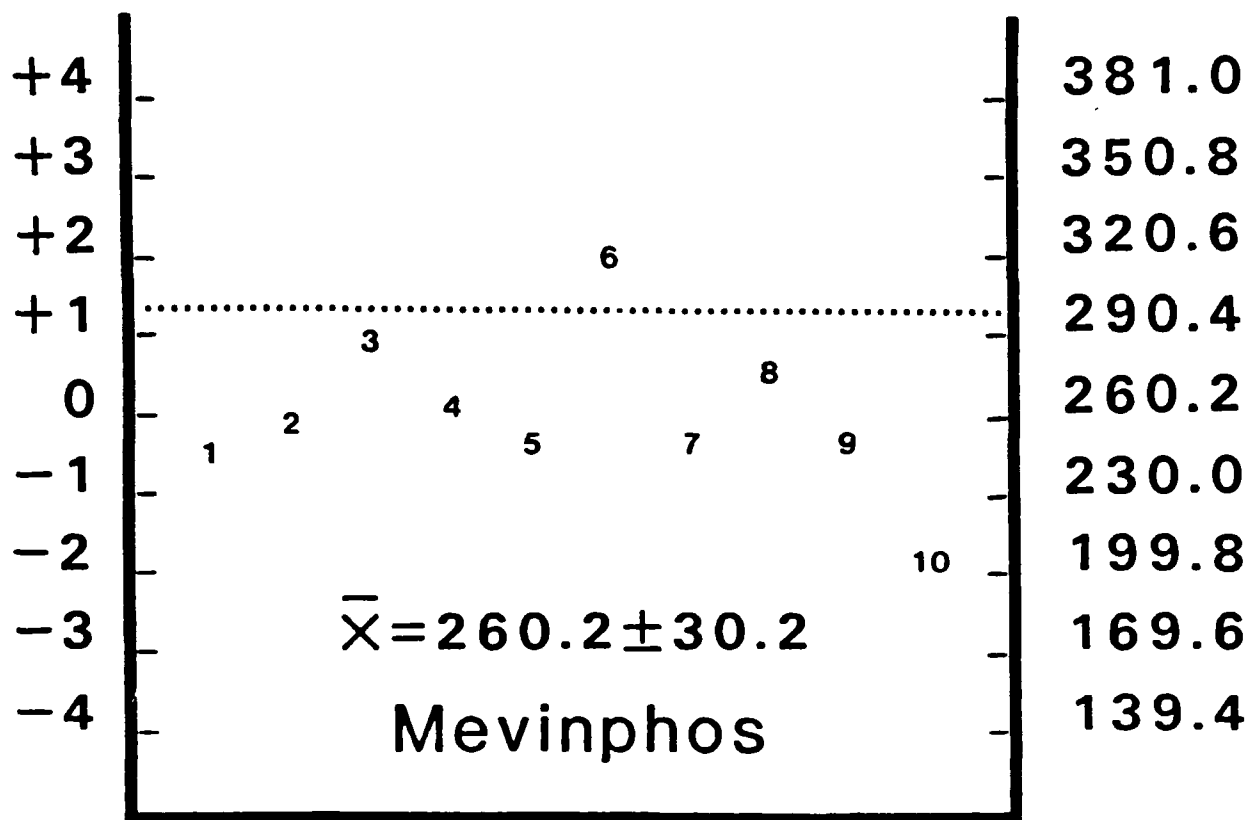
Fig. 5. Normal probability plot of arm patch samples fortified with 300 ng mevinphos. Numbers represent individual samples. Dashed line represents expected recovery of fortified concentrations (300 ng).
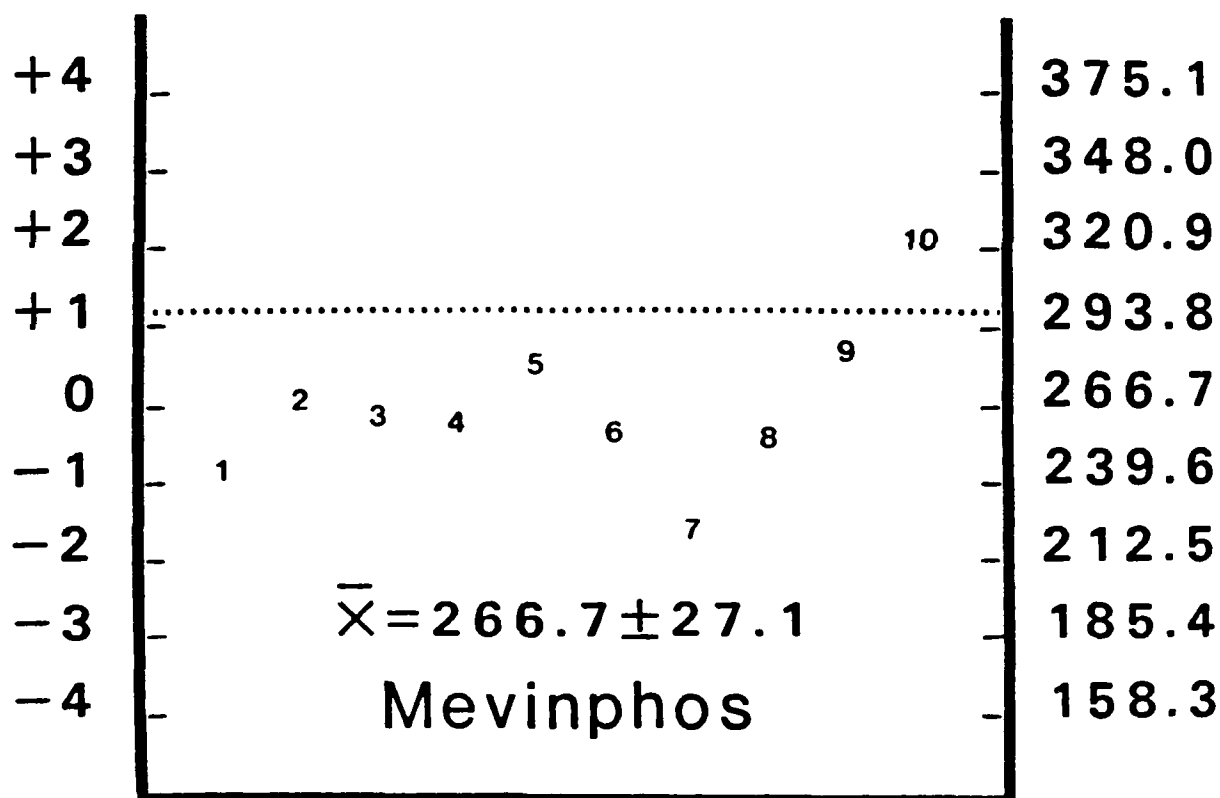
Fig. 6. Normal probability plot of leaf punch samples
fortified with 300 ng mevinphos. Numbers represent
individual samples. Dashed line represents expected
recovery of fortified concentrations (300 ng).
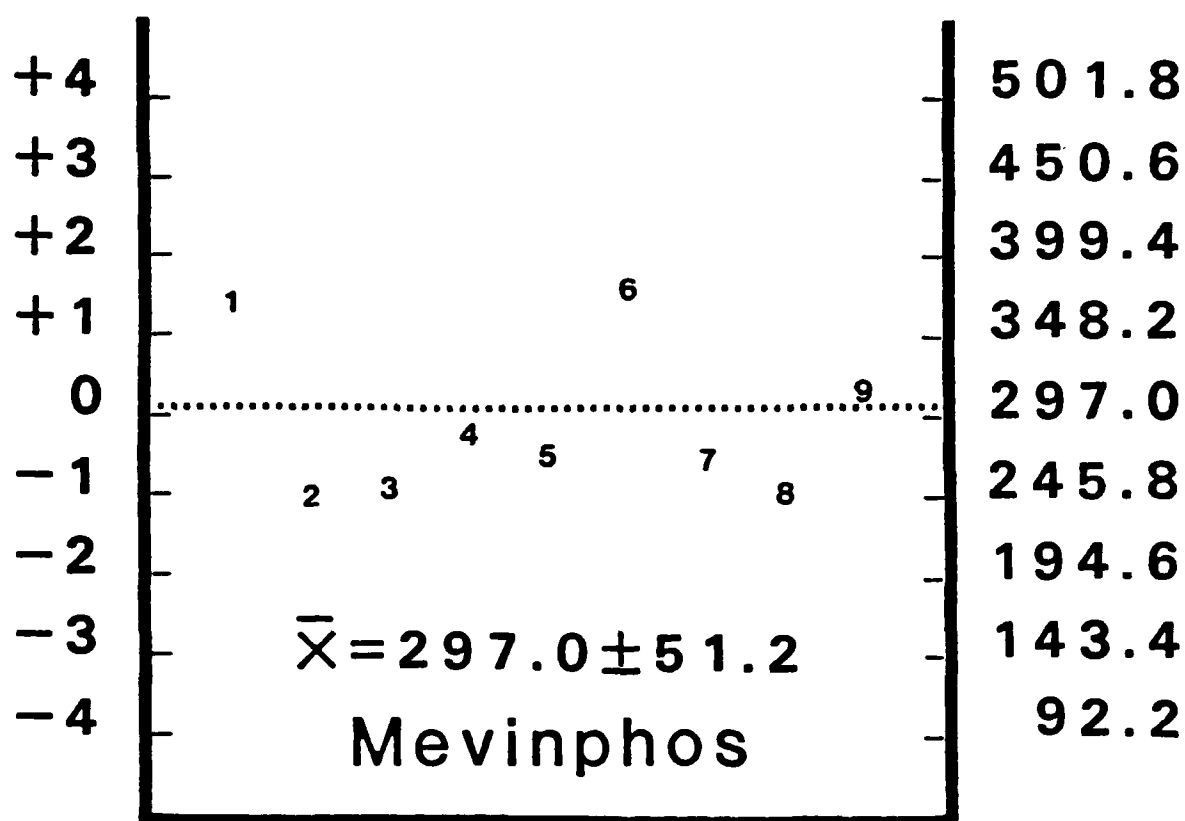
Fig. 7. Normal probability plot of glove samples
fortified with 300 ng mevinphos. Numbers represent
individual samples. Dashed line represents expected
recovery of fortified concentrations (300 ng).

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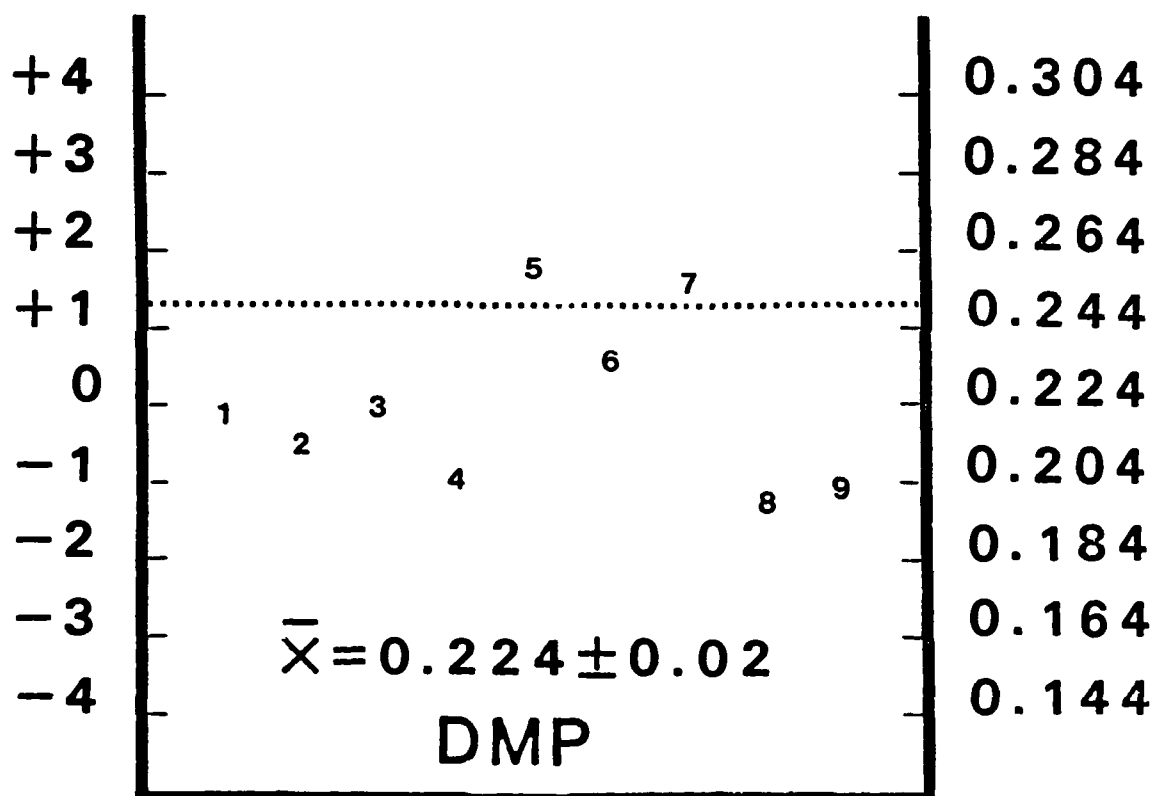
Fig. 8. Normal probability plot of urine samples fortified with 0.25 ug/ml dimethylphosphate (DMP). Numbers represent individual samples. Dashed line represents expected recovery of fortified concentrations (0.25 ug/ml).
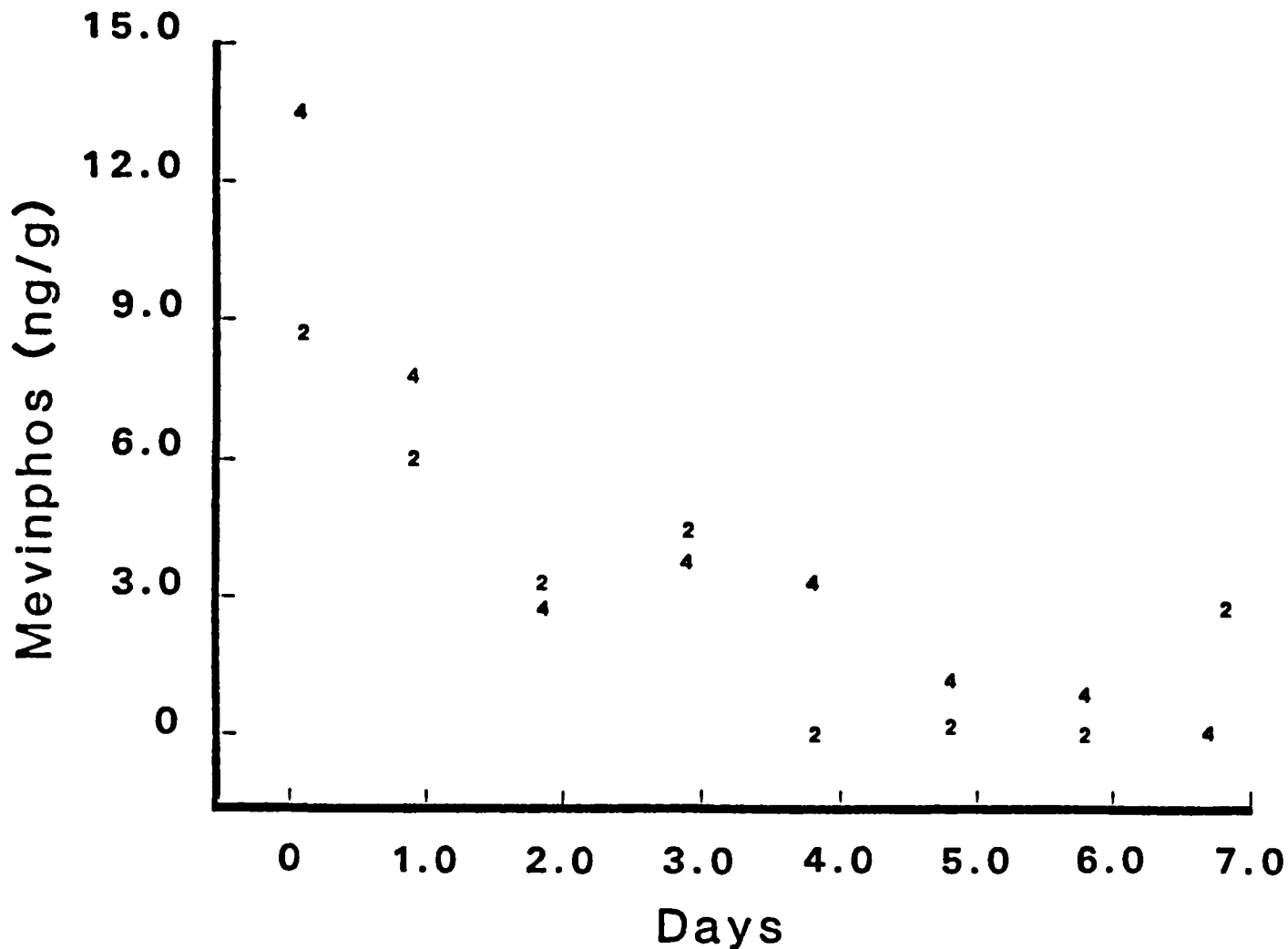
Fig. 9. Decline or loss of residues of Phosdrin[R] detected as cis-mevinphos in soil samples collected from sites 2 and 4 within a turnip field treated with an aerial application of Phosdrin[R] 4EC at the rate of 0.5 pint per acre (17 December 1982, 1500 hours).
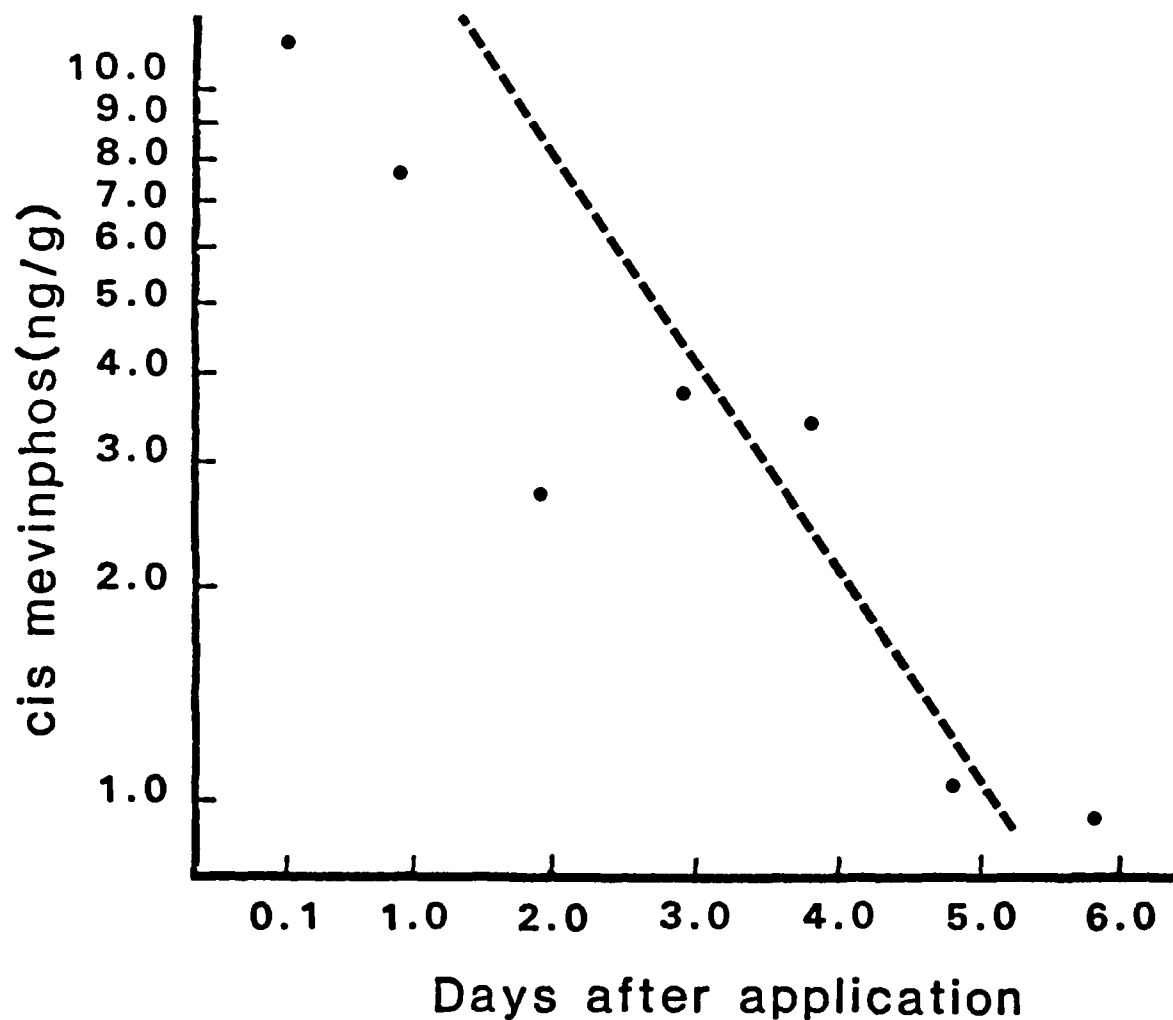
Fig. 10. Semilogarithmic display of residue levels of cis-mevinphos detected in soil from site 4 to estimate rate of decline or loss and the half-life of Phosdrin(R) in soil after application of Phosdrin(R) 4EC at the rate of 0.5 pint per acre (17 December 1982, 1500 hours).
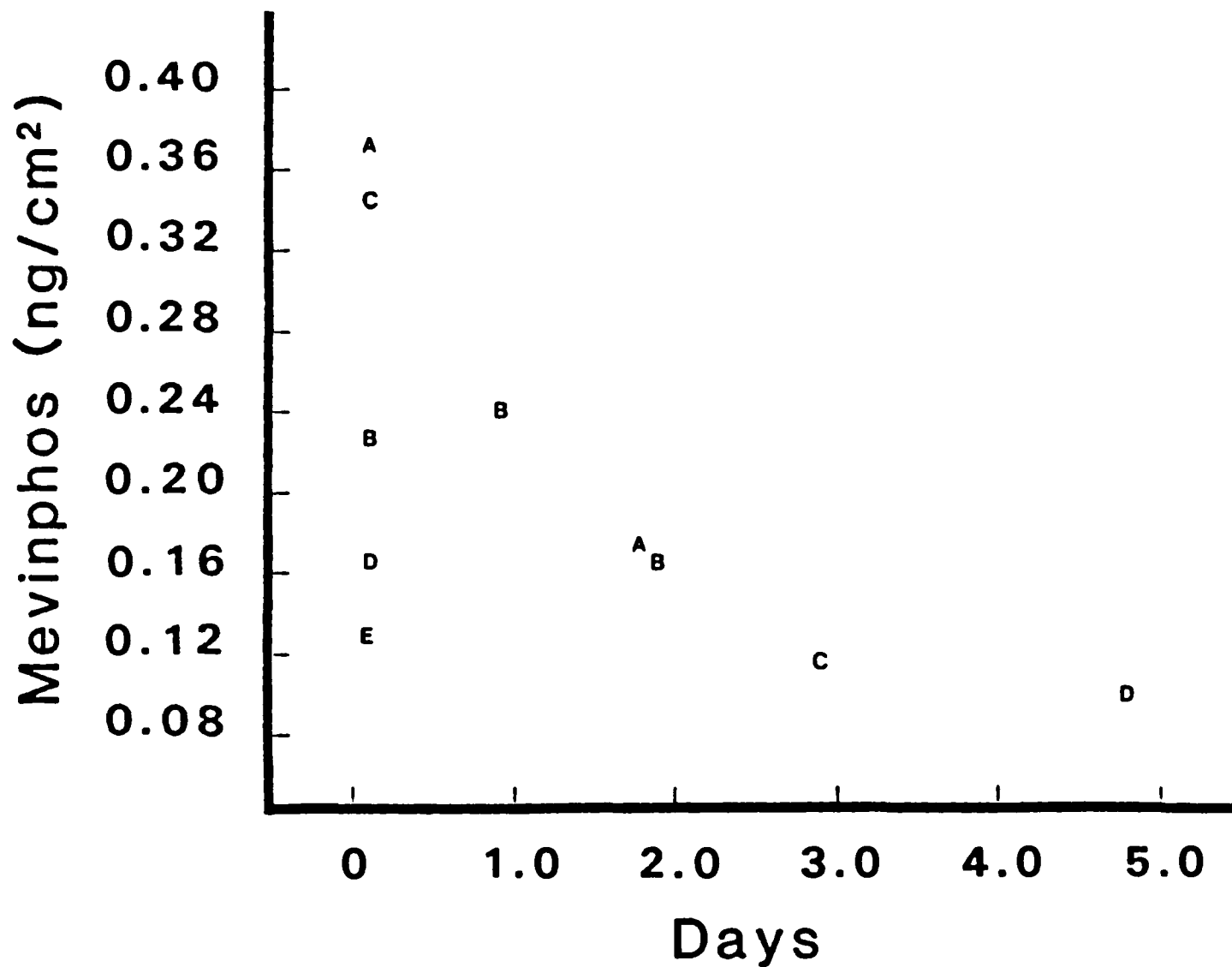
Fig. 11. Decline or loss of Phosdrin(R) detected as cis-mevinphos in leaf punches collected from turnip foliage along rows from the west edge of the field following an aerial application of Phosdrin(R) 4EC (0.5 pint per acre) on 17 December 1982 at 1500 hours. Letters refer to rows within the field (see Fig. 2).

Table 1. Physical characteristics of female workers involved in harvesting turnips after application of Phosdrin[R] 4EC.

Worker Number	Physical Characteristics[a]	
	Age	Weight (Kg)
9	31	-
34	14	50 (110)
38	11	40 (87)
39	14	-
42	13	55 (121)
44	40	59 (130)

[a] Weight in kilograms. Values enclosed are pounds.

Table 2. Physical characteristics of male workers involved in harvesting turnips after application of Phosdrin[R] 4EC.

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| | Physical Characteristics[a] | |
Worker Number	Age	Weight (Kg)
2	53	88 (193)
5	36	109 (240)
14	16	-
19	13	52 (114)
20	12	43 (94)
31	8	25 (55)
32	10	29 (63)
47	55	89 (196)
50	35	69 (152)
52	24	68 (149)
55	34	54 (118)

[a] Weight in kilograms. Values enclosed are pounds.

Table 3. Deposition and loss of mevinphos detected as cis-mevinphos in soil collected from Site 1 (Fig. 1) following aerial application of Phosdrin(R) 4EC at 0.5 pint per acre.

TIME POST APPLICATION		ng/g
Hours	Days	cis-mevinphos
3	0.13	44.00
35	1.45	0.00
74	3.08	3.77
117	4.88	2.25
152	6.33	0.62
191	7.96	0.00
230	9.58	0.00
269	11.21	1.17

Table 4. Deposition and loss of mevinphos detected as cis- mevinphos in soil collected from Site 3 (Fig. 1) following aerial application of Phosdrin(R) 4EC at 0.5 pint per acre.

TIME POST APPLICATION		ng/g
Hours	Days	cis-mevinphos
3	0.13	0.00
35	1.45	0.00
74	3.08	0.00
117	4.88	0.81
152	6.33	0.00
191	7.96	0.00
230	9.58	0.00
269	11.21	1.17

Table 5. Deposition and loss of mevinphos detected as cis-mevinphos in soil collected from Site 5 (Fig. 1) following aerial application of Phosdrin(R) 4EC at 0.5 pint per acre.

TIME POST APPLICATION		ng/g
Hours	Days	cis-mevinphos
3	0.13	1.29
35	1.45	17.10
74	3.08	3.65
117	4.88	0.00
152	6.33	0.27
191	7.96	1.87
230	9.58	0.38
269	11.21	1.86

Table 6. Deposition and loss of mevinphos detected as cis-mevinphos in soil collected from Site 2 (Fig. 1) following aerial application of Phosdrin(R) 4EC at 0.5 pint per acre.

| TIME POST APPLICATION | | ng/g |
Hours	Days	cis-mevinphos
3	0.13	8.67
35	1.45	5.95
74	3.08	3.33
117	4.88	4.46
152	6.33	0.00
191	7.96	0.51
230	9.58	0.00
269	11.21	2.82

Table 7. Deposition and loss of mevinphos detected as cis-mevinphos in soil collected from Site 4 (Fig. 1) following aerial application of Phosdrin(R) 4EC at 0.5 pint per acre.

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TIME POST APPLICATION		ng/g
Hours	Days	cis-mevinphos
3	0.13	13.50
35	1.45	7.71
74	3.08	2.71
117	4.88	3.74
152	6.33	3.37
191	7.96	1.11
230	9.58	0.95
269	11.21	0.00

===

Table 8. Concentrations of Phosdrin[R] detected as cis-mevinphos in leaf punches collected from rows on the first day of application.

Row	Distance (m) from west edge of field	Time of sample collection	Mevinphos concentration (ng/cm^2)
A	19	206	0.37
B	38	213	0.23
C	57	219	0.35
D	76	226	0.16
E	95	225	0.13

Table 9. Deposition and loss of Phosdrin[R] detected as cis-mevinphos (ng/cm^2) on leaf punches collected from row A (19 m from west edge of field) following aerial application of Phosdrin[R] 4EC (0.5 pints per acre).

Post application time		Residue concentration
Hours	Days	Cis-Mevinphos (ng/cm^2)
3	0.1	0.37
36	0.9	0.00
74	1.8	0.17
152	3.8	0.00
192	4.8	0.00

Table 10. Deposition and loss of Phosdrin[R] detected as cis-mevinphos (ng/cm^2) on leaf punches collected from row B (38 m from west edge of field) following aerial application of Phosdrin[R] 4EC (0.5 pints per acre).

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Post application time		Residue concentration
Hours	Days	Cis-Mevinphos (ng/cm^2)
4	0.1	0.23
37	0.9	0.24
75	1.9	0.16
117	2.9	0.00
192	4.8	0.00

==

Table 11. Deposition and loss of Phosdrin(R) detected as cis-mevinphos (ng/cm^2) on leaf punches collected from row C (57 m from west edge of field) following aerial application of Phosdrin(R) 4EC (0.5 pints per acre).

Post application time		Residue concentration
Hours	Days	Cis-Mevinphos (ng/cm^2)
4	0.1	0.35
76	1.9	0.00
117	2.9	0.11
153	3.8	0.00
192	4.8	0.00

Table 12. Deposition and loss of Phosdrin(R) detected as cis-mevinphos (ng/cm^2) on leaf punches collected from row D (76 m from west edge of field) following aerial application of Phosdrin(R) 4EC (0.5 pints per acre).

Post application time		Residue concentration
Hours	Days	Cis-Mevinphos (ng/cm^2)
4	0.1	0.16
37	0.9	0.00
76	1.9	0.00
117	2.9	0.00
192	4.8	0.10

Table 13. Deposition and loss of Phosdrin(R) detected as cis-mevinphos (ng/cm^2) on leaf punches collected from row E (95 m from west edge of field) following aerial application of Phosdrin(R) 4EC (0.5 pints per acre).

Post application time		Residue concentration
Hours	Days	Cis-Mevinphos (ng/cm^2)
4	0.1	0.13
37	0.9	0.00
76	1.9	0.00
117	2.9	0.00
153	3.8	0.00
192	4.8	0.00

Table 14. Residue concentrations of cis-mevinphos on sampling devices (arm patches, gloves, and air samplers) worn by female workers involved in harvesting turnips after application of Phosdrin[R] 4EC.

Worker Number	Residue Concentration Cis-Mevinphos (ng)		
	Arm patch	Gloves	Air sampler
9	0.00	0.00	-
34	0.00	-	-
38	0.00	0.00	-
39	0.00	-	-
42	0.00	0.00	-
44	0.00	-	0.00

Table 15. Residue concentrations of cis-mevinphos on sampling devices (arm patches, gloves, and air samplers) worn by male workers involved in harvesting turnips after application of Phosdrin[R] 4EC.

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Worker Number	Residue Concentration Cis-Mevinphos (ng)		
	Arm patch	Gloves	Air sampler
2	0.00	0.00	-
5	0.00	0.00	-
14	0.00	0.00	-
19	0.00	-	0.00
20	130.00	-	-
31	0.00	-	-
32	0.00	0.00	-
47	0.00	0.00	-
50	0.00	0.00	0.00
52	0.00	-	0.00
55	-	-	0.00

Table 16. Urinary metabolite, dimethylphosphate (ug/ml) detected in urines collected from six female workers while harvesting turnips treated with Phosdrin(R) 4EC. FMV = first morning void (0530-0700).

Worker Number	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolite (ug/ml) Dimethylphosphate (DMP)
9	1	1	1030	0.00
	2	2	FMV	0.01
34	1	1	0800	0.00
	2	1	1100	0.02
	3	2	FMV	0.00
38	1	1	0800	0.00
	2	2	FMV	0.00
39	1	1	0800	0.01
	2	1	1100	0.01
	3	2	FMV	0.07
42	1	1	0800	0.00
	2	1	1110	0.00
44	1	1	0800	0.00
	2	1	1105	0.00
	3	2	FMV	0.01

Table 17. Urinary metabolite, dimethylphosphate (ug/ml) detected in urines collected from eleven male workers while harvesting turnips treated with Phosdrin(R) 4EC. FMV = first morning void (0530-0700).

Worker Number	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolite (ug/ml) Dimethylphosphate (DMP)
2	1	1	0800	0.00
	2	1	1100	0.00
	3	2	FMV	0.00
5	1	1	0800	0.01
	2	1	1045	0.00
14	1	1	0800	0.02
	2	1	1100	0.00
19	1	1	0800	0.00
	2	1	1045	0.00
	3	2	FMV	0.01
20	1	1	0800	0.00
	2	1	1045	0.00
	3	2	FMV	0.01
31	1	1	0800	0.00
	2	1	1100	0.01
	3	2	FMV	0.01
32	1	1	0800	0.00
	2	1	1105	0.00
	3	2	FMV	0.00
47	1	1	0800	0.00
	2	1	1100	0.03
50	1	1	0800	0.00
	2	1	1105	0.00
52	1	1	0800	0.00
	2	1	1100	0.00
55	1	1	0800	0.00
	2	1	1120	-

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Table 18. Temperature extremes at the study site between the date of application (17 December) of mevinphos and the date of harvest of turnip greens (27 December).

Day (December 1982)	Maximum Temperature (°F)	Minimum Temperature (°F)	Rainfall (in)
17	75	48	-
18	78	57	-
19	80	51	-
20	74	50	-
21	79	59	-
22	81	60	-
23	82	64	-
24	84	69	-
25	84	65	-
26	77	51	-
27	59	47	-

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LITERATURE CITED

Abbadie, D., M. Colle, J. Battin. 1980. Intoxication by organophosphorous insecticides. A case history of a 2 year old infant. Pediatrie 35(6): 545-552.

Beynon, K. I., D. H. Hutson, and A. N. Wright. 1973. The metabolism and degradation of vinyl phosphate insecticides in Residue Reviews. Springer-Verlag, New York.

Bondy, M. K., R. H. Lebow, M. O'Malley, T. Reilly. 1976. Occupational health and safety for agricultural workers. DHEW (NIOSH) Publ. No. 77-150. Washington, D.C.

Casida, J. E., P. E. Gatterdam, J. B. Knaak, R. D. Lance, and R. P. Niedermeier. 1958. Bovine metabolism of organophosphorous insecticides. Subacute feeding studies with 0,0-dimethyl 1-carbomethoxy-1-propen-1-yl phosphate. J. Agr. Food Chem. 6:658-662.

Conover, W. J. 1980. Practical nonparametric statistics, 2ed. John Wiley & Sons, New York.

Eto, M. 1979. Organophosphorus pesticides: organic and biological chemistry. CRC Press, Inc., Boca Raton, FL.

Federal Working Group on Pest Management. 1974. Occupational exposure to
pesticides. Report to the Federal Working Group on Pest Management from
the Task Group on Occupation Exposure to Pesticides. 155 pp.

Fukuto, T. R., E. O. Horning, R. L. Metcalf, and M. Y. Winston. 1961. The
configuration of the alpha and beta isomers of methyl 3-
(dimethoxyphosphinyloxy)crotonate (Phosdrin[R]). J. Org. Chem. 26:
4620.

Gunther, F. A., J. H. Barkley, and W. E. Westlake. 1974. Worker environment
research. II. Sampling and processing techniques for determining
dislodgable pesticide residues on leaf surfaces. Bull. Env. Cont. Tox.
12(6):641-644.

Haley, T. J., E. R. Reichert, and H. W. Klemmer. 1978. Acute human poisoning
with parathion and mevinphos. Fed. Proc. Fed. Am. Soc. Exp. Biol. 37(3):
247.

Hayes, W. J., Jr. 1982. Pesticides studies in man. Williams & Wilkins,
Baltimore/London. 455 pp.

Hutson, D. H., B. A. Pickering and C. Donninger. 1972. Phosphoric acid
triester-glutathione alkyltransferase. A mechanism for the
detoxification of dimethyl phosphate triesters. Biochem. J. 127:285-293.

Maddy, K. T., and S. C. Edminston. 1982. Pesticide safety program of the California Department of Food and Agriculture based upon measurements of potential workplace exposure and the elimination of excess exposures. In J. R. Plimmer, ed., ACS Symposium Series, No. 182., American Chemical Society, Washington, DC.

McCraw, B. D. 1979. Easy gardening...turnips and mustards. Texas Agricultural Extension Service. Publ. No. L-1589. 4 unnumbered pp.

Merck Index. 1976. Ninth Ed. Merck & Co., Inc., Rahway, N.J.

Mollhagen, T., C. C. Dary, A. Guillen, Jr., and V. F. Cox. 1985. An assessment of cucumber harvesters to methomyl. Draft submitted to U.S. Environmental Protection Agency, Washington, DC.

Morello, A., A. Vardanis, and E. Y. Spencer. 1968a. Comparative metabolism of two vinyl phosphorothionate isomers (Thiono Phosdrin) by the mouse and the fly. Biochem. Pharmacol. 17:1795-1802.

Morello, A., A. Vardanis, and E. Y. Spencer. 1968b. The role of glutathione in the detoxification of some dimethyl vinyl organophosphorus compounds. Abstracts 155th Meeting American Chemical Society, San Francisco, April 1-5, A-51.

Morello, A., A. Vardanis, and E. Y. Spencer. 1968c. Mechanism of detoxication of some organophosphorous compounds: The role of glutathione-dependent demethylation. Can. J. Biochem. 46:885-892.

Murphy, S. D. 1975. Pesticides in toxicology, the basic science of poisons. Macmillan Publishing Co., Inc., New York. 768 pp.

Shell Chemical Company, Agricultural Chemicals. 1982. Label: Phosdrin[R] 4EC Insecticide. Houston, TX.

Zavaleta, A. N. 1981. Introduction - Mexican American health status: selected topics from the borderlands. Borderlands J. 4(1):1-6.

Zweig, G., R. Gao, J. M. Witt, W. J. Popendorf, and K. T. Bogen. 1985. Exposure of strawberry harvesters to carbaryl in Dermal Exposure Related to Pesticide Use. American Chemical Society, Washington, D.C.

Appendix A

Chromatographic Summaries

The tables that follow in this section are summaries of the chromatographic sequence of injected standards for autocalibration and the companion quality controls for each substrate.

Table A1. Chromatographic summary of injection sequence for recovery of mevinphos from soil samples (10 g) fortified with 150 ng cis-mevinphos.

Sequence	Sample[a]/ Type	Observed Recovery (ng)	Peak Area	Peak Retention Time	Percent Recovery
1	Standard	148.0	222831	1.62	-
2	Blank	1.96	2913	1.60	-
3	Q.C.	126.0	187574	1.63	84.0
4	Q.C.	133.0	197564	1.63	88.7
5	Autocal	168.0	249177	1.62	-
6	Q.C.	112.0	185420	1.63	74.7
7	Q.C.	106.0	175610	1.65	70.7
8	Q.C.	113.0	188086	1.62	75.3
9	Autocal	160.0	265169	1.62	-
10	Q.C.	122.0	215895	1.63	81.3
11	Q.C.	98.0	172839	1.63	65.3
12	Q.C.	103.0	182116	1.62	68.7
13	Autocal	154.0	272427	1.62	-
14	Q.C.	103.0	187228	1.63	68.7
15	Q.C.	108.0	196458	1.65	72.0

[a]/ Sequence for recovery of 150 ng standard, blank, and quality control samples fortified with 150 ng autocalibration on 150 ng standard.

Table A2. Chromatographic summary of injection sequence for recovery of mevinphos from gauze patches (100 cm^2) fortified with 300 ng cis-mevinphos.

Sequence	Sample[a] Type	Observed Recovery (ng)	Peak Area	Peak Retention Time	Percent Recovery
1	Standard	-	255594	1.73	-
2	Blank	0.0	-	-	-
3	Q.C.	245.0	208645	1.78	81.7
4	Q.C.	258.0	219899	1.78	86.0
5	Q.C.	288.0	245055	1.78	96.0
6	Q.C.	262.0	223096	1.77	87.3
7	Q.C.	250.0	212809	1.73	83.3
8	Q.C.	319.0	220927	1.75	106.0
9	Q.C.	250.0	213310	1.77	83.3
10	Q.C.	276.0	235265	1.73	92.0
11	Q.C.	250.0	212699	1.75	83.3

[a] Sequence for recovery of 300 ng standard, blank, and quality control samples fortified with 300 ng cis-mevinphos.

Table A3. Chromatographic summary of injection sequence for recovery of mevinphos from gloves (549.7 cm^2) fortified with 300 ng cis-mevinphos.

Sequence	Sample[a]/ Type	Observed Recovery (ng)	Peak Area	Peak Retention Time	Percent[b]/ Recovery
1	Standard	-	91362	3.37	-
2	Autocal	-	70943	3.37	-
3	Autocal Straight Spike	-	557674	3.35	-
4	Blank	-	-	-	-
5	Q.C.	368.0	228144	3.38	122.7
6	Q.C.	247.0	152983	3.40	82.3
7	Autocal	352.0	654864	3.37	-
8	Q.C.	249.0	181338	3.40	83.0
9	Q.C.	287.0	208885	3.43	95.7
10	Autocal	323.0	704913	3.33	-
11	Q.C.	272.0	212902	3.40	90.7
12	Q.C.	379.0	297094	3.38	126.3
13	Q.C.	265.0	207533	3.40	88.3
14	Q.C.	250.0	588712	3.52	83.3
15	Q.C.	301.0	709293	3.37	100.3

a/ Sequence for recovery of 300 ng standard, blank, straight spike, and quality control samples fortified with 300 ng cis-mevinphos.

b/ Percent recovery based on straight spike (Peak area = 557674) used as standard.

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Table A4. Chromatographic summary of injection sequence for recovery of mevinphos from leaf samples (50 cm^2) fortified with 300 ng cis-mevinphos.

Sequence	Sample[a] Type	Observed Recovery (ng)	Peak Area	Peak Retention Time	Percent[b] Recovery Autocal	Straight Spike
1	Standard	-	226029	1.65	-	-
2	Autocal	345.0	260045	1.65	-	-
3	Straight Spike	254.0	219837	1.65	-	-
4	Blank	0.0	-	-	-	-
5	Q.C.	206.0	178639	1.67	68.7	81.3
6	Q.C.	227.0	197462	1.67	75.7	89.7
7	Autocal	234.0	202806	1.67	-	-
8	Autocal	385.0	260336	1.67	-	-
9	Autocal	304.0	263588	1.67	-	-
10	Q.C.	219.0	192606	1.67	73.0	87.7
11	Q.C.	218.0	191548	1.68	72.7	87.0

Sequence	Sample[a] Type	Observed Recovery (ng)	Peak Area	Peak Retention Time	Percent[b] Recovery	
					Autocal	Straight Spike
12	Q.C.	235.0	206826	1.67	78.3	94.0
13	Autocal	244.0	213966	1.67	-	-
14	Autocal	277.0	197218	1.67	-	-
15	Q.C.	215.0	189094	1.68	71.2	86.0
16	Autocal	468.0	411575	1.65	-	-
17	Autocal	291.0	398708	1.65	-	-
18	Q.C.	288.0	382601	1.65	96.0	-
19	Q.C.	324.0	430637	1.67	108.0	-
20	Q.C.	224.0	297404	1.63	74.7	-
21	Q.C.	246.0	327278	1.65	82.0	-

[a] Sequence for recovery of 300 ng standard, blank, straight spike, and quality control samples fortified with 300 ng cis-mevinphos.

[b] Percent recovery based on autocalibration and straight spike (Peak area = 219837) used as standard.

Table A5. Chromatographic summary of injection sequence for recovery of dimethylphosphate (DMP) from urine samples fortified with 0.25 ug/ml DMP.

Sequence	Sample[a/] Type	Observed Recovery (ug/ml)	Peak Area	Peak Retention Time	Percent Recovery
1	Standard	0.229	337433	2.53	-
2	Autocal	0.257	346448	2.53	-
3	Q.C.	0.220	304654	2.53	88.0
4	Q.C.	0.214	296536	2.53	85.6
5	Q.C.	0.225	311605	2.53	90.0
6	Autocal	0.245	339299	2.52	-
7	Q.C.	0.204	277315	2.53	81.6
8	Q.C.	0.260	352994	2.53	104.0
9	Q.C.	0.236	320959	2.53	94.4
10	Q.C.	0.256	335202	2.53	102.4
11	Autocal	0.246	327867	2.52	-
12	Q.C.	0.199	260707	2.53	79.6
13	Q.C.	0.202	265265	2.53	80.8

a/ Sequence for recovery of 0.25 ug/ml standard and quality control samples fortified with 0.25 ug/ml autocalibration on 0.25 ug/ml standard.

Appendix B

Additional Results

The tables that follow in this section are additional results which may be useful in drawing conclusions about information presented in the text.

Table B1.   Confirmation of cis-mevinphos in air cartridges by two column method.

| | Column Type | | | |
| | 10% DC200 | | SE 30/OV210 | |
Sample	Peak Area	Peak Retention Time	Peak Area	Peak Retention Time
2	27772	3.68	31193	0.67
5	19042	3.72	70666	0.67
6	18076	3.70	58128	0.67
Autocal	398997	3.52	135721	0.62
Autocal	410806	3.52	117235	0.62

Table B2. Residue concentrations of cis-mevinphos on sampling devices (arm patches and gloves) worn by agricultural workers involved in harvesting turnips after application of Phosdrin(R) 4EC. M = male; F = female.

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Worker Number	Sex	Residue Concentration Cis-Mevinphos (ng)	
		Arm patch	Gloves
1	M	0.00	-
3	F	0.00	-
4	M	0.00	-
6	M	0.00	-
7	M	-	0.00
8	M	0.00	-
10	M	0.00	-
11	M	0.00	-
12	M	0.00	-
13	M	0.00	-
16	M	0.00	-
17	M	0.00	-
18	M	0.00	-
22	M	4.72	-
23	M	0.00	-

Table B2 Cont.

Worker Number	Residue Concentration Cis-Mevinphos (ng)		
	Sex	Arm patch	Gloves
30	M	0.00	-
33	F	0.00	0.00
35	F	0.00	-
36	F	0.00	-
37	F	0.00	-
40	F	0.00	-
41	F	0.00	0.00
45	F	-	0.00
46	M	0.00	-
49	M	0.00	-
51	M	0.00	-
53	F	0.00	-
54	F	0.00	-
56	M	0.00	-
57	F	0.00	-

Table B3. Urinary metabolite, dimethylphosphate (ug/ml) detected in urines collected from agricultural workers while harvesting turnips treated with Phosdrin(R) 4EC. FMV = first morning void (0530-0700); M = male; F = female.

Worker Number	Sex	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolite (ug/ml) Dimethylphosphate (DMP)
1	M	1	1	0800	0.03
		2	2	FMV	0.00
3	F	1	1	0800	0.00
		2	1	1100	0.01
4	M	1	1	0800	0.00
		2	1	1045	0.00
		3	2	FMV	0.00
6	M	1	1	0800	0.00
		2	1	1100	0.00
7	M	1	1	0800	0.00
		2	1	1105	0.01
8	M	2	1	1100	0.00
10	M	1	1	0800	0.00
		2	1	1100	0.00
11	M	1	1	0800	0.00
		2	2	1045	0.01
12	M	1	1	0800	0.00
		2	1	1045	0.01
13	M	1	1	0800	0.00
		2	1	1100	0.00
15	M	1	1	0800	0.01
		2	1	1100	0.01
16	M	1	1	0800	0.04
		2	1	1100	0.05
		3	2	FMV	0.02
17	M	1	1	0800	0.01
		2	1	1045	0.00
		3	2	FMV	0.00

Table B3. Cont.

Worker Number	Sex	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolite (ug/ml) Dimethylphosphate (DMP)
18	M	1	1	0800	0.02
		2	1	1045	0.01
		3	2	FMV	0.00
21	M	2	1	1100	0.00
		3	2	FMV	0.00
22	M	1	1	0800	0.00
		2	1	1105	0.00
		3	2	FMV	0.00
23	M	1	1	0800	0.01
		2	1	1100	0.01
		3	2	FMV	0.00
30	M	1	1	0800	0.00
		2	1	1045	0.00
		3	2	FMV	0.04
33	F	1	1	0800	0.01
		2	1	1100	0.00
35	F	2	1	1110	0.00
36	F	1	1	0800	0.01
		2	1	1110	0.01
37	F	1	1	0800	0.00
		2	1	1120	0.00
40	F	1	1	0800	0.02
		2	1	1100	0.01
		3	2	FMV	0.07
41	F	1	1	0800	0.00
		2	1	1100	0.00
45	F	1	1	0800	0.01
		2	1	1105	0.00

Table B3. Cont.

Worker Number	Sex	Void Number	Day of Void Collection	Time of Void Collection	Urinary Metabolite (ug/ml) Dimethylphosphate (DMP)
46	M	1	1	0800	0.00
		2	1	1100	0.00
		3	2	FMV	0.00
49	M	1	1	0800	0.03
		2	1	1110	0.01
51	M	1	1	1110	0.00
53	F	1	1	0800	0.01
		2	2	FMV	0.02
54	F	1	1	0800	0.00
		2	1	1045	0.00
		3	2	FMV	0.00
56	M	1	2	FMV	0.00
57	F	1	2	FMV	0.00

Appendix C

Methods

Extraction of Insecticides from Soil

1. Weigh 10 g of soil and place in a 250 ml Erlenmeyer flask.

2. Extract twice with 50 mls of acetone, 15 min.

3. Filter, extract and evaporate to 5 mls.

4. Check sample for OP's using FPD.

5. Prepare a florisil column and pass sample through collecting the
   6 and 15% eluates; 6 and 15% ethyl ether in petroleum ether.
   Evaporate samples to 5 mls and take to chromatography lab.
   (Note) Step 5 only applies when extracting soil for organochlorines.

Extraction of Plant Tissue (Leaves) for Dislodgable Residues

1. Take 50 cm^2 or 10 large leaf punches and weigh them.

2. Place the samples in 120 cc urine specimen cups and add to each 3 drops of surfactant (Witconol NP-100 @ 0.5% concentration) and 75 mls H$_2$O.

3. Extract for 15 minutes using the shaker in the round set at the fastest speed possible.

4. Pass the extract to a 1,000 ml (dilute sample extract volume to 500 mls with deionized H$_2$O) separatory funnel and re-extract the sample as before for a second time.

5. Collect both extracts in separatory funnels and adjust the volume to approximately 600 mls using 5% Na$_2$SO$_4$.

6. Extract the sample contained in the separatory funnels three times with 150 mls of Dichloromethane (Methylene chloride).

7. Collect both extracts and dry with Na$_2$SO$_4$ granules.

8. Evaporate to 0.5 mls and adjust volume to 5.0 mls using methanol.

9. Take samples to chemist for the addition of the internal standard.

1. Place one 4" X 4" gauze patch in a 500 ml Erlenmeyer flask and add 150 mls of methanol.

2. Extract twice using a Burrell Wrist-Action Shaker set at #6.

3. Collect to extracts and dry using Na_2SO_4 and evaporate to 5 mls.

4. Take to chemist for the addition of the internal standard.

Extraction of Bond Elute Cartridges

for Organophosphates and Organochlorine

1. Pass 100 mls of acetone through the cartridge at approximately 5 mls a minute.

2. Dry with Na_2SO_4.

3. Evaporate to 5 mls and take to GC room.

ALKYL PHOSPHATES by Benzyl Method

Preparation of Standards & Solutions:

1. Prepare an alkyl phosphate standard at the following concentrations: Prepare two standards daily.

KDMP	.25 ug/ml
KDEP	.25 ug/ml
KDMTP	.50 ug/ml
KDETP	.50 ug/ml

2. Prepare 3-benzyl-1-p-toyltriayene derivatizing reagent:
    250 mg above in 200 mls chloroform
    (must prepare this daily)

3. Prepare NaCl/HCl solution: 100 g NaCl
    175 ml 12 N HCl
    Bring up to 1 liter with H_2O

Procedure:

1. Place 1 ml of urine sample in 30 ml micro impinger tube.

2. Bring up to 20 ml mark with CH_3CN (acetonitrile). Add approximately 200 mg NaCl (small spatula full).

3. Azeotrope at approximately 90-95° C, almost to dryness. (Do not Dry)

4. Add approximately 5 mls additional acetonitrile and azeotrope to approximately 1 ml.

5. Derivatize with 20 mls benzyl derivatizing reagent and evaporate to 1 ml, placing a one ball snyder column on impinger tube.

6. Let solution set for about 20 minutes.

7. Add 15 mls NaCl/HCl solution.

8. Extract three times with 6.0 mls ethyl ether. Do this using glass stoppers and vortexing each extraction for 2 minutes.
    HINT: Easiest to remove organic layer with 5 ml macropipet.

9. Dry with Na_2SO_4.

10. Evaporate to 0.1 ml.

11. Adjust to 1 ml with acetone.
    Note: For standard, dilute to 100 mls in volumetric flask.

Reid, S. J. and Watts, R. R. (1981). A method for the determination of dialkyl phosphate residues in urine. J. Analyt. Tox. 5, 126-132.

Extraction of Gloves for Pesticides

1. Cut gloves into approximately 1 inch square pieces.

2. Place sample into 1000 ml Erlenmeyer flask and extract with methanol (200 ml portions) three times on wrist-action shaker for 20, 15, and 15 minutes.

3. Decant through glasswool in funnel into second 1000 ml Erlenmeyer flask. Place sufficient sodium sulfate to absorb any moisture in the extract. Transfer to round bottom evaporating flask.

4. During second wrist-action extraction evaporate samples down so second extraction will fit into round bottom evaporating flask.

5. Repeat for third extraction.

6. Bring down to approximately 1 ml.

7. Prepare columns necessary:

   Pack with glasswool at the tip about 1 cm high.
   Add approximately 5.5 grams sodium sulfate (one large glass scoop full)

8. Transfer sample from round bottom into column and collect in 50 ml tube. Rinse four times with 5 ml increments of desired final solvent.

9. Evaporate under nitrogen, purge to approximately 2 mls. Vortex and centrifuge sample.

10. Transfer to centrifuge tube. Rinse 50 ml tube twice with 2 ml aliquots of solvent. Add to transferred solvent.

11. Re-evaporate to desired volume. Vortex and centrifuge.

12. Take to GC lab.

Gas Chromatographic Conditions for Detection of Cis-Mevinphos

Column 1

Instrument - Tracor 222 gas chromatograph

Column - 4% SE30/6% OV210

Flow rate 20 cc/min., 200° C.

Detector F.P.D., phosphorous mode

Input attenuation 10^3

Output attenuation 32

Bucking range 6

Detector flow control

    O_2 85 ml/min.

    H 100 ml/min.

Column 2

Instrument - Tracor 222 gas chromatograph

Column - 10% DC 200

Flow rate 50 cc/min., 165° C.

Detector F.P.D., phosphorous mode

Input attenuation 10^3

Output attenuation 64

Bucking range 6

Detector flow control

    O_2 150 ml/min.

    H 150 ml/min.