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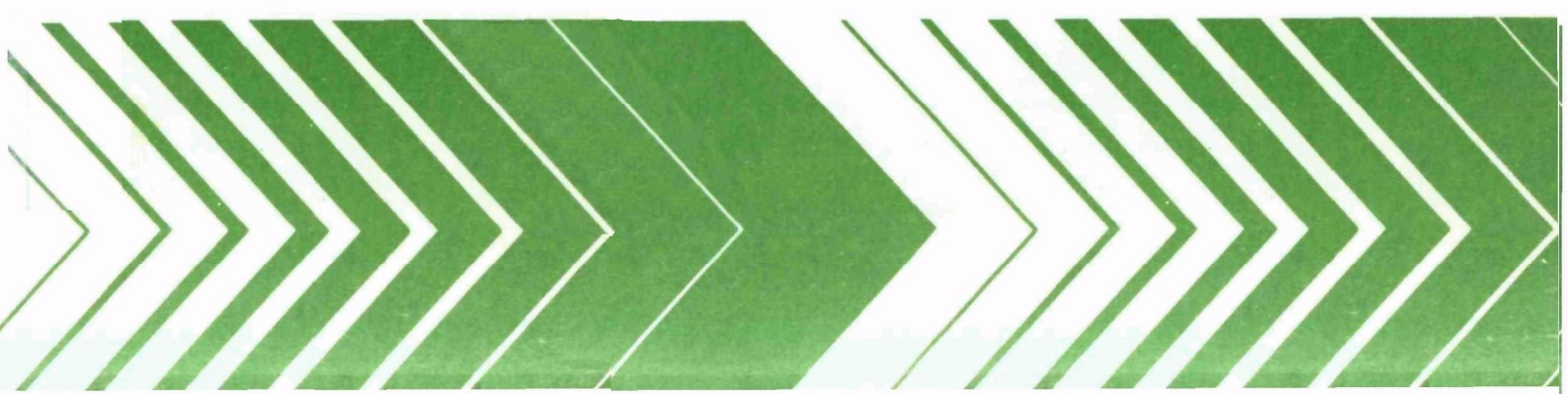
Adsorption, Movement, and Biological Degradation of Large Concentrations of Selected Pesticides in Soils



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EPA-600/2-80-124
August 1980

ADSORPTION, MOVEMENT, AND BIOLOGICAL DEGRADATION OF LARGE CONCENTRATIONS OF SELECTED PESTICIDES IN SOILS

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and intergrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communication link between the researcher and the user community.

This report presents the results of a study on the behavior of selected pesticides in soils when the pesticide is present at large concentrations. The work was conducted because of uncertainty whether the existing low-concentration agricultural data base could be extrapolated to predict the behavior of large concentrations of pesticides in soils at disposal sites.

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ABSTRACT

Because of the importance of soil in biologically reducing the quantity and retarding the rate of pollutant movement into groundwater, this laboratory study was initiated to evaluate the adsorption, mobility, and degradation of large concentrations of the pesticides atrazine, methyl parathion, terbacil, trifluralin, and 2,4-D in soils representing four major soil orders in the United States.

Equilibrium adsorption isotherms of the non-linear Freundlich type were obtained for all pesticides and the four soils. Pesticide solution concentrations used in the study ranged from zero to the aqueous solubility limit of each pesticide. The mobility of each pesticide increased as the concentration of the pesticide in the soil solution phase increased. These results were in agreement with the equilibrium adsorption isotherm data. Pesticide degradation rates and soil microbial populations generally declined as the pesticide concentration in the soil increased; however, some soils were able to degrade a pesticide at all concentrations studied, while others remained essentially steril throughout the incubation period (50 to 80 days). As shown by measurements of $^{14}CO_2$ evolution, total CO_2 evolution was not always a good indication of pesticide degradation. Several pesticide metabolites were formed and identified in various soil-pesticide systems. The quantities of trifluralin and atrazine "bound" to the soil at the end of the incubation period were measured and in some cases appeared to be related to types of metabolites formed during biological degradation.

The observed increase in pesticide mobility for large pesticide concentrations in the soil invalidates, in many cases, the usefulness of the existing low concentration data base for designing pesticide waste disposal sites. Owing to the increased mobility and lower microbial decompostion rates of many pesticides when introduced into soils at waste disposal concentrations, the potential for groundwater contamination is increased signitifantly. The data presented in this report should be given consideration when designing waste disposal sites for pesticides. The low concentration data base for pesticide mobility may be reasonable when considering pesticides with low aqueous solubilities; however, this should not be accepted without verification.

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CONTENTS

FIGURES

TABLES

ACKNOWLEDGEMENTS

The assistance of Mr. R. E. Jessup (University of Florida) in developing numerical solutions to the conceptual mathematical models used to describe pesticide adsorption and mobility in soils is gratefully acknowledged. Also, the cooperation and overall project coordination by Dr. M. H. Roulier (EPA, Municipal Environmental Research Laboratory, Cincinnati, Ohio) as the Project Officer is appreciated.

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Eli Lilly for Trefluralin (technical material, formulation, ^{14}C-trifluralin, authentic metabolites);
Kerr-McGee for Methyl Parathion (formulation);
Monsanto for Methyl Parathion (technical material);
Thompson-Hayward for 2,4-D (formulation).

SECTION 1

INTRODUCTION

Because of a continued increase in the number and quantity of pesticide compounds being placed on the market, the safe disposal of surplus and/or waste pesticide materials has become an acute problem (von Rumker, et al., 1974). Incineration, encapsulation, isolation in underground caves and mines, chemical stabilization, land spreading and landfills are some of the procedures being considered for the disposal of pesticides and other hazardous wastes (Schomaker, 1976; von Everdingen and Freeze, 1971; Wilkinson, et al., 1978). Of these methods, disposal by landfills and land spreading appear to be more common and economical (Fields and Lindsey, 1975; Lindsey, et al., 1976). Placing hazardous wastes in the land has come under attack recently (Atkins, 1972; Rouston and Wildung, 1969) because there is no guarantee that the hazardous chemicals disposed of in this manner will not migrate from the disposal site to potable water supplies.

In general, pesticide applications associated with agricultural production have had very little adverse effect on the soil microbial activity (Cole, 1976; Hubbell, et al., 1973; Jensen, 1962; Kaiser, et al., 1970; Newman and Downing, 1958; Roslycky, 1977). However, reports on soil microbial activity where large concentrations were used have been contradictory and inconclusive. For example, Ou et al. (1978a) observed 2,4-D (2,4-dichlorophenoxyacetic acid) degradation at concentrations of 5,000 and 20,000 μg/g of soil (ppm) for one soil type and no degradation at the same concentrations for another soil. Soil respiration and bacterial, fungal and actinomycete populations were significantly reduced in the soil unable to degrade 2,4-D. They concluded that the physical and chemical properties of the soil as well as the 2,4-D concentration were important factors in governing microbial activity and pesticide degradation in soils receiving large pesticide concentrations.

Trifluralin (α,α,α-trifluro-2,6-dinitro-N, N-dipropyl-p-toluidine) and atrazine (2-chloro-4-ethylamine-6-isopropylamino-s-triazine) are commonly used herbicides. Trifluralin applications of 3 kg/ha (1.4 ppm) have been shown not to influence soil bacterial, fungal and actinomycete populations significantly (Tyunaeva, 1974). However, when 1.1 kg/ha (0.5 ppm) was applied per year over a five year period, bacterial populations were inhibited while fungal and actinomycete populations were enhanced (Breazeale and Camper, 1970). When analytical grade trifluralin was incorporated into the soil at concentrations of 5,000 ppm, CO_2 evolution and bacterial populations were inhibited while streptomycete populations were stimulated. Stojanovic et al. (1972) has shown that formulated trifluralin stimulated CO_2 evolution and streptomycete populations while inhibiting bacterial

populations in soil. Atrazine was shown not to inhibit soil respiration at concentrations associated with agricultural production (Kaiser, et al., 1970; Eno, 1962). Cole (1976) and Voets et al. (1974) have shown that soil bacterial and fungal populations were not affected at rates below 4 kg/ha (1.8 ppm). However, Stojanovic et al. (1972) reported that atrazine inhibited soil respiration and bacterial populations at 5,000 ppm but had no effect on fungal populations.

A thorough understanding of the various processes that influence the persistence, retention, and leaching of pesticides in soils is required to develop technology for the selection and management of pesticide disposal sites involving soils. The fate of pesticides in soils when applied at concentrations similar to those associated with agricultural practices has been well-documented in several reviews (Bailey and White, 1970; Sanborn, et al., 1977). However, the direct extrapolation of this data base to systems containing large pesticide concentrations, such as those occurring at or below disposal sites, may not be feasible (Davidson, et al., 1976).

Laboratory experiments were initiated to investigate the physical, chemical and microbiological behavior of five pesticides in five soils when the pesticide was present at large concentrations. The objectives of the study were to: 1) Measure and describe pesticide adsorption in selected soil-water systems over a wide range of chemical concentrations (zero to water solubility), 2) Measure mobility and distribution of pesticides in selected soils, when applied or initially present in soil at large concentrations, 3) Measure chemical and microbial degradation rate, and identify metabolites produced in soil-pesticide systems receiving large pesticide concentrations, and 4) Measure the influence of large pesticide concentrations on soil microbial activity and respiration rate for selected soil-pesticide systems.

SECTION 2

CONCLUSIONS

1. Equilibrium adsorption isotherms for pesticides and soils considered in this study were nonlinear. The Freundlich equation described the full range of pesticide solution concentrations (zero to aqueous solubility limit) studied. The adsorption "sites" for the pesticide were apparently never saturated in any soil-pesticide system investigated.

2. Pesticide mobility was inversely related to the pesticide concentration in the soil solution phase when the adsorption isotherm was nonlinear ($N < 1.0$). 2,4-D at 5,000 µg/ml was nearly as mobile as the chloride ion. The dependence of the mobility on pesticide solution concentration could be predicted and described by the equilibrium adsorption isotherm.

3. $^{14}CO_2$ evolution rate from a ^{14}C-ring labeled pesticide was a good indicator of pesticide degradation rate in soils containing large pesticide concentrations. Total CO_2 evolution, however, did not always represent the actual degradation of a pesticide. For this reason, the biological activity of soils containing low pesticide concentrations may, in many cases, be unrelated to the behavior and degradation of pesticides at large concentrations in the soil.

4. Moderately persistent pesticides such as atrazine and trifluralin, degrade slowly forming a number of metabolites when present in soils at high and low concentrations. These pesticides and metabolite products have the potential to become "bound" to the soil matrix. Bound residue was defined in this study to be the ^{14}C-labeled material remaining in the soil after recommended extraction procedures had been employed.

5. The less persistent pesticides such as 2,4-D and methyl parathion may or may not degrade when applied to a soil at high concentrations. Factors that determine the degradation rate were pesticide concentration, chemical formulation, nutrients in the soil, soil type, soil pH, temperature, soil-water content, soil organic matter content, texture, and the presence of a microbial population capable of degrading the pesticide. If the pesticide was degraded, the time required for degradation to begin was longer for large concentrations (>50 ppm) than for low concentrations. The lag period was directly related to pesticide concentration.

6. Pesticide mobility and degradation were described using adsorption and biological degradation parameters measured during this study. Conceptual or process based mathematical models were used to describe pesticide

mobility. The models were well suited for estimating the concentration distribution and mobility of pesticides associated with waste disposal sites.

7. Bound residues were formed at all concentrations studied (10 to 20,000 ppm). The percent of binding was higher for low concentrations; however, the amount bound (atrazine or trifluralin) increased as the pesticide concentration increased. The toxicity and chemical nature of the "bound residues" were not studied in detail.

8. At low pesticide concentrations (<50 ppm), microbial activity (indicated by total CO_2 evolution, and bacterial, fungal and actinomycete population) was generally not affected. Microbial activity may be enhanced or inhibited when a large amount of pesticide is applied to a soil. When degradation occured at large concentrations, microbial activity was enhanced. Moreover, formulation chemicals may stimulate microbial activity by serving as energy or nutrient sources. If pesticide degradation does not occur, microbial activity may be either enhanced or inhibited.

9. Based on the results of this study, groundwater contamination may be a significant problem when highly soluble pesticides are placed in waste disposal sites subject to considerable leaching. The potential for groundwater contamination, on the other hand, is not as great for pesticides with low solubilities.

SECTION 3

RECOMMENDATIONS

1. Total CO_2 evolution or soil respiration should not be used as the only measurement to estimate pesticide degradation in soils receiving or containing large pesticide concentrations.

2. Because this study considered only systems involving the presence of one pesticide, additional studies need to be conducted to establish the degradation, adsorption, and movement of pesticides in systems containing mixtures of several pesticides at high and low concentrations. This type of information is more relevant to actual pesticide disposal sites.

3. Identify procedures for stimulating pesticide degradation in waste disposal sites involving soils.

4. Establish the major soil parameters and properties which determine the potential for a given soil to degrade a high concentration of a given pesticide. Factors to consider are microbial population and species, soil pH, organic matter content, cation exchange capacity, soil-water content, temperature, etc.

5. Determine the mechanisms responsible for the formation of "bound" residues. Evaluate stability and/or phytotoxicity of bound residues.

6. Develop protocols for site evaluation and selection for pesticide disposal using surface soils or landfills. Protocols should consider single as well as mixtures of pesticides.

SECTION 4

MATERIALS AND METHODS

SOILS

Soils used in this study were selected on the basis of their geographic and taxonomic representation of major soil orders in the United States. State Conservationists for the Soil Conservation Service in selected regions were asked to identify the major soil series in their area for a selected soil order and to ship 735 kg (air-dry) of the Ap horizon of that soil. A soil profile description, sample site location, previous crop and management history, and climatic conditions at the site were provided with each soil series selected and studied. Soils selected were: Webster silty clay loam (Typic Haplaquolls) from Iowa, Cecil sandy loam (Typic Hapludults) from Georgia, Glendale sandy clay loam (Typic Torrifluvents) from New Mexico, Eustis fine sand (Typic Quartzipsamments), and Terra Ceia muck (Typic Mediasaprista) from Florida.

The soils were air-dried and sieved to pass a 2-mm screen prior to being stored. Selected physical and chemical properties of the mineral soils are given in Table 1. Terra Ceia muck is characterized by 81% organic matter, 19% total mineral content, CEC of 350 meq/100g and pH of 6.4.

PESTICIDES

The pesticides used in this study were selected based upon their present and anticipated usage as well as their different chemical properties. The production and use of herbicides has increased significantly in the past few years and at the present time herbicides represent the largest group of pesticides on the market. Because of this market shift in pesticide production, the herbicides were identified as a group of chemicals requiring major attention. The following description of each pesticide used in the study illustrates the diversity in chemical properties and toxicity of the selected compounds. It was believed that this range in chemical properties (Tabel 2) provided the necessary information needed to evaluate the problems associated with introducing large pesticide concentrations into the soil environment.

1) Atrazine (Herbicide): (2-chloro-4-ethylamino-6-isopropylamino-s-triazine). Low solubility in water (Table 2), but highly soluble in chloroform, methanol, and ether. Losses due to chemical and microbial degradation are significant. Leaching from soils may be limited due to adsorption on certain soil constituents. Acute oral LD_{50} to rats 3080 mg/kg.

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF THE MINERAL SOILS USED IN THIS STUDY

SOIL	PARTICLE SIZE FRACTION (%) Sand	Silt	Clay	pH (1:1 paste) Water	1N KCl	CEC (meq/100g)	Organic C (%)	Base Saturation (%)	Extractable Acidity (meq/100g)
Webster	18.4	45.3	38.3	7.3	6.5	54.7	3.87	91	5.15
Cecil	65.8	19.5	14.7	5.6	4.8	6.8	0.90	31	4.68
Glendale	50.7	16.4	22.9	7.4	6.5	35.8	0.50	90	3.74
Eustis	93.8	3.0	3.2	5.6	4.1	5.2	0.56	10	4.68

TABLE 2. PROPERTIES OF PESTICIDES USED IN THIS STUDY

Common Name	Molecular Weight	Vapor Pressure (mmHg x 10^6)	Aqueous Solubility (g/100 ml H_2O)	Melting Point
Atrazine	215.7	1.4 (30° C)	0.0033 (27° C)	173-175° C
Methyl parathion	263.2	9.5 (20° C)	0.0055-0.0060 (25° C)	35-36° C
Terbicil	216.7	0.48 (29.5° C)	0.071 (25° C)	175-177° C
Trifluralin	335.3	199 (29.5° C)	1 x 10^{-4} (27° C)	48.5-49.0° C
2,4-D	221.0	n.d.*	0.09 (25° C)	135-138° C
2,4-D Amine	266.1	0.001 (28° C)	300 (20° C)	85-87° C

*not determined

2) Methyl Parathion (Insecticide): (0-0-dimethyl-0-p-nitrophenyl phosphorothioate). Technical grade is a liquid. Low solubility in water (Table 2), but soluble in most organic solvents. Highly toxic and degrades readily in a soil environment producing some metabolites that are equally toxic. Acute oral LD_{50} to rats is 9-25 mg/kg.
3) Terbacil (Herbicide): (3-tert-butyl-5-chloro-6-methyl uracil). soluble in water (Table 2) and soluble in most organic solvents. mobile in soils due to relatively low adsorption. Acute oral LD_{50} for rats between 5,000-7,000 mg/kg.
4) Trifluralin (Herbicide): (α,α,α-trifluoro-2,6-dinitro-N, N-dipropyl-p-toluidine). Almost insoluble in water (Table 2) but very soluble in most organic solvents. Volatile unless incorporated into the soil immediately following application. Microbial and photo-degradation play a significant role in dissipation from soil. Adsorption on organic matter and clay colloids retards leaching from soils. Acute oral LD_{50} for rats greater than 10,000 mg/kg.
5) 2,4-D (Herbicide): (2,4-dichlorophenoxyacetic acid). Somewhat soluble in water (Table 2), and very soluble (30-60%) in acetone and alcohols. Undergoes microbial degradation in soils, but losses due to photodecomposition are minimal. Because of low adsorption in soils, it is readily leached. Acute oral LD_{50} for formulations are in the range of 300-1000 mg/kg rats, guinea pigs, and rabbits.

Formulated and technical grade materials fortified with ^{14}C materials were used to study mobility, adsorption-desorption, microbial degradation and accumulation of metabolites in soils at various pesticide concentrations. Stock solutions of each pesticide were prepared in 0.01N $CaCl_2$ using the commercial stock solution made up to the aqueous solubility limit of the pesticide. Solutions of lower concentrations were prepared by successive dilutions of the original stock solution. A mixture of antibiotics consisting of Penicillin G at 1 µg/ml and Polymixin B sulfate at 5 µg/ml (Sigma Chemical Co., St. Louis, MO) was added to all pesticide solutions to prevent microbial degradation during storage and use.

The commercial formulation of 2,4-D was Ded-Weed 40 (Thomson-Hayward Chemical Co., Kansas City, MO), a dimethylamine salt of 2,4-D (41% acid equivalent). The stock solution of commercially formulated atrazine was prepared using AATREX 80W (80% wettable powder; Ciba-Geigy Corp., Greensboro, NC). A concentrated xylene solution of methyl parathion (80% solution; Monsanto Co., Agricultural Division, St. Louis, MO) was diluted in 0.01N $CaCl_2$ to give the desired stock concentration. The commercial form of trifluralin was Treflan (Elanco Products Co., a division of Eli Lilly and Co., Indianapolis, IN; 44.5% trifluralin and 55.4% inert ingredients). The technical grade form of each pesticide was at least 97% pure. All pesticide solutions were spiked with the appropriate uniformly ring-labeled ^{14}C compound (except for trifluralin) to give specific activities in the range of 2-5 nCi/ml. Trifluralin was ^{14}C-labeled at the $-CF_3$ position.

ADSORPTION ISOTHERMS

Equilibrium adsorption isotherms for all soil-pesticide combinations were measured using the batch procedure. Equilibrium was achieved by

shaking duplicate samples of 5 or 10 g of soil with 10 ml of pesticide solution in Pyrex serew-cap glass test tubes for 48 hrs. Preliminary experiments had indicated that there was no measurable increase in pesticide adsorption beyond this time. Following equilibration, the test tubes were centrifuged at 800 g for 10 minutes and the ^{14}C-activity in 1-ml aliquots of the clear supernatant solution was assayed by liquid scintillation counting. Decreases in pesticide solution concentration were attributed to adsorption by the soil. All adsorption experiments were performed at a constant temperture (23 ± 1° C).

PESTICIDE DISPLACEMENT THROUGH SOILS

Pesticide movement through water-saturated columns of Webster, Cecil, and Eustis soils was studied using the miscible displacement technique described by Davidson et al. (1968). Air-dry soil was packed in small increments into glass cylinders (15 cm long; 45 cm^2 cross-sectional area). Medium porosity fritted glass plates served to retain the soil in the column. The soil was initially saturated with 0.01 N $CaCl_2$ solution. A known volume of pesticide solution at a desired concentration was introduced into the soil at a constant flux using a constant-volume peristaltic pump. After a specific volume of pesticide solution had been applied, the pesticide solution was subsequently displaced through the soil column with 0.01 N $CaCl_2$ at the same flux. Effluent solutions were collected in 5 or 10 ml aliquots using an automatic fraction collector. A pulse of ^3H_2O (specific activity = 5 nCi/ml) was also displaced through each soil column to characterize the transport of non-adsorbed solutes. The activity of ^{14}C and ^3H in effluent fractions was assayed by liquid scintillation. The counting efficiencies exceeded 90% for ^{14}C and 50% for ^3H in all cases.

The column experiments consisted of displacing 2,4-D amine solutions at two concentrations (50 and 5,000 µg/ml) through columns of Cecil, Eustis and Webster soils, and 5 and 50 µg/ml solutions of atrazine through a Eustis soil. All displacements were performed at a Darcy flux of approximately 0.22 cm/hr to ensure near-equilibrium conditions for pesticide adsorption during flow. The total volume of water held in the soil column was gravimetrically determined at the end of each displacement by extruding the soil from the glass cylinders and oven-drying. The number of pore volumes (V/V_o) of solution displaced through the column was calculated by dividing the cumulative outflow volume (V) by total water volume (V_o) in the soil column. Effluent pesticide concentrations are expressed as relative concentrations (C/C_o), where C and C_o are, respectively, effluent and input concentrations. Plots of C/C_o versus V/V_o are referred to as breakthrough curves (or BTC).

Air-dry soil was packed into 3.2-cm diameter lucite cylinders composed of 1-cm sections supported by a V-shaped container that permitted observation of the wetting front position with time. Technical or analytical grade pesticide was dissolved in benzene and was spiked with ^{14}C-labeled compound. The benzene solution was mixed with air-dry soil (to give 200 or 2,000 µg pf pesticide/g of soil and 10 nCi/g soil) and the benzene evaporated. In order to simulate a waste disposal site, the pesticide-spiked soil was packed into the top 1.5 cm of the soil column. Infiltra-

tion of water into horizontal columns of soil was controlled by maintaining the soil surface at a negative pressure (-4 cm of water) using a fritted-glass plate and a constant-head burette. The fritted-glass plate apparatus was filled with 0.01 N $CaCl_2$ and the desired negative pressure applied before it was placed in contact with the soil. Measurement of time in all experiments commenced the instant contact was established between the fritted-glass plate and soil surface. Water entering the soil was measured volumetrically using a constant-head burette connected to the fritted-glass plate apparatus. Measurements of distance to the wetting front (zero at the contact plane between soil and plate) were visually observed. When flow had proceeded for the desired time (i.e., until the wetting front had advanced to about 30 cm), the water supply was discontinued and the soil column was immediately cut into 1-cm segments. About one-half of the soil contained in each 1-cm segment was oven-dried at 105° C for 24 hours to determine the gravimetric soil-water content. The remaining one-half of the soil from each 1-cm-segment was dried in a vacuum desiccator over P_2O_5 or H_2SO_4 for a 24-48 hour period. About 0.5-0.7 g of the desiccator-dried soil was then combusted in a Packard Model 306B sample oxidizer; the $^{14}CO_2$ evolved by combustion was trapped in a premixed organic amine-fluor cocktail and assayed by liquid scintillation. The pesticide concentrations were calculated using the specific activity (dpm/µg pesticide) of the pesticide-spiked soil sample. The pesticide concentrations determined in the above manner represent the sum of adsorbed and solution-phase concentrations and were expressed as µg pesticide/g oven-dry soil.

PESTICIDE DEGRADATION AND SOIL RESPIRATION

Each soil was initially wet to a soil-water content corresponding to 30% of the 0.33 bar soil-water tension and incubated for one week at 25° C. Following incubation, each soil was then mixed thoroughly with a specific quantity of pesticide fortified with ^{14}C-pesticide at 1 µCi/100 g of soil and sufficient water was added to bring the soil up to 0.33 bar soil-water tension. For pesticide degradation and soil respiration experiments, 100 g (oven-dry basis) of each pesticide-treated soil was placed in a 250 ml Erlenmeyer flask. Special care was taken when mixing the pesticide with the soil to ensure a uniform distribution of the pesticide within the soil. Technical grade and formulated materials of each pesticide were used. The flasks were then connected to a plexiglass manifold and CO_2-free water-saturated air passed through the manifold into the falsks at a flow rate of 10 ml/min per flask. For pesticides with high vapor pressures, the air leaving the flask was passed through 40 ml of ethylene glycol to absorb the volatilized pesticide. The air leaving each flask was also bubbled through a KOH solution (0.1-0.5N) to absorb the evolved CO_2. At frequent intervals, the KOH solutions were replaced with fresh KOH solutions and the total CO_2 concentrations in the KOH solutions were determined by titration. $^{14}CO_2$ activity in the KOH solution was determined by liquid scintillation counting.

SOIL MICROBIAL POPULATIONS

For the microbial enumeration experiments, the experimental set-up was essentially the same as that for the degradation experiment, except

250 g of each pesticide-treated soil (10 to 20,000 µg/g) was placed in a 500 ml Erlenmeyer flask and no ^{14}C-labeled pesticide was used. Ten gram soil samples were withdrawn weekly from each flask. Bacterial, fungal and actinomycete populations in the samples were determined using a dilution plate count method. The number of microorganisms were expressed as colony forming units (cfu) per gram of oven-dry soil. Bacterial populations were determined using a TGY medium consisting of 5 g tryptone, 5 g of glucose, 4 g of yeast extract, and 18 g of agar in 1,000 ml of distilled water. The pH of the medium after autoclaving was 7.0. Bacterial colonies in the plates were counted after 48 to 52 hours at 28° C. Fungi were enumerated in Martin's (Martin, 1950) Rose Bengal-streptomycin agar (RBS agar). The pH of the fungal medium after autoclaving was 6.0. Fungal colonies were determined after 60 to 72 hours at 28° C. Actinomycetes were plated on starch-casein agar (SC agar) supplemented with antibiotics cycloheximide 50 µg/ml and nystatin 50 µg/ml (Williams and Davis, 1965). The pH of the actinomycete medium after autoclaving was 7.2. The actinomycete colonies were counted after 12 to 14 days at 25° C.

TABLE 3. SOLVENTS USED FOR PESTICIDE EXTRACTION FROM SOIL

Pesticide	Solvent
2,4-D	Ether Ethyl
Trifluralin	1) Benzene/Ethyl Acetate (3:1) 2) MeOH
Atrazine	MeOH (soxhlet)
Methyl Parathion	Hexane:Acetone (80:20)

METABOLITE IDENTIFICATION

Soil treatments and incubation were essentially the same as for the pesticide degradation experiments, except 150 g of soil were used and 2 µCi ^{14}C-pesticide per 100 g soil were added. Ten gram soil samples were withdrawn biweekly. The soil samples were extracted three times with the appropriate solvent (Table 3). The 20,000 µg/g samples were extracted four times because of their high pesticide concentrations. The extracted soil was then air dried and stored in a cold chamber prior to analysis for "bound" ^{14}C. The extracts were concentrated to 10 ml on a rotary evaporator, or in a Danish Kuderna evaporator, then further concentrated using a gentle stream of N_2 and an aliquot was assayed for ^{14}C. The extracts were further concentrated with N_2 to one ml and an aliquot equivalent to 15,000 dpm of each sample was streaked on a thin layer plate (see Table 4). The TLC plates were developed and placed on Kodak on-screen x-ray film (NS-57)

for one month. Radioactive streaks on the TLC plates were scraped and the radioactivity eluted with two ml of solvent (Table 3). The percentage of radioactivity in each separate radioactive component on the TLC plates was determined by liquid scintillation counting.

The unextractable "bound" portion of the ^{14}C-residue was determined by oxidizing the extracted soil samples in a stream of O_2 at 800° C according to the modified method of Watts (1971). The air dried extracted soil was placed directly in the oven at 800° C and the O_2 stream which passed through the soil was bubbled directly into 15 ml of phenethylamine CO_2-trapping cocktail solution. Complete combustion took approximately five minutes. Then N_2 was purged through the system to eliminate O_2 and the trapped $^{14}CO_2$ was assayed.

A Varian Aerograph Series 2100 gas chromatograph (GC) with one flame ionization and three electron capture detectors was used for the gas chromatography work. 2,4-D analysis consisted of quanitfication of the butoxyethyl ester of 2,4-D which was prepared as follows: 1) Five ml of acetyl chloride was added dropwise to cold butoxyethanol (final volume equal to 100 ml); 2) 0.1 ml of this solution was then added to a test tube containing the extracted 2,4-D. The tube was sealed and held at 80° C for 30 minutes; 3) The tube was cooled and 2.0 ml of hexane was added; 4) The hexane solution was then extracted three times with 0.2 M K_2HPO_4 and 5) A small amount of anhydrous sodium sulfate was then added to the hexane solution to dry the sample. The GC column was 1.8 m x 2 mm i.d. glass packed with 3% QF-1 80/100 on Gas Chrom Q and operated at 200° C. The injection port and detector temperatures were 250° and 300° C, respectively. The same column was used for trifluralin but was operated at 140° C. Trifluralin and its metabolites were assayed without modification.

Atrazine and its dealkylated metabolites were assayed using a 5% CBWX 20 M 60/80 mesh Gas Chrom Q packed in a 1.8 m x 2 mm i.d. glass column and utilizing a flame ionization detector. The hydroxy metabolites of atrazine were methylated and then assayed on the CBWX column using a flame ionization detector. Injector, column and detector temperatures were 250°, 200° and 300° C, respectively.

Mass spectral analyses for trifluralin were performed using a Finnigan Model 1015C chemical inozation quadruple mass spectrometer equipped with a Varian 1400 gas chromatograph as the inlet source without a separator. The mass spectrometer (MS) was interfaced to a System Industries 150 computer data acquisition system. The 1.8 m x 2 mm i.d. glass column was packed with 3% QF-1 on 100/120 mesh Gas Chrom Q. Methane was used as the carrier gas at a flow rate of 18 ml/min and passed directly into the ion source where the pressure was maintained at 1.0 torr. The injector, column and transfer line temperatures were 240°, 140° and 230° C, respectively.

In addition to mass spectra, the computer data system provided reconstructed gas chromatograms (RGC) and limited mass range searches (LMS). RGC's represent the normalized total ion current plotted versus the spectrum number.

TABLE 4. THIN LAYER CHROMATOGRAPHIC SYSTEMS

Pesticide	TLC Solvent Systems	TLC Plates*	TCL Scraping Eluting Solvent
2,4-D	n-Butanol:Acetic Acid:H_2O (4:1:1.8)	Silica gel 60F-254 (20 x 20 x 0.2 mm)	Ether
Trifluralin	Hexane:MeOH (97:3)	Silica gel 60F-254 (20 x 20 x 0.2 mm)	Ethyl Acetate
Atrazine	$CHCl_3$:Acetone:Acetic Acid (9:1:1)	Aluminum Oxide (20 x 20 x 0.2 mm)	$CHCl_3$:Acetic Acid (9:1)
Methyl Parathion	Hexane:Acetone (80:20)	Silica gel 60F-254 (20 x 20 x 0.2 mm)	

*All were Brinkman

SECTION 5

RESULTS AND DISCUSSION

ADSORPTION AND MOBILITY

Adsorption Experiments

Equilibrium adsorption isotherms were determined for each soil-pesticide combination by measuring pesticide adsorption at five or more concentrations ranging from zero to the pesticide's aqueous solubility. All adsorption isotherms considered in this study, with the exception of 2,4-D and the Glendale soil, were described by the Freundlich equation ($S = KC^N$), where K and N are constants, and S and C are adsorbed ($\mu M/kg$ soil) and solution ($\mu M/\ell$) phase pesticide concentrations. The values of the Freundlich adsorption constants, K and N, for each soil-pesticide combination studied were obtained using a least-square fit procedure to the adsorption data. These values are presented in Table 5.

Equilibrium adsorption isotherms should be independent of the soil to solution ratio employed in the batch adsorption procedure. This has not always been true for some published data (Grover and Hance, 1970; Hance 1977). The results presented in Figure 1 illustrate that no difference was observed between the 2,4-D amine and Webster soil adsorption isotherms conducted at soil:solution ratios ranging from 1:2 to 1:10. The independence of the adsorption isotherm to soil solution rate used in the batch adsorption procedure was shown to be consistent for the other soil-pesticide systems considered in this study. These results are in agreement with those of Green and Obien (1969), Nearpass (1967), and Dao and Lavy (1978). This concept is important when using the Freundlich equation and its constants, K and N, to predict pesticide partitioning between soil and solution phases in systems where soil:solution ratios are known but not constant (e.g., soil profile, runoff water containing sediments, etc.).

The type and quantity of specific electrolytes in the water frequently influence the adsorption of pesticides. The sensitivity of pesticide adsorption characteristics to electrolytes depends upon the adsorption mechanism between the pesticide and solid phase. For example, 2,4-D amine adsorption increases in the presence of calcium (Figures 2 and 3) for both Cecil and Webster soils. This phenomenon, however, is not consistent for all soil-pesticide systems (Abernathy and Davidson, 1971). Based upon the results presented in Figures 2 and 3 one needs to be aware of the type and quantity of electrolytes present in the water and their influence on pesticide adsorption.

TABLE 5. FREUNDLICH CONSTANTS CALCULATED FROM EQUILIBRIUM ADSORPTION ISOTHERMS FOR VARIOUS SOIL-PESTICIDE COMBINATIONS

PESTICIDE	SOIL	K_M†	K_G‡	N	K_{OC}‡
Atrazine	Webster	9.12	6.03	0.73	155.8
	Cecil	0.84	0.89	1.04	98.9
	Glendale	0.69	0.62	0.93	124.0
	Eustis	0.85	0.62	0.79	110.7
	Average ± % CV*	2.87 ± 145	2.04 ± 131	0.87 ± 16	122.3 ± 20
Methyl Parathion	Webster	18.67	13.39	0.75	346.0
	Cecil	4.81	3.95	0.85	438.6
	Glendale	6.05	3.57	0.61	714.5
	Eustis	3.30	2.72	0.86	486.4
	Average ± % CV	8.21 ± 86	5.91 ± 85	0.77 ± 15	496.4 ± 32
Terbacil	Webster	2.96	2.46	0.88	63.6
	Cecil	0.39	0.38	0.99	42.2
	Glendale	0.42	0.38	0.93	76.0
	Eustis	0.15	0.12	0.88	21.4
	Average ± % CV	0.98 ± 135	0.83 ± 130	0.92 ± 6	50.8 ± 47
Trifluralin	Webster	2.49	2.93	1.15	75.7
	Cecil	0.43	0.46	1.05	50.7
	Glendale	1.31	1.60	1.18	177.8
	Eustis	0.23	0.24	1.06	43.2
	Average ± % CV	1.11 ± 92	1.31 ± 94	1.11 ± 6	86.8 ± 72
2,4-D Amine	Webster	7.27	4.62	0.70	119.4
	Cecil	0.84	0.65	0.83	72.2
	Glendale	--	--	--	--
	Eustis	1.14	0.76	0.73	135.7
	Average ± % CV	3.08 ± 118	2.01 ± 112	0.75 ± 9	109.1 ± 30

†K_M Freundlich constant when solution and adsorbed phase concentrations are expressed as µM/l and µM/kg of soil.

‡K_G Freundlich constant for solution and adsorbed phase concnetrations are as µg/ml and µg/g of soil [$K_G = K_M(MW/1{,}000)^{1-N}$], when MW is the pesticide's molecular weight.

‡K_{OC} Freundlich constant for solution and adsorbed phase expressed as µg/ml and µg/g of organic carbon.

*CV is the coefficient of variation, % CV = (standard deviation/average x 100.

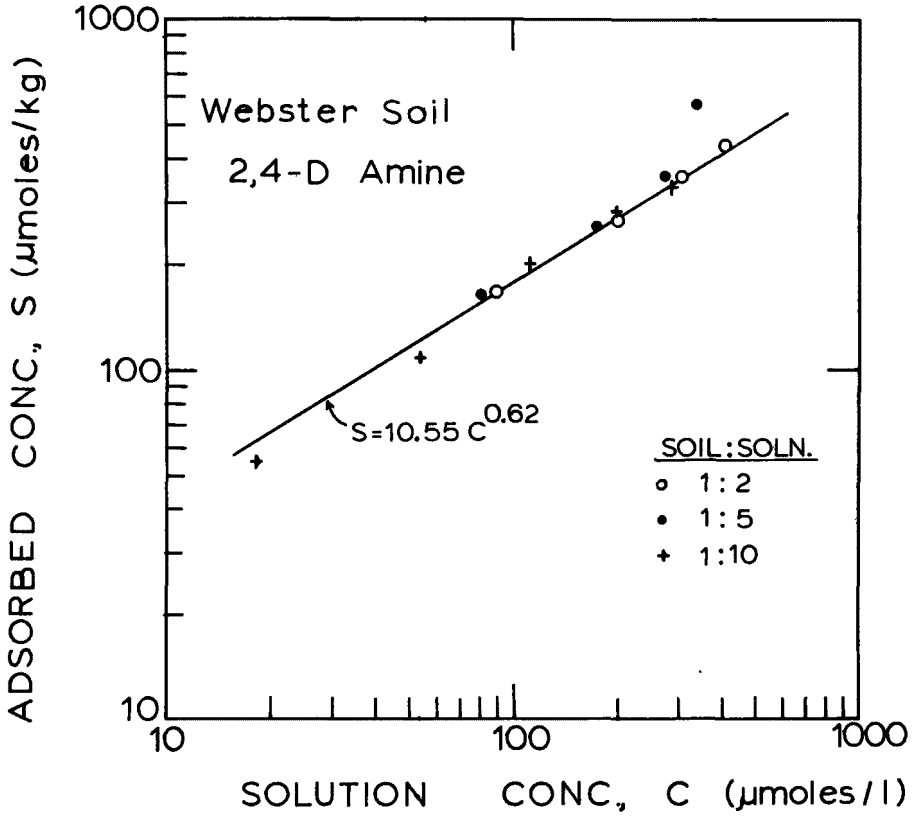

Figure 1. Adsorption isotherm for 2,4-D amine and Webster soil. Data obtained using soil:solution ratios of 1:2, 1:5 and 1:10.

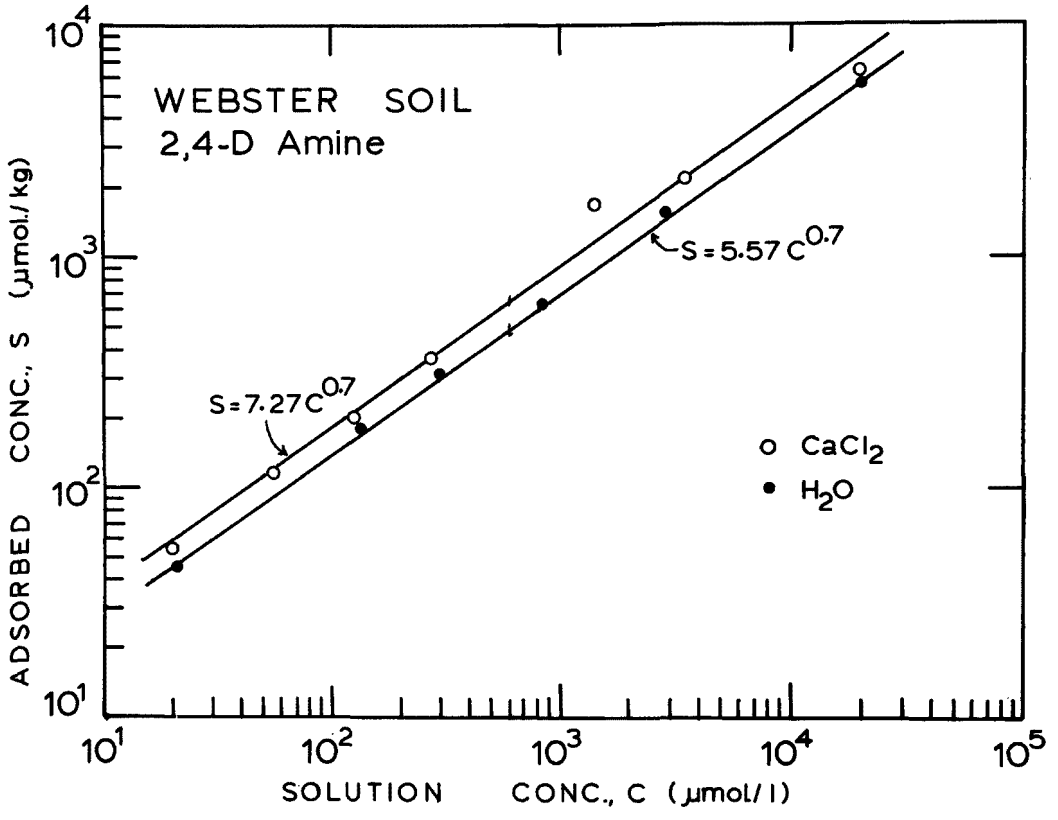

Figure 2. Adsorption isotherm for 2,4-D amine and Webster soil. 2,4-D was applied to soil in distilled water or 0.01 N $CaCl_2$.

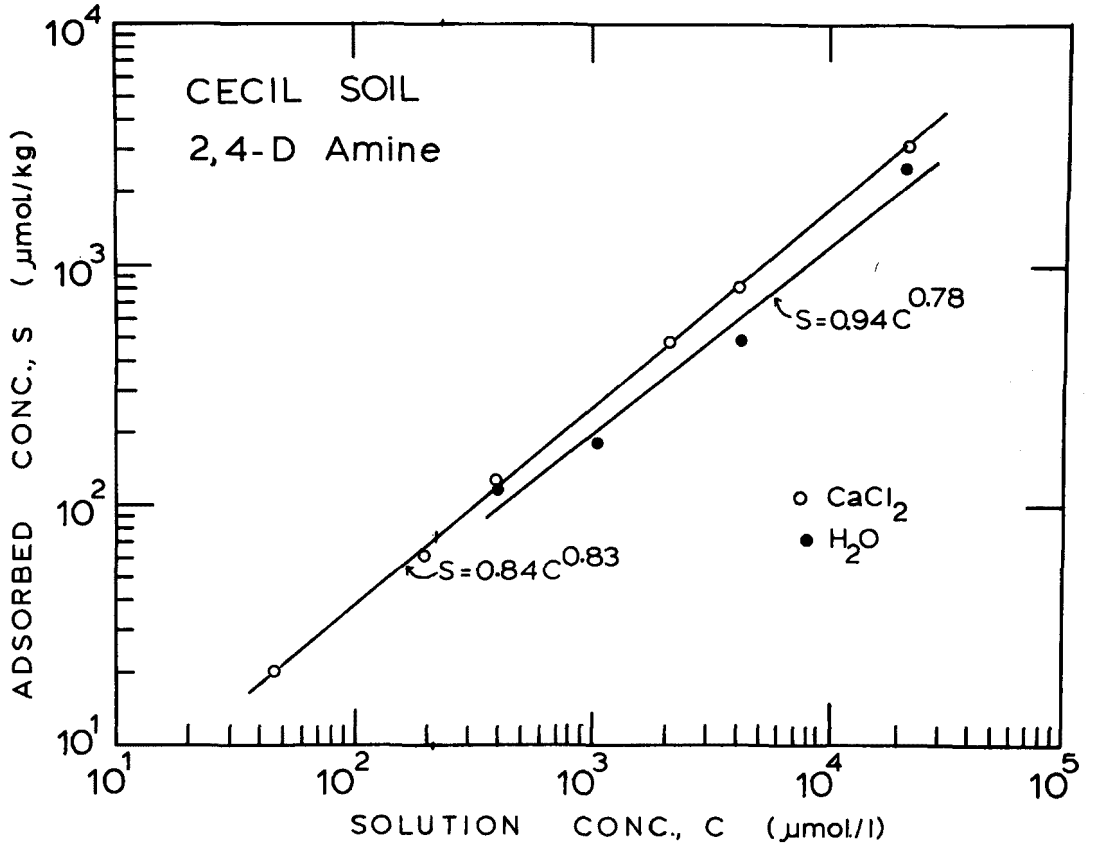

Figure 3. Adsorption isotherm for 2,4-D amine and Cecil soil. 2,4-D was applied to soil in distilled water or 0.01 N $CaCl_2$.

Adsorption isotherms for atrazine, methyl parathion, terbacil, trifluralin, and 2,4-D amine and four soils are presented in Figures 4-8. Because of the large quantity of pesticide adsorbed by the Terra Ceia muck, it was not included in these figures. The Freundlich adsorption constants which describe the data for each isotherm are shown adjacent to the best-fit line (least-squares) through the data. Note that for all pesticide-soil systems studied, with the exception of trifluralin, N in the Freundlich equation is less than one.

To achieve the high solution concentrations of trifluralin shown in Figure 7, it was necessary to use a 1% solution of a nonionic surfactant (Triton X-100; polyoxyethylene ethers). Decreasing solution concentrations of the surfactant due to its adsorption on the soil (Valoras et al., 1969), could lead to a reduction in pesticide solubility and promote precipitation of the trifluralin, especially at the higher concentrations. In this study, the amount of pesticide adsorbed by the soil was measured from the change in solution concentration. Thus, any decrease in pesticide concentration in the solution phase due to precipitation would have been erroneously attributed to adsorption by the soil. If precipitation had occurred primarily at the higher trifluralin concentrations, a value of N greater than 1.0 would be anticipated. It should also be recognized that the presence of surfactants can drastically increase or decrease pesticide adsorption on soils (Hugenberger, et al., 1972). The surfactant may compete with the pesticide for adsorption sites on the soil, or it could enhance the lipophillic nature or the soil surface and thereby increase pesticide adsorption.

The adsorption data for 2,4-D amine and the Glendale soil are not included in Figure 8 or Table 5 because a calcium salt of 2,4-D was formed in this soil and precipitated out of solution making it impossible to measure 2,4-D adsorption at large herbicide concentrations. The Glendale soil contains a large quantity of calcium carbonate. The quantity of 2,4-D amine precipitated increased as the herbicide concentration in solution prior to contact with the soil increased. The precipitation of 2,4-D as a calcium salt in the Glendale soil was confirmed through analytical procedures (mass spectroscopy).

Two important conclusions can be made based on the data presented in Table 5. First, the fact that the Freundlich equation describes all pesticide adsorption isotherms over a wide concentration range suggests that adsorption sites were not saturated at any concentration considered in this study. The amount of pesticide adsorbed by the soil continued to increase, at a decreasing rate, with each increase in solution concentration. This behavior may not, however, hold for other pesticide adsorbents (Weber and Usinowicz, 1973). Second, contrary to a frequent assumption, pesticide adsorption isotherms are generally nonlinear, that is, N is greater or less than one (Table 5). Linear adsorption isotherms have been generally accepted for low pesticide concentrations because it simplified computer simulation modeling (Davidson, et al, 1968; Davidson and Chang, 1972; Hugenberger, et al., 1972; Kay and Elrick, 1967).

Because soil organic carbon content generally correlates well with pesticide adsorption, the use of an adsorption paratition coefficient based

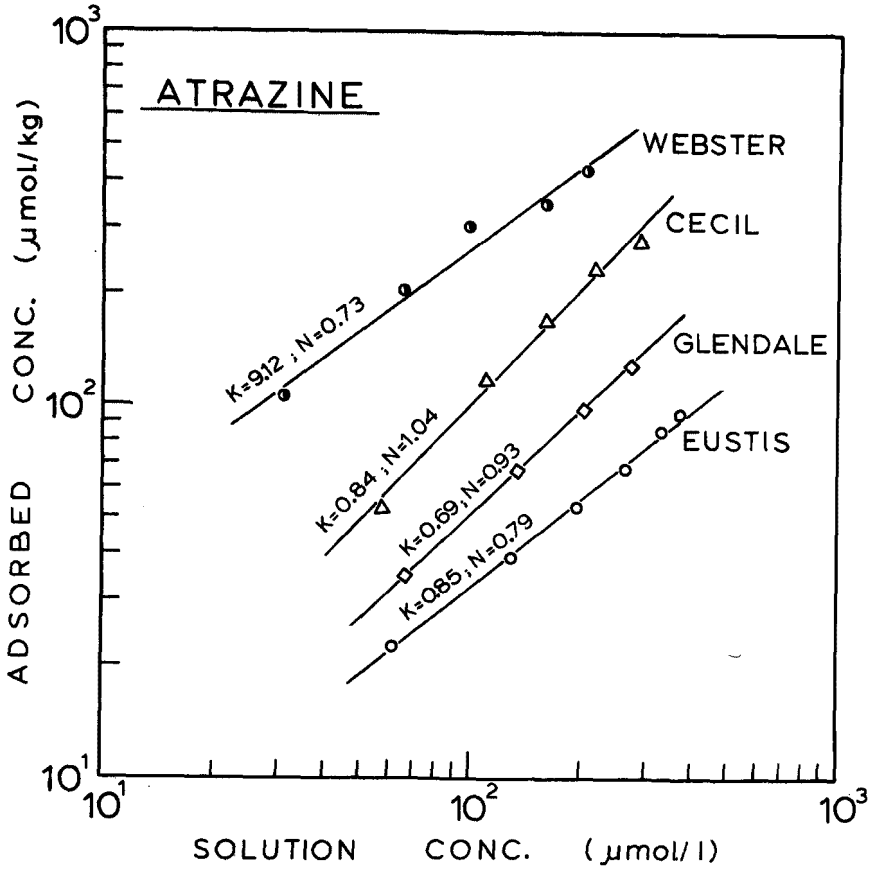

Figure 4. Adsorption isotherms for atrazine and Webster, Cecil, Glendale and Eustis soils. Freundlich constants (K and N) for each isotherm, determined by least-squares fit to the data, are also shown.

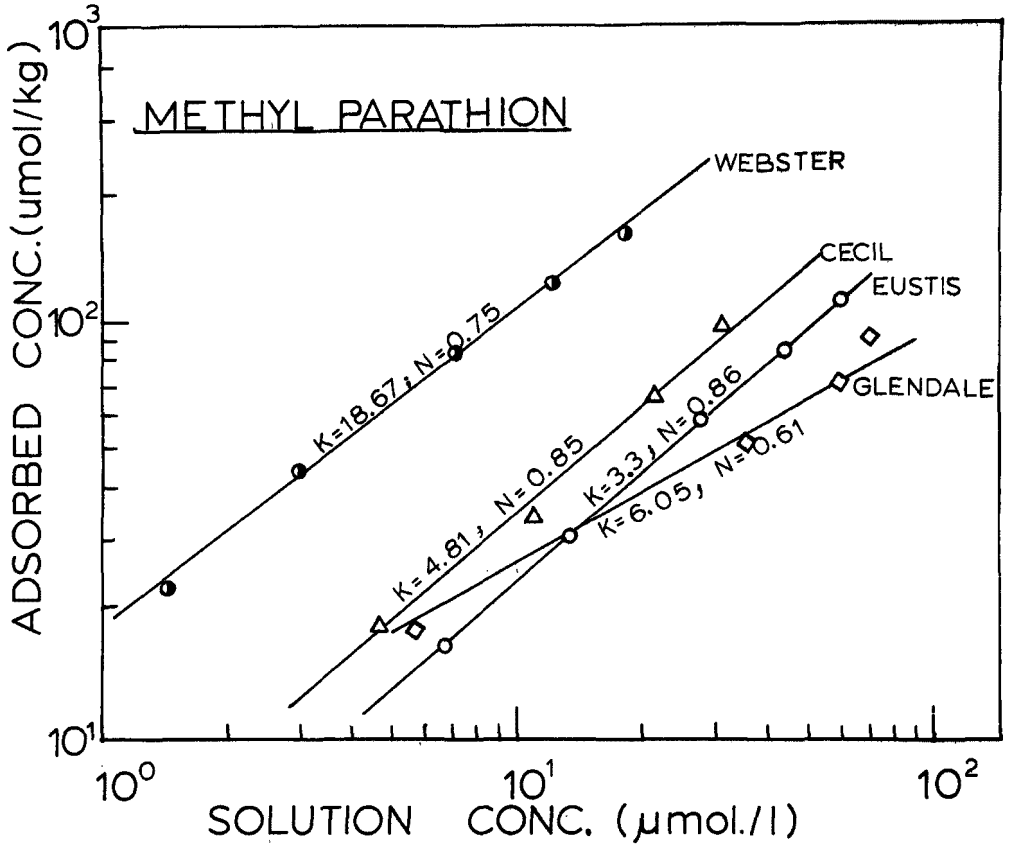

Figure 5. Adsorption isotherms for methyl parathion and Webster, Cecil, Glendale and Eustis soils. Freundlich constants (K and N) for each isotherm, determined by least-squares fit to the data, are also shown.

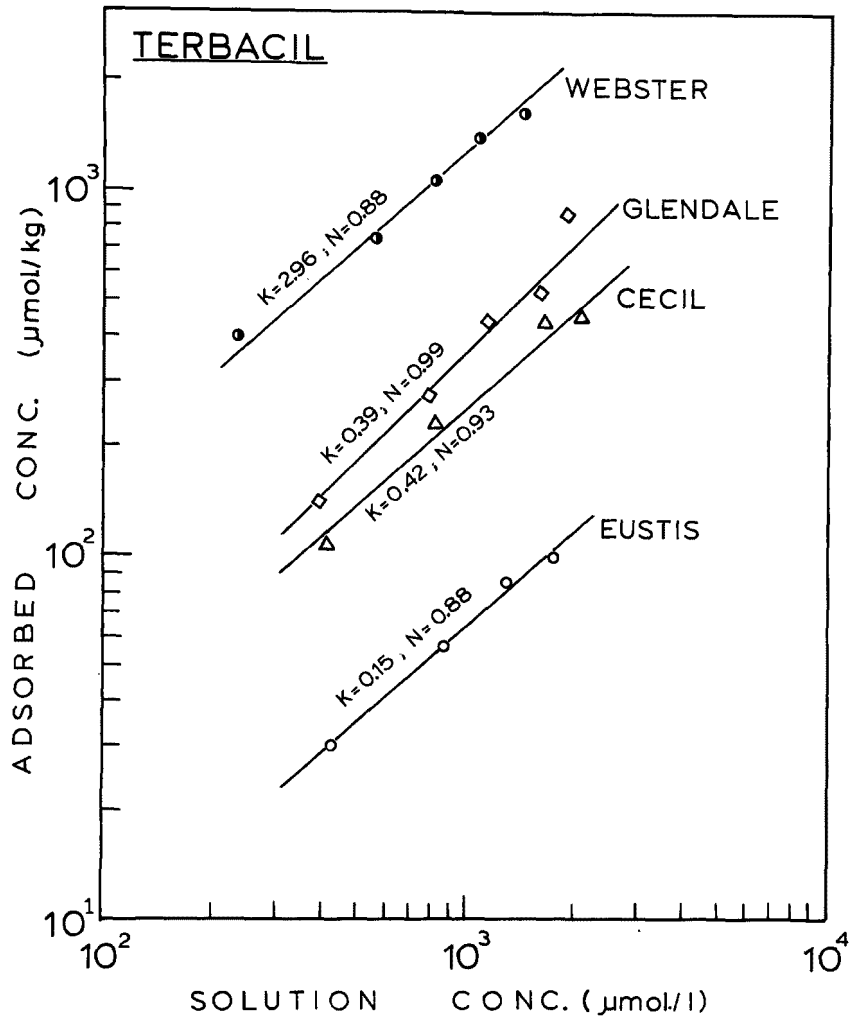

Figure 6. Adsorption isotherms for terbacil and Webster, Cecil, Glendale and Eustis soils. Freundlich constants (K and N) for each isotherm determined by least-squares fit to data, are also shown.

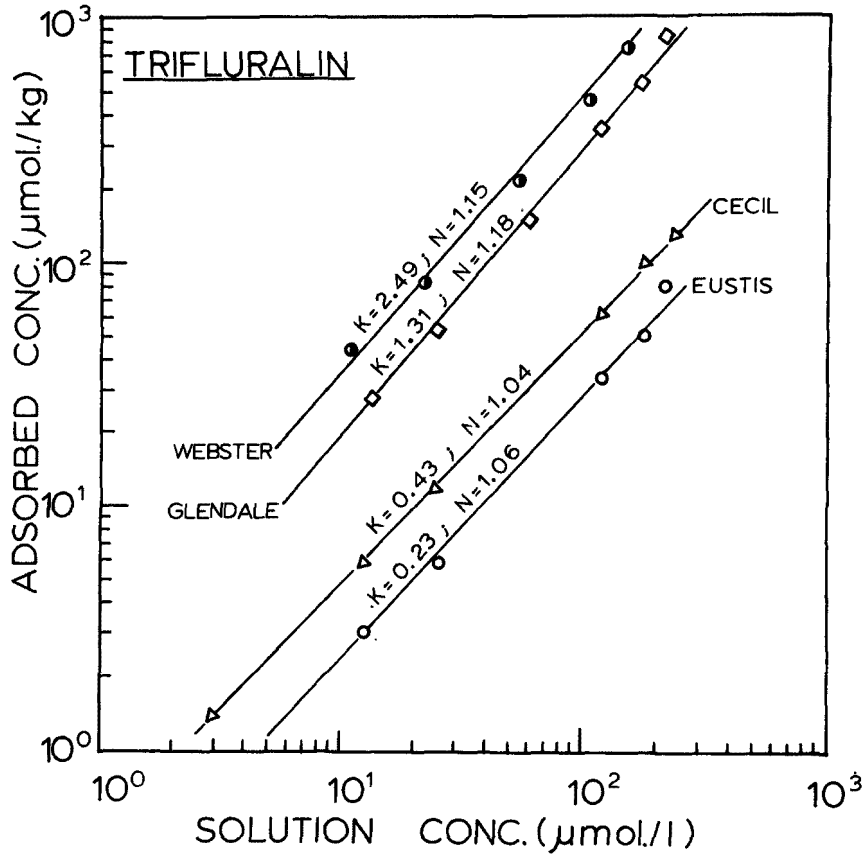

Figure 7. Adsorption isotherms for trifluralin and Webster, Cecil, Glendale and Eustis soils. Freundlich constants (K and N) for each isotherm, determined by least squares fit to data, are also shown.

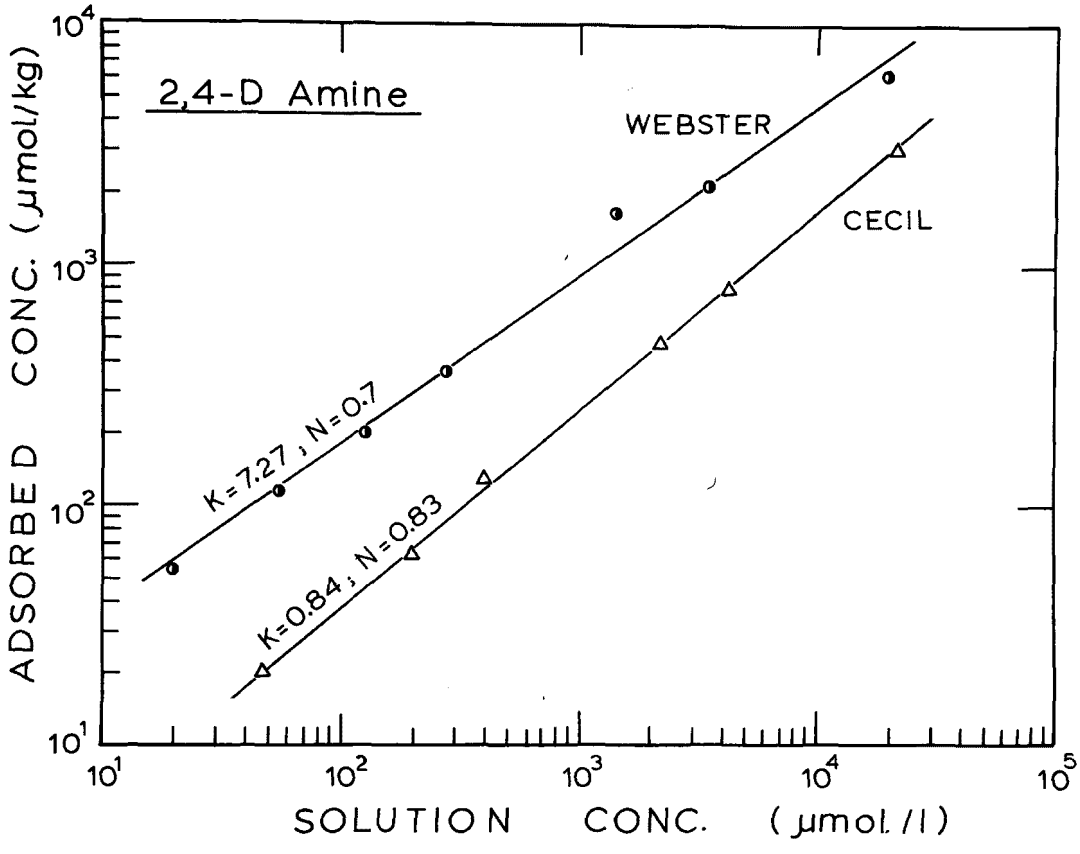

Figure 8. Adsorption isotherms for 2,4-D amine and Webster and Cecil soils. Freundlich constants (K and N) for each isotherm, determined by least-squares fit to data, are also shown.

upon organic carbon content rather than total soil mass has been proposed by Lambert (1968) and Hamaker and Thompson (1971). Using this procedure, the amount of pesticide adsorbed was expressed as μg/g organic carbon and the Freundlich constant (K_{OC}) for each adsorption isotherm was computed. These values are also presented in Table 5. It is apparent that the values of K_{OC} for a given pesticide are much less variable (smaller percent CV) among the four soils studied than are the K values uncorrected for organic carbon. These results are in general agreement with the observations of Hamaker (1975) where the K_{OC} values for a given pesticide were nearly independent of soil type. It should be recognized, however, that other factors such as soil pH, clay content, and cation exchange capacity may also play a significant role in determining pesticide adsorption by soils (Bailey and White, 1970). On the basis of the K_{OC} values listed in Table 5, the extent of pesticide adsorption in soils was in the order of terbacil < trifluralin < 2,4-D amine < atrazine < methyl parathion.

COLUMN DISPLACEMENT EXPERIMENTS

The partial differential equation generally assumed to describe the movement of pesticides and other adsorbed solutes through soils under steady-state water flow conditions is (Van Genuchten, et al., 1974):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho}{\theta} \frac{\partial S}{\partial t} \qquad [1]$$

where t is time (days), D is dispersion coefficient (cm^2/day), x is distance (cm), v is average pore-water velocity (cm/day), ρ is soil bulk density (g/cm^3), θ is volumetric soil-water content (cm^3/cm^3), and C and S are solution and adsorbed pesticide phase (μg/ml and μg/g), respectively. When the adsorption isotherm obeys the Freundlich equation, the convective-dispersive solute transport model (Equation 1) reduces to:

$$R(C) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \qquad [2]$$

where,

$$R(C) = [1 + \rho K N C^{N-1}] \qquad [3]$$

The retardation term R(C) is a quantitative index of the pesticide's mobility in that its value is equal to the ratio of the positions of the adsorbed and nonadsorbed solute fronts in soil. The value of the adsorption coefficient K in Equation [3] for nonadsorbed solutes (e.g., chloride or ^3H_2O) is equal to zero; hence, R(C) = 1. For adsorbed solutes, R(C) is greater than one because the value of K is larger than zero. Thus, larger values of R(C) indicate reduced pesticide mobility in soils. It may be noted from Equation [3] that for the case of nonlinear adsorption isotherms (N < 1), the value of the retardation term increases with decreasing solution concentration C, while for a linear isotherm (N = 1), R(C) is independent of pesticide solution concentration. Thus, the mobility of pesticides and other adsorbed solutes through soils is directly influenced by the shape of the equilibrium adsorption isotherms.

Effluent breakthrough curves (BTC) were measured for 2,4-D amine at two input concentrations (C_o = 50 and 5,000 µg/ml) and tritated water (^3H_2O) using columns of Webster, Cecil and Eustis soils. These BTC are shown in Figures 9, 10 and 11. Tritiated water represents a nonadsorbed solute and serves as a reference for the adsorbed solutes (2,4-D amine in this case). A shift of the BTC for adsorbed solutes to the right of ^3H_2O BTC is due to an adsorption-induced retardation. The greater the right-hand shift of the BTC, the greater the adsorption; thus, a decrease in mobility. It is apparent from the data presented in Figures 9, 10 and 11 that the mobility of 2,4-D amine was significantly increased as the input concentration (C_o) increased from 50 to 5,000 µg/ml. Note that for the 5,000 µg/ml input concentration, 2,4-D amine was nearly as mobile as was ^3H_2O. The effect of increased mobility at high concentration was more pronounced in the Webster soil (Figure 9) than in the Cecil (Figure 10) or Eustis soil (Figure 11). These column results are consistent with Equation [3] and the measured nonlinear adsorption isotherms (Table 5) for 2,4-D amine.

Breakthrough curves for the displacement of atrazine through the Eustis soil at two herbicide input concentrations (C_o = 5 and 50 µg/ml) and ^3H_2O are presented in Figure 12. The trend of increased mobility at higher atrazine solution concentrations again is evident. However, the differences in pesticide mobility between the two concentrations were not as large for atrazine (Figure 12) as they were for 2,4-D amine (Figures 9-11). Deviations of the adsorption isotherms from linearity, i.e., constant retardation term, increase exponentially as the concentration differences become larger and/or as N approaches zero (Davidson, et al., 1976; Hamaker and Thompson, 1972). In this study, atrazine concentrations varied only by ten-fold while the 2,4-D amine concentrations varied by 100-fold. Furthermore, the isotherm for 2,4-D amine adsorption in Webster soil was more nonlinear than that for the Eustis soil-atrazine system (Table 5).

The position of the BTC for an adsorbed solute is governed by the nature of the equilibrium adsorption isotherm (Equation 3), whereas the shape of the BTC (i.e., symmetry or lack of it) is defined by nonlinearity of the adsorption isotherm and the kinetics of adsorption-desorption processes. Symmetrical BTC are obtained when adsorption is an instantaneous process and the adsorption isotherm is linear. For nonequilibrium adsorption conditions during flow, asymmetrical BTC are generally obtained (Van Genuchten, et al., 1974; Rao, et al., 1979). All of the pesticide BTC measured in this study (Figures 9-12) were asymmetrical in shape with extensive "tailing" observed as C/C_o approached 1.0 or zero. Tailing was absent in ^3H_2O breakthrough curves. The extent of the asymmetrical shape of each pesticide BTC exceeded that which could be attributed to the nonlinear nature of the adsorption isotherms. Hence, much of the asymmetry measured for the pesticide BTC may be attributed to nonequilibrium conditions which exist in the soil columns during flow. Rao et al. (1979) presented an evaluation of two conceptual models where nonequilibrium during flow was attributed to either kinetics-controlled or diffusion-controled adsorption-desorption processes.

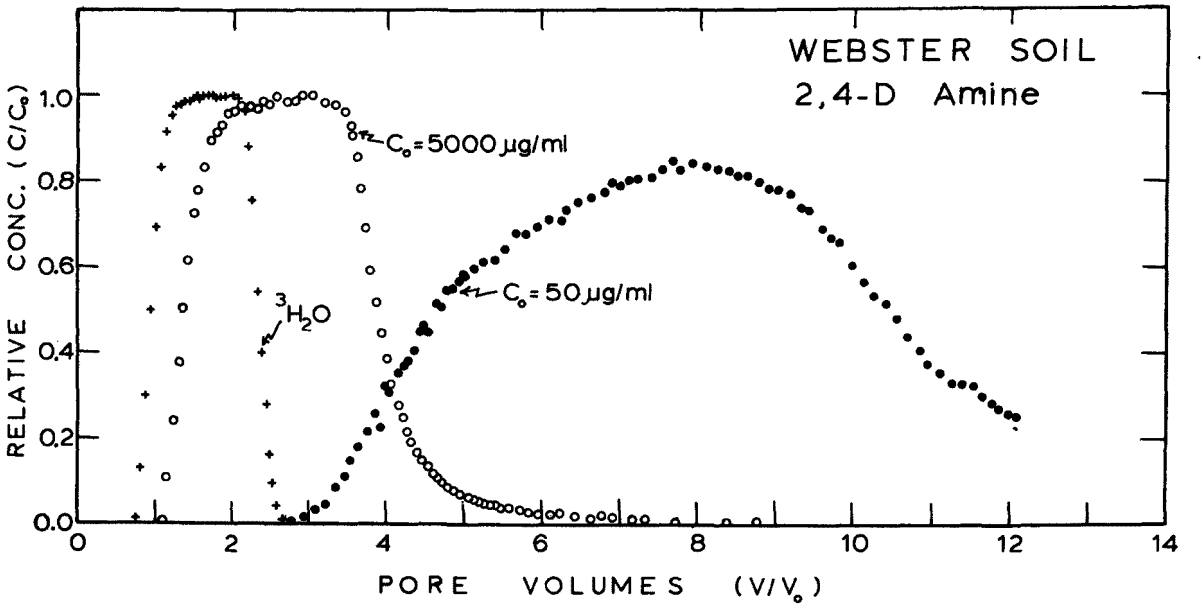

Figure 9. Effluent breakthrough curves for 2,4-D amine (C_O = 50 and 5,000 µg/ml) and for tritiated water displacement through Webster soil column.

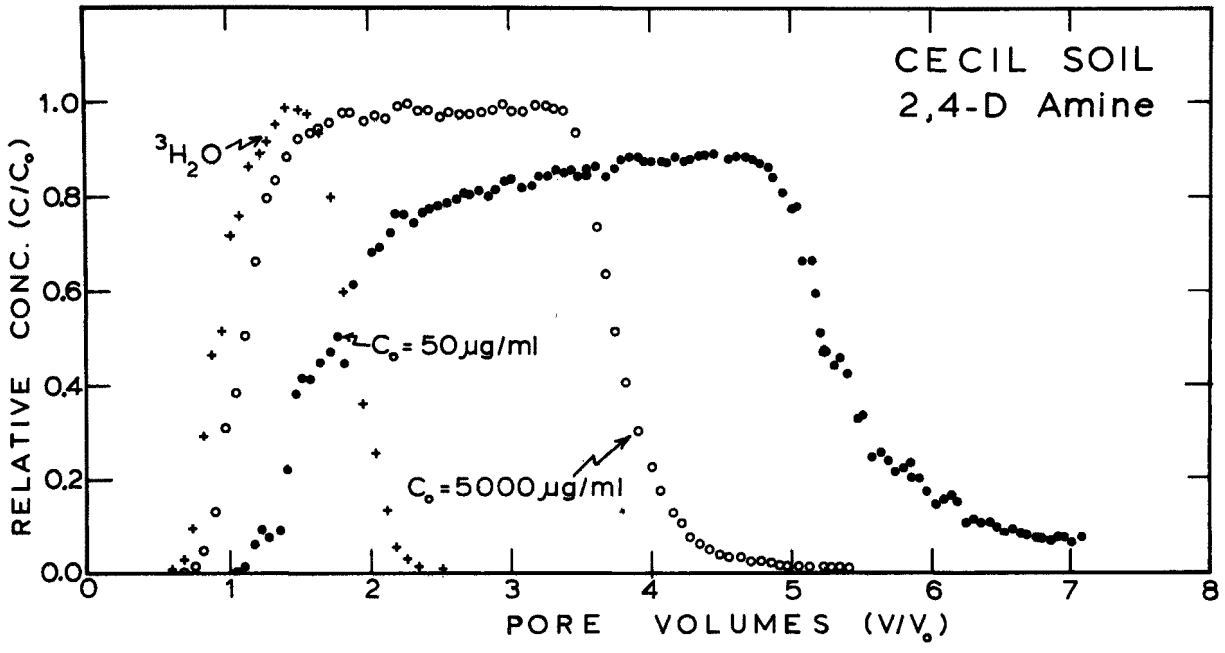

Figure 10. Effluent breakthrough curves for 2,4-D amine (C_o = 50 and 5,000 µg/ml) and for tritiated water displacement through Cecil soil column.

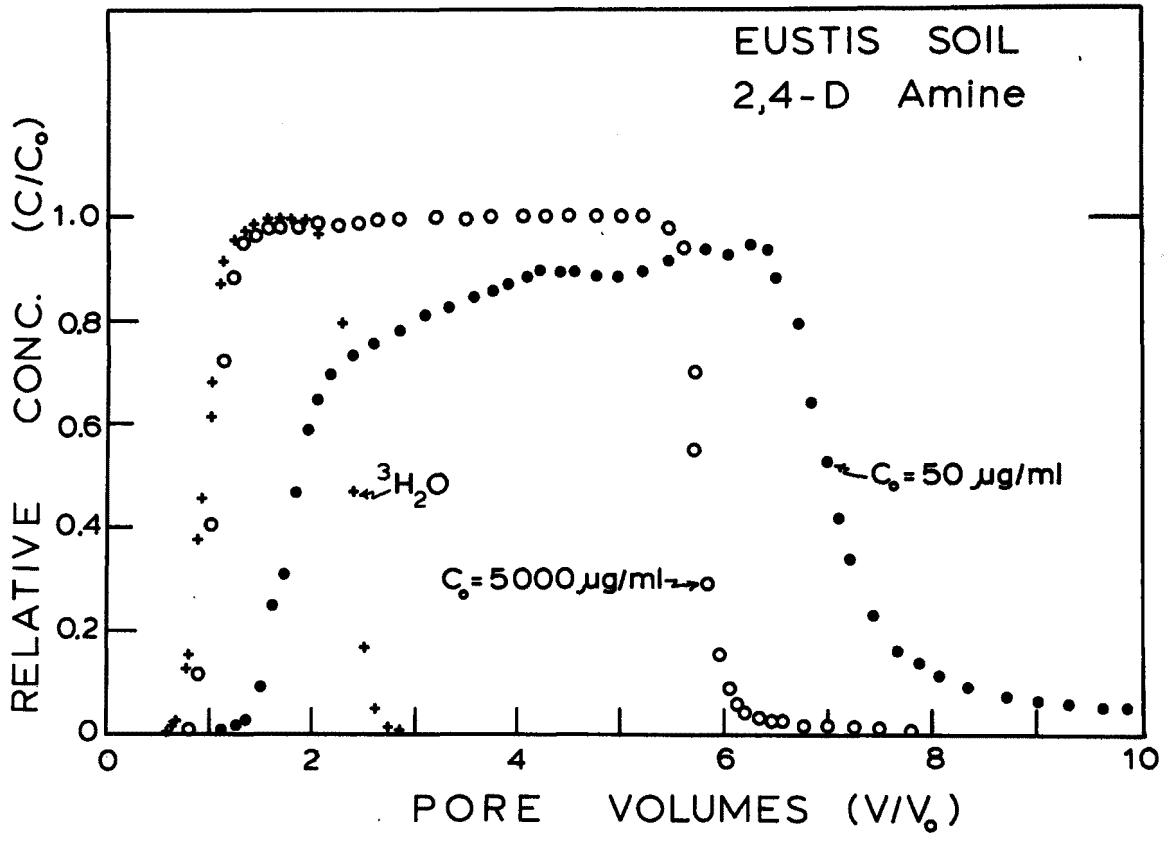

Figure 11. Effluent breakthrough curves for 2,4-D amine (C_o = 50 and 5,000 µg/ml) and for tritiated water displacement through Eustis soil column.

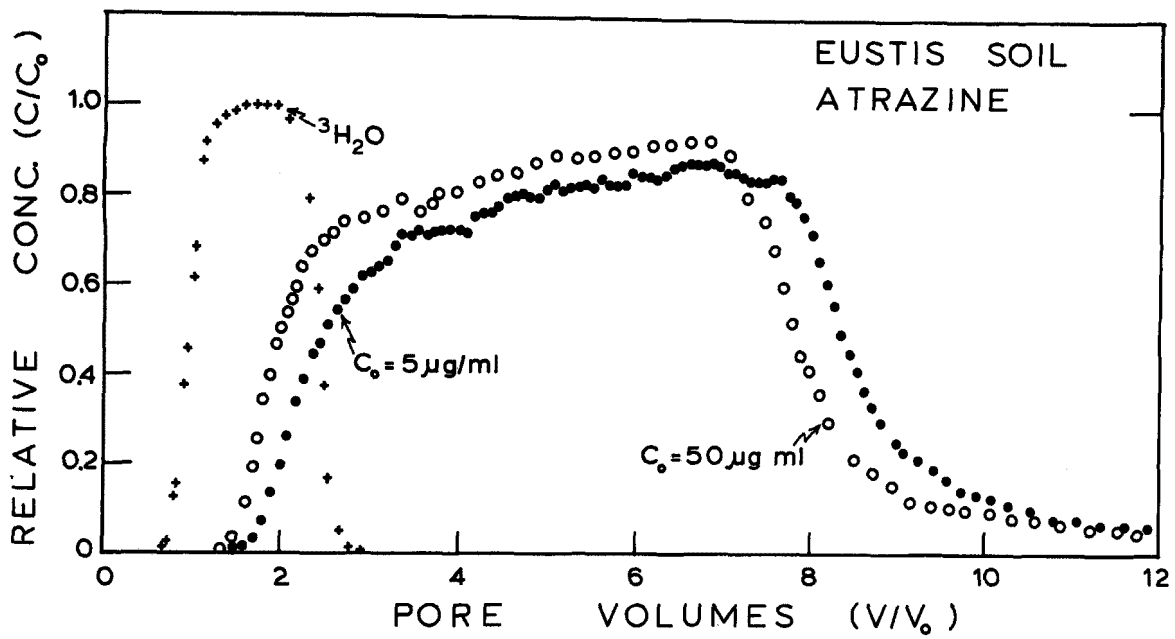

Figure 12. Effluent breakthrough curves for atrazine (C_o = 5 and 50 µg/ml) and for tritiated water displacement through Eustis soil column.

The illustrated increase in pesticide mobility at high concentrations limits the usefulness of the present low concentration data base for developing safe management practices for pesticide disposal in the soil. However, underestimation of pesticide movement by assuming linear adsorption isotherms may not be severe for pesticides with low aqueous solubilities. Ou et al. (1978a, 1978b) showed that for high loading rates, up to 20,000 µg 2,4-D/g soil, there was a significant decrease in the pesticide degradation rate with a concomitant depression of total microbial activity in the soil. Thus, due to rapid leaching and minimal microbial decomposition of pesticides at high concentrations, the potential for groundwater contamination with pesticides is increased.

SIMULATION OF PESTICIDE MOBILITY IN SOILS

Several conceptual models have been proposed and evaluated for describing the solute adsorption-desorption term ($\partial S/\partial t$) in Equation [1]. Because many of these models are based on the assumption of instantaneous adsorption and linear isotherms, they fail to describe experimental data (Davidson, et al., 1976). Models based on first-order or other reversible kinetic adsorption-desorption processes were found to simulate experimental data reasonably well at low pore-water velocities but failed at high pore-water velocities (Davidson and McDougal, 1973).

Recent attempts to model the asymmetry or "tailing" in experimental breakthrough curves thought to be associated with nonequilibrium adsorption may be classified into two groups. In the first group, physical processes are assumed responsible for the observed tailing. In these models, the soil-water regime was divided into mobile and immobile regions. Although the solute adsorption-desorption was assumed to be instantaneous, the rate at which adsorbent molecules approached a fraction of the adsorption sites was governed by diffusion through the stagnant soil-water region (Skopp and Warrick, 1974; Van Genuchten and Wierenga, 1976). The assumption that a wide-range in pore-water velocities would result in the observed tailing has been evaluated by Rao et al. (1976), using a capillary bundle model. In a variation of the latter approach, Skopp et al. (1977) considered convective-dispersive solute transport in a system consisting of two soil-water phases where the mass transfer of the solute between these phases obeyed a first-order kinetic process.

In the second group of conceptual models, the observed excessive asymmetry in the solute breakthrough curves was attributed to chemical processes. Adsorption-desorption isotherms for these models were assumed nonsingular (Van Genuchten, et al., 1974; Hornsby and Davidson, 1973). Because these models assume instantaneous equilibrium between the adsorbed and solution phases, they failed to describe experimental data for high pore-water velocities. Furthermore, the physical and/or chemical justification for the nonsingularity in the adsorption-desorption isotherms has been questioned. More recently, Selim et al. (1976) and Cameron and Klute (1977) have proposed to two-site adsorption-desorption model for describing asymmetrical breakthrough data. Because nonsingular adsorption isotherms observed earlier could be simulated using this model (Davidson, et al., 1976; Selim, et al., 1976) and because justifications for such a

conceptualization may be found in the chromatography literature (Giddings, 1965), a thorough evaluation of the two-site adsorption-desorption model appears warranted.

Agreement between model simulations and experimental data is generally used as a criterion for verification of conceptual models. Davidson et al. (1976) discussed the limitations of such an approach when model parameters were estimated by "best-fit" to experimental data and not by independent measurements. However, due to the present inadequacy of experimental techniques, independent determination of model parameters may not always be feasible. However, for curve-fitting procedures to be valid for model verification purposes, the same set of parameters estimated from a given experiment should be used to predict experimental results obtained under different conditions (e.g., column length and input concentrations, etc.).

In the model proposed by Selim et al. (1976) to describe the adsorption term $\partial S/\partial t$ in Equation [1], two groups of adsorption sites were assumed to be responsible for solute adsorption by soils; one group of sites achieved instantaneous equilibrium (type-1) while the other group was time-dependent (type-2). Using this approach, the time rate of change in the adsorbed phase concentration ($\partial S/\partial t$ in Equation 1) may be expressed as,

$$\frac{\rho}{\theta}\frac{\partial S}{\partial t} = \left[\frac{\rho K_1 N C^{N-1}}{\theta}\right]\frac{\partial C}{\partial t} + \left[k_1 C^N - \frac{k_2 \rho}{\theta} S_2\right] \qquad [4]$$

where K_1 and N are constants associated with instantaneous adsorption on type-1 sites, k_1 and k_2 are, respectively, forward and backward rate coefficients (day^{-1}) for kinetic adsorption on the type-2 sites, S_2 is adsorbed phase concentrationon the kinetic sites, and other terms are as defined previously. Note that at equilibrium, total adsorption is the sum of the two types of sites and described by the Freundlich equation:

$$S = S_1 + S_2 = K_1 C^N + K_2 C^N = K C^N \qquad [5]$$

where $K = (K_1 + K_2)$, K_1, K_2, and N are Freundlich constants, S_1 and S_2 ($\mu g/g$) are adsorbed phase concentrations on type-1 and type-2 sites, respectively, and K and S are defined on the basis of total solute adsorbed. Note that the exponent N in Equation [5] was assumed identical for both sites. Assuming that type-1 sites represent some fraction F of the total available adsorption sites, the following relationships may be stated:

$$K_1 = FK \qquad [6a]$$

$$K_2 = (1-F)K \qquad [6b]$$

By assuming a linear equilibrium adsorption isotherm (i.e., N = 1 in Equations [4] and [5]), an analytical solution to the two-site adsorption model (i.e., Equation [4] coupled with Equation [1]), has been obtained by Cameron and Klute (1977). Numerical solutions for nonlinear adsorption isotherms as well as the more general case when adsorption on both sites is kinetic-controlled were presented by Selim et al. (1976).

In the conceptual model (Equation [1]), the values of the experimental variables K, N, θ, ρ, and v are known. The dispersion coefficient, D, for each soil was estimated from tritiated water breakthrough curves using the method proposed by Rose and Passioura (1972). Experimental methods are unavailable to independently measure the values of F, K_1 and K_2. It may be noted from equations [4], [5] and [6] that,

$$K_2 = (1 - F)K = (\theta k_1/\rho k_2) \qquad [7]$$

and

$$k_2 = \theta k_1/(1 - F)\rho K \qquad [8]$$

Since the value of k_2 can be calculated given K, F, and k_1, the problem now reduces to that of estimation of the two unknown parameters F and k_1.

The model parameters were estimated using a nonlinear least-squares (NLLS) optimization procedure (Meeter and Wolfe, 1968) to fit the model prediction to measured BTC at low input concentrations. This iterative technique is based on minimizing the differences between simulated and measured BTC data by successive refinement of the initial parameter values; the estimates at each iteration are obtained by a combination of Gaussian method and steepest descent method described by Marquardt (1963). These estimates of model parameters were then used to verify the conceptual models by comparing the predicted and the measured BTC obtained at a higher input concentration. Conversely, the model parameters obtained by fitting to high concentration BTC data were also used to predict low concentration BTC data. Model verification procedures similar to this approach have been employed by Gaudet et al. (1977), O'Connor et al. (1976), and Van Genuchten and Wierenga (1977).

A finite-difference scheme was used to solve the model (Equations [1] and [4]) subject to the following initial and boundary conditions:

$$C = 0, \quad S = 0, \quad 0 \leq x \leq L, \quad t = 0 \qquad [9a]$$

$$vC - D\frac{\partial C}{\partial x} = \begin{cases} vC_o, & x = 0, \quad t \leq t_1 \\ 0, & x = 0, \quad t > t_1 \end{cases} \qquad [9b]$$

$$\frac{\partial C}{\partial x} = 0, \qquad x = L, \qquad t > 0 \qquad [9c]$$

These conditions are applicable for a soil column of L length (cm), initially void of pesticide, to which a pesticide solution of C_o (μg/ml) concentration is applied at an average pore-water velocity of v (cm/day) for a period of t_1 days, and then leached through the soil with a pesticide-free solution. All computations were performed on an AMDAHL 470 V/6-11 digital computer (soft-ware compatible with IBM 370/165 systems) with the aid of computer programs written in FORTRAN IV language.

Measured and simulated BTC for 2,4-D amine displacement through a water-saturated Cecil soil column are presented in Figure 13. Pesticide mobility was greater for high input concentrations as indicated by the left-hand shift of the BTC for C_o = 5,000 µg/ml compared to that for C_o = 50 µg/ml. This increased pesticide mobility at higher concentrations is due to the nonlinearity of the adsorption isotherm (Rao et al., 1979). The simulated curves, shown as solid lines in Figure 13, were calculated using the two-site model, where the parameters F and k_1 were estimated by curve-fitting to the C_o = 50 µg/ml BTC data. Independently measured values of K and N (Table 5) along with the estimated values of F, k_1, and k_2 were used to predict the BTC for C_o = 5,000 µg/ml. The agreement between the simulations (solid lines in Figure 13) and the measured BTC is only fair. Therefore, the model parameters K, N, F, k_1, and k_2 were re-estimated using a 4-parameter fit procedure and the C_o = 50 µg/ml BTC data. Improved prediction (dashed lines in Figure 13) of the measured BTC using the four parameter fit procedure is evident.

The values of the model parameters K, N, F, k_1, and k_2 estimated from 2,4-D amine data for C_o = 50 µg/ml by varying two parameters (F and k_1) or four parameters (K, N, F and k_1) in the NLLS procedure are presented in Table 6. More than a two-fold increase in K value and a small decrease in N over that obtained from an equilibrium adsorption isotherm was necessary to describe the BTC data for both input concentrations. Furthermore, the two estimates of the k_1 and k_2 values were also different. Note that about 60 to 70% of the total adsorption sites were required to be kinetic (i.e., type-2 sites) in order to describe the extensive tailing in the measured BTC.

Unlike the BTC for the pesticides, those for ^3H_2O displacement through the three soils were symmetrical and sigmoidal in shape (see Figures 9, 10, and 11). Excellent descriptions of the BTC were obtained using the convective-dispersive transport model (Equation 1) where all the soil-water was assumed to be mobile. A conceptual model where the soil and soil-water are partitioned into mobile and immobile phases failed to describe the BTC for ^3H_2O for the three soils studied (Rao et al., 1979). These results suggest that while Equation [1] correctly represented nonadsorbed solute transport processes, the nonequilibrium adsorption-desorption phenomenon were not adequately described by Equation [4]. Additional studies need to be carried out to identify the causes of nonequilibrium conditions for pesticide adsorption-desorption during transport in soils.

INFILTRATION EXPERIMENTS

Pesticide transport in soils during transient, unsaturated, and one-dimensional water flow was investigated using hand packed horizontal soil columns. In order to simulate a waste disposal site, the top 1.5 cm of each soil column was packed with pesticide-treated soil (2,000 µg pesticide/g soil), and 0.01 N $CaCl_2$ was infiltrated into the soil at a constant negative head (-4 cm of water). During infiltration, the rate of wetting front advance was recorded by visual observations. The soil column was cut into 1-cm segments at the end of the infiltration. In each soil segment, the total amount of pesticide (sum of solution, adsorbed, and solid

TABLE 6. COMPARISON OF MODEL PARAMETER VALUES EXTIMATED FROM THE 2,4-D AMINE BREAKTHROUGH DATA (C_o = 50 µg/ml) FOR CECIL SOIL BY VARYING EITHER TWO OR FOUR PARAMETERS IN THE NONLINEAR LEAST-SQUARES CURVE-FITTING PROCEDURE

PARAMETER	CECIL -2,4-D AMINE	
	2-parameter Fit	4-parameter Fit
N	0.83*	0.73
K	0.664*	1.604
k_1	0.324	0.425
F	0.488	0.265
k_1 (day^{-1})	0.271	0.515
k_2 (day^{-1})	0.222	0.122
k_1/k_2	1.220	4.221

*These values of the Freundlich constants were obtained independently from the equilibrium adsorption isotherm.

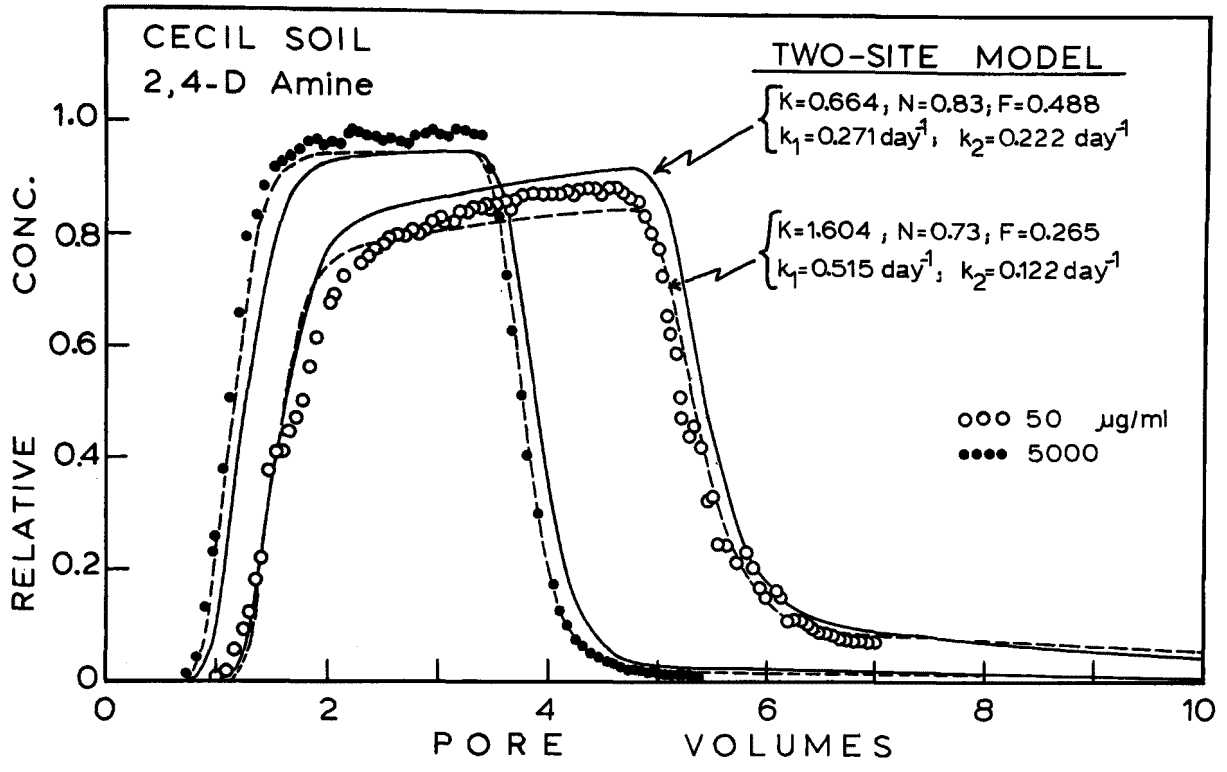

Figure 13. Measured and simulated breakthrough curves for 2,4-D amine displacement through Cecil soil column. Parameter values used to calculate the solid lines were obtained from a 2-parameter fit, and those for dashed lines were estimated from a 4-parameter fit to C_o = 50 µg/ml data.

phases) was determined by combustion, while the soil-water content was measured by oven-drying.

The depth (X_p) to which the pesticide front moved in a soil due to water infiltration was dependent upon the wetting front depth (X_w), the pesticide adsorption isotherm constants (K and N), and the aqueous solubility (C_s) of the pesticide. The relationship between these variables may be expressed as:

$$\frac{X_w}{X_p} \simeq 1 + \frac{\rho K C_s^{N-1}}{\bar{\theta}} \qquad [10]$$

where, ρ is the soil bulk density (g/cm^3) and $\bar{\theta}$ is the average soil-water content (cm^3/cm^3) in the wetted zone behind the wetting front. It should be noted that for the case of a linear adsorption isotherm (N = 1), Equation [10] is exact and the retardation of the pesticide front due to adsorption is independent of concentration, while for the nonlinear isotherm case, Equation [10] is only an approximation.

Assuming that Darcy's law is valid for unsaturated water flow in soils, the rate of the advance of the wetting front is given by (Kirkham and Powers, 1972):

$$X_w = mt^{1/2} \qquad [11]$$

where, m is a constant and t is time (min). In the present study, Equation [11] described ($r^2 \geq 0.95$) the advance of the wetting front for all soil columns considered. The values of m and other pertinent data for the infiltration experiments are summarized in Table 7.

Measured pesticide concentration profiles and soil-water content distributions at the end of infiltration in Eustis, Cecil, and Webster soil columns are shown in Figures 14 and 15. Because the final wetting front position in each soil column was different, for ease of comparison the ordinate in Figures 14 and 15 is plotted as soil depth relative to the wetting front depth (i.e., X/X_w). Except for the 2,4-D-Eustis and the terbicil-Eustis data, the relative mobilities of the pesticides are in general agreement with those anticipated from the equilibrium adsorption isotherms and pesticide aqueous solubilities. The measured mobility of terbacil and 2,4-D in the Eustis soil (Figure 14) was nearly the same although the adsorption coefficient for 2,4-D is greater than that for terbacil in Eustis soil (see Tables 5 and 7). The importance of aqueous solubility is demonstrated by the atrazine data in the Eustis soil (Figure 14 and Table 7). Note that the volume of water infiltrated into the soil column could solubilize and transport only about 4% of the total pesticide present in the top 1.5 cm segment; thus, most of the atrazine does not appear to have moved. The retardation factors, (X_w/X_p), calculated by Equation [10] are generally larger than those measured in the infiltration experiments (Table 7). Similar results were reported by Wood and Davidson (1975) for transient-flow studies and by Davidson and Chang (1972) for saturated flow experiments. The kinetics of pesticide adsorption-desorption in soils are

TABLE 7. PHYSICAL DATA FOR INFILTRATION EXPERIMENTS

SOIL	PESTICIDE	C_s (μg/ml)	ρ (g/cm^3)	X_w (cm)	m* ($cm/min^{1/2}$)	X_w/X_p Measured	X_w/X_p Calculated**	Volume of water applied (ml)	Pesticide Recovery (%)
Eustis	Atrazine	33	1.67	21.3	3.195	2.50	3.03	44	>100
Eustis	2,4-D	650	1.69	30.0	3.854	1.05	1.89	68	>100
Eustis	Terbacil	710	1.64	29.5	4.039	1.11	1.37	63	91
Cecil	Terbacil	710	1.51	28.4	0.705	1.49	3.03	68	93
Webster	Terbacil	710	1.40	24.1	0.543	4.16	4.55	67	99

*see Equation [11]

**see Equation [10]

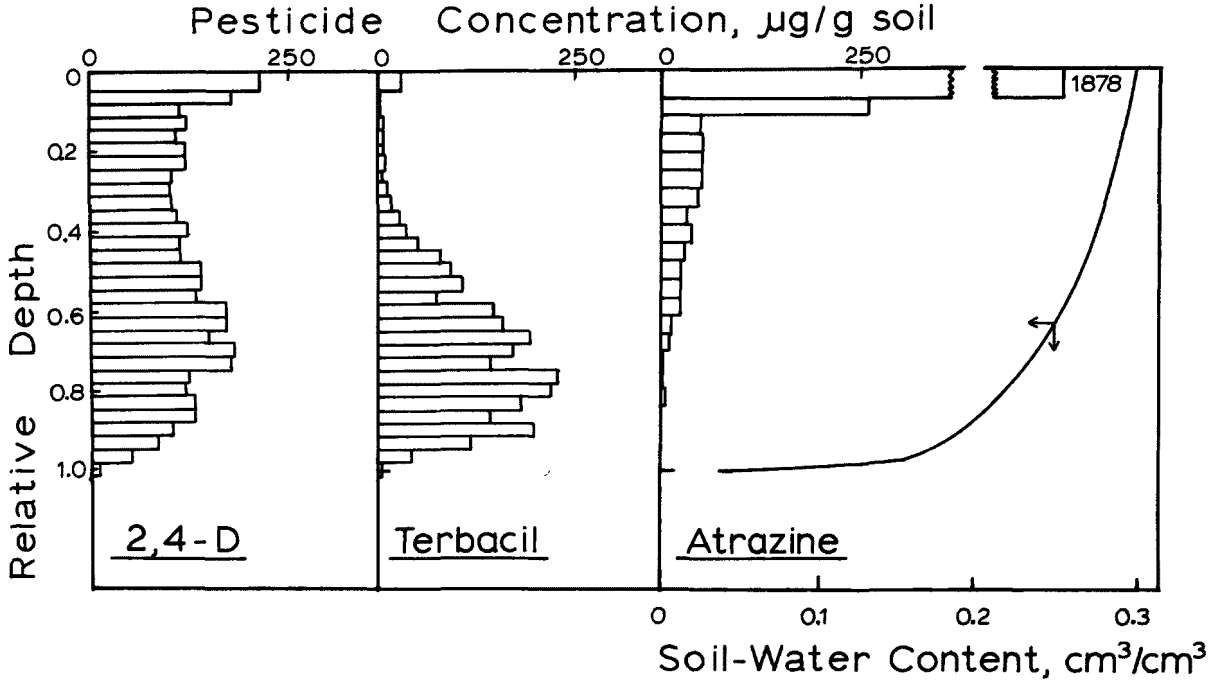

Figure 14. Soil-water content (solid line) and 2,4-D, terbacil and atrazine concentration distribution in Eustis soil following infiltration of water to approximately 30-cm. Soil was initially air dry and herbicide was in top 1.5 cm. of soil (2,000 µg/g of soil).

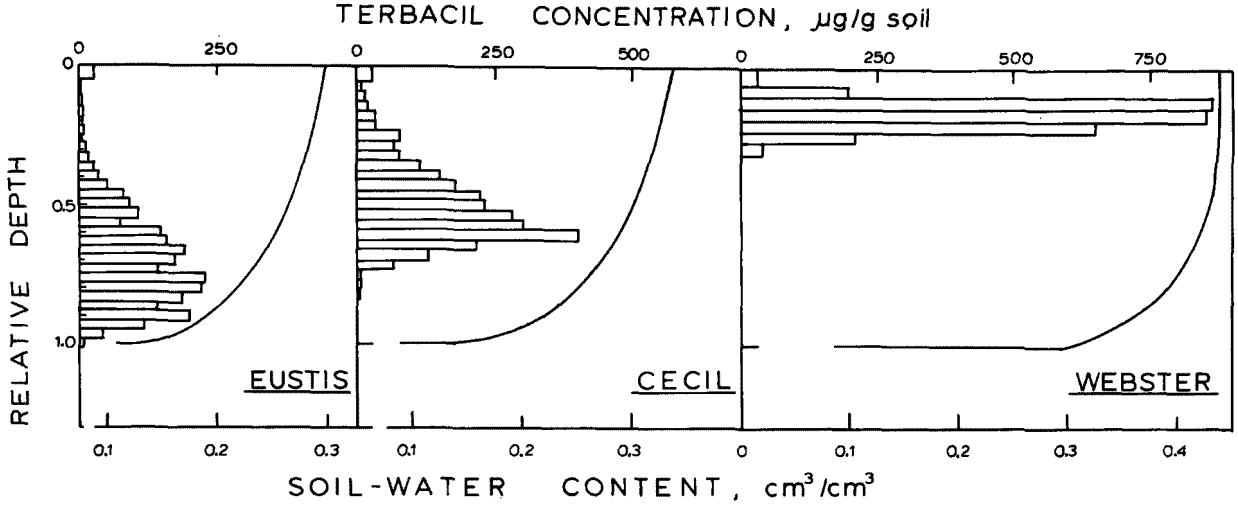

Figure 15. Soil-water content (solid lines) and terbacil concentration distributions in Eustis, Cecil and Webster soils following infiltration of water to approximately 30-cm. Soils were initially air dry and herbicide was in top 1.5-cm of soil (2,000 µg/g of soil).

not understood well enough at this time (Rao et al., 1979) to describe modeling the nonequilibrium conditions for pesticide adsorption-desorption during transient soil-water flow. Additional studies are needed in this area.

MICROBIAL ACTIVITY AND DEGRADATION

Total CO_2 evolution (respiration) is generally a good indicator of soil microbial activity. This procedure was used by Stojanovic et al. (1972) to estimate pesticide degradation rates in soil systems receiving large pesticide concentrations. A more direct procedure for determining pesticide degradation, however, is to measure $^{14}CO_2$ evolution from uniformly ring-labeled ($^{14}CF_3$ position for trifluralin) pesticides. In this study, the accuracy of total CO_2 evolution as an estimate of pesticide degradation was compared with that obtained using $^{14}CO_2$ evolution.

ATRAZINE

Soil respiration rates from Cecil soil treated with 10 ppm of technical grade atrazine generally were not different from the soil without atrazine during the entire incubation period of 82 days (Figure 16). Soil respiration rates for the 1,000 and 20,000 ppm treatments were generally smaller than the untreated soil with the inhibition being the greatest for the 20,000 ppm treatment. Total CO_2 evolution from the Cecil soil receiving 10, 1,000 and 20,000 ppm of formulated atrazine was enhanced, especially during the first 16 days of incubation and the stimulation was greatest for the 1,000 and 20,000 ppm treatments. Both technical grade and formulated atrazine at concentrations of 10, 1,000 and 20,000 ppm enhanced the CO_2 evolution from the Webster soil (Figure 17), with CO_2 evolution being greater for the largest herbicide concentration.

For incubation periods up to 70 days, 80-90% of the ^{14}C-activity extracted from the Webster soil was in the form of intact atrazine; the remainder of the ^{14}C-activity existed as metabolites. More extensive break-down occured in the soil treated with 10 ppm of technical grade atrazine and then only after incubation exceeding 80 days. A small portion (less than 1%) of the applied ^{14}C from all treatments was lost as $^{14}CO_2$ during the entire incubation period.

The breakdown of atrazine in Cecil soil was more rapid and more extensive than it was in the Webster soil. However, the amount degradated declined with increasing concentrations. In the case of the 10 ppm treatment, there was a substantial breakdown of atrazine. After 63 days of incubation of the technical material, 14% of the ^{14}C remained as the parent compound; for the case of formulated atrazine incubated for 75 days, 40% was intact atrazine. Cecil soil treated with 1,000 ppm of atrazine exhibited somewhat less breakdown. After 55 to 63 days of incubation with the technical grade material, 70 to 82% of the ^{14}C extracted was parent atrazine; and after 75 days of incubation with the formulated herbicide, 50% of the herbicide was unchanged. In the Cecil soil fortified with 20,000 ppm, even less breakdown occurred; after incubation for 75 days, 80% of the ^{14}C remaining was atrazine. Similar to the Webster soil, only a small quantity of the

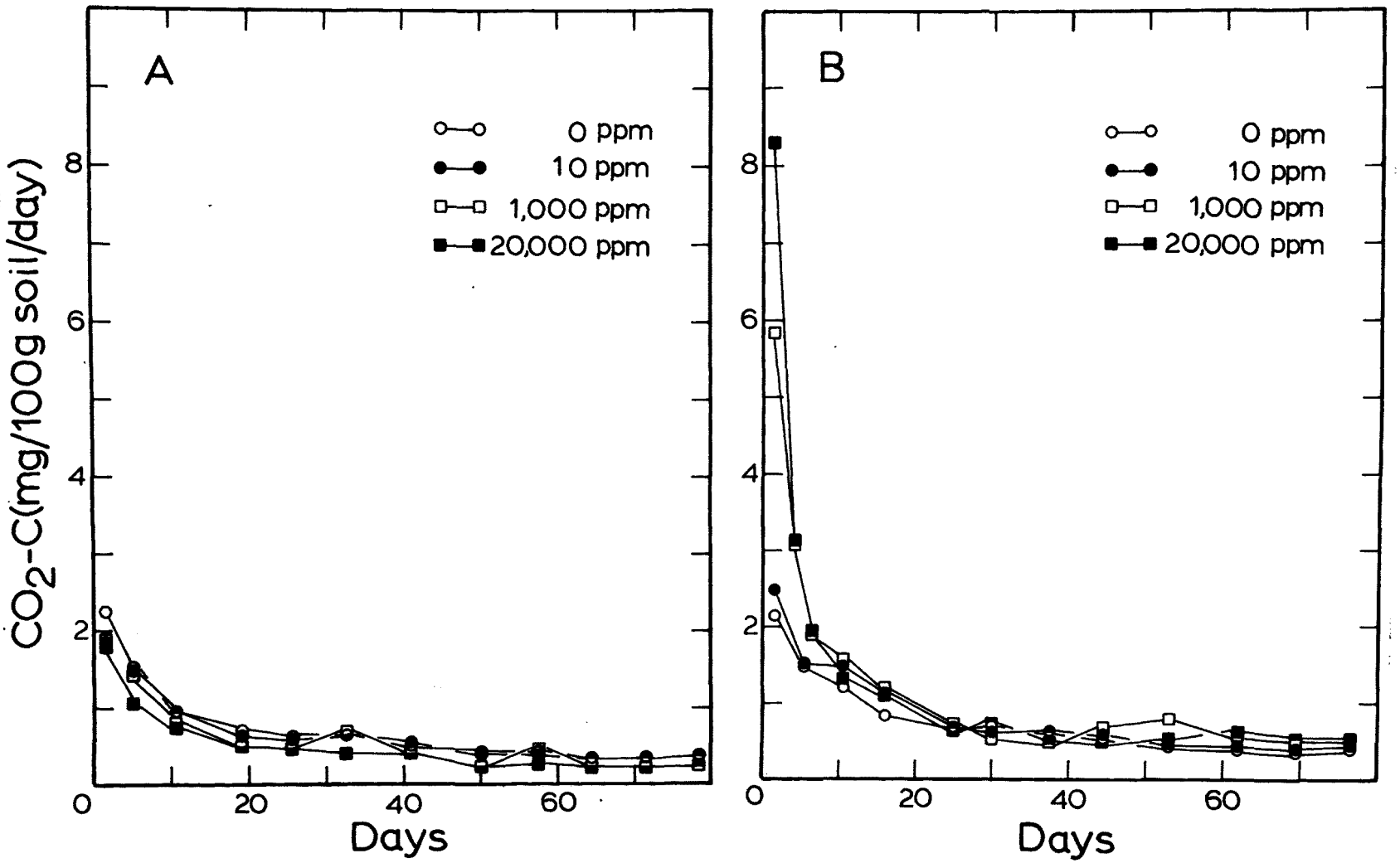

Figure 16. CO_2 evolution rate from the Cecil soil receiving various concentrations of atrazine. (A) Technical grade; (B) Formulated atrazine.

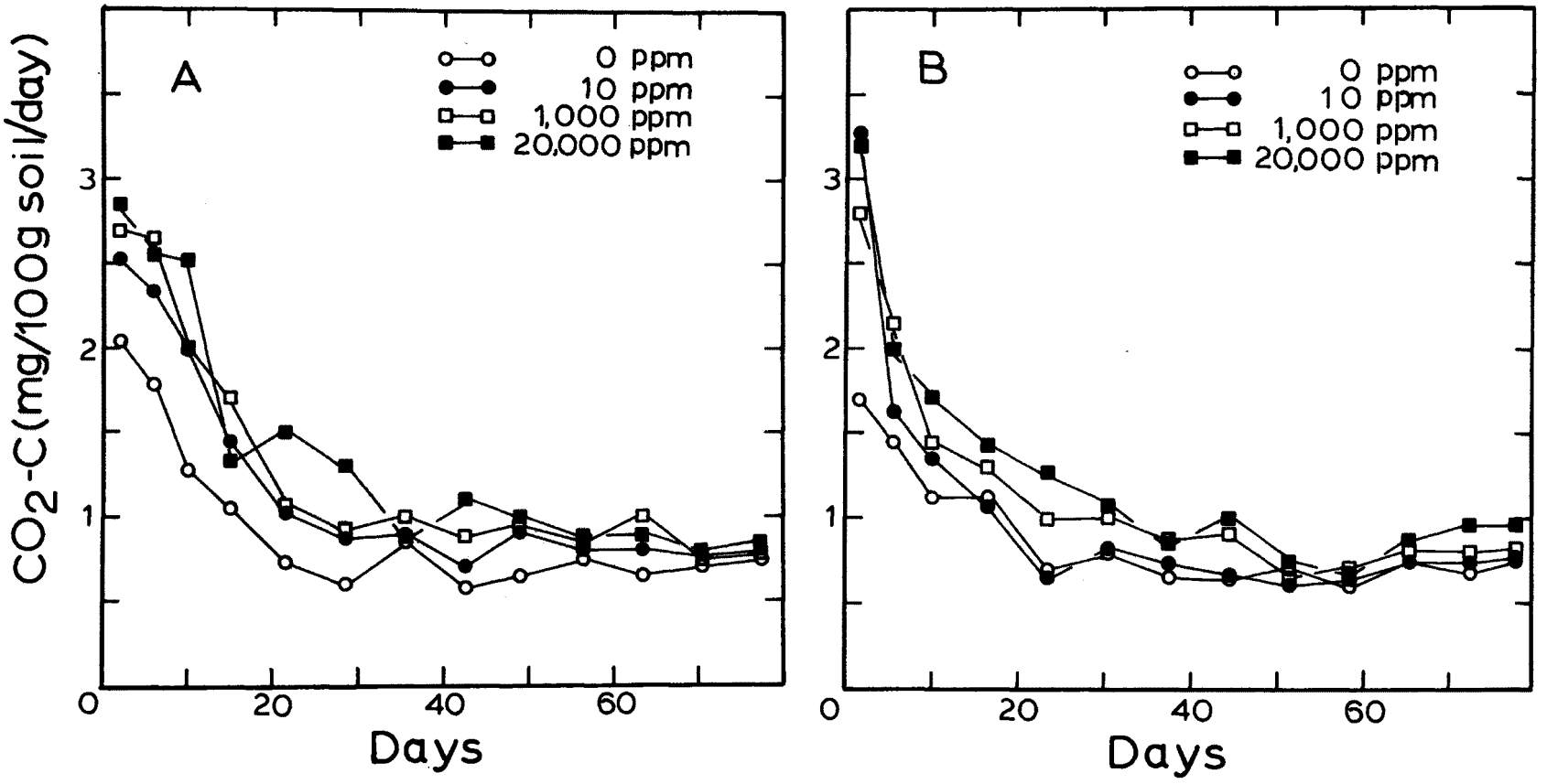

Figure 17. CO_2 evolution rate from the Webster soil receiving various concentrations of atrazine. (A) Technical grade; (B) Formulated atrazine.

total ^{14}C-activity (less than 1%) was degraded to $^{14}CO_2$ in the Cecil soil.

Technical grade and formulated atrazine at concentrations of 10, 1,000 and 20,000 ppm did not have a significant effect on bacterial populations in the Cecil or Webster soils, except for the 20,000 ppm formulated atrazine concentration in the Cecil soil (Table 8). The bacterial population in this treatment was nearly four times higher than the untreated soil following eleven weeks of incubation.

The number of fungi in the technical grade treated Cecil soil at 10, 1,000 and 20,000 ppm were not significantly different from the untreated soil following eleven weeks of incubation (Table 9). Fungal populations in the technical grade treated Webster soil at the same application rates were, however, significantly higher ($p < 0.01$). Fungal populations in all the formulation atrazine treated soils, but one, were not significantly different. Fungal populations in the Cecil soil treated with 20,000 ppm of formulated atrazine were reduced significantly ($p < 0.01$) during the first seven weeks of incubation.

Technical grade and formulated atrazine at concentrations of 10, 1,000 and 20,000 ppm showed no consistent effect on the actinomycete populations in the Cecil or Webster soils, except for the Cecil soil which received 20,000 ppm of formulated atrazine (Table 10). In this treatment, actinomycete populations were reduced significantly ($p < 0.01$).

METHYL PARATHION

Total CO_2 evolution from the Webster soil containing 24.5 and 10,015 ppm of technical grade and formulated methyl parathion were generally not different from an untreated soil (Table 11), except during the first few days of incubation. CO_2 evolution was somewhat greater for the treatments receiving a pesticide during the first few days of incubation than for the untreated soils. Unlike the Webster soil, total CO_2 evolution from the Cecil soil containing 10,015 ppm of methyl parathion was reduced (Table 12). The reduction was somewhat greater for the Webster soil receiving the formulated material. Apparently, the formulation chemicals at this concentration exhibited an inhibitory effect on soil respiration in the Cecil soil, but not for the Webster soil. CO_2 evolution from the Cecil soil receiving 24.5 ppm of technical grade or formulated methyl parathion was not different from the untreated soil.

Both technical grade and formulated methyl parathion at 24.5 ppm were degraded rapidly to CO_2, H_2O and simple inorganic ions in the Webster and Cecil soils as indicated by $^{14}CO_2$ evolution from uniformly ring labeled ^{14}C-methyl parathion (Table 13). More than half of the ^{14}C-methyl parathion added was mineralized to $^{14}CO_2$ in 10 days in the Webster and Cecil soils. Degradation rates were greater in the Webster soil than the Cecil soil. Degradation rates from the soil receiving the technical grade material were somewhat greater than those receiving the formulated material. At the end of 52 days of incubation, 75% to 85% of ^{14}C-methyl parathion in the 24.5 ppm treatments was degraded to $^{14}CO_2$. Lichtenstein, et al. (1977) reported that up to 43% of the ^{14}C-ring labeled methyl parathion applied to a soil

TABLE 8. EFFECT OF TECHNICAL GRADE AND FORMULATED ATRAZINE ON BACTERIAL POPULATIONS IN CECIL AND WEBSTER SOILS

Concentration of atrazine ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-6}) Time (Weeks) 0.1	1	2	3	4	5
0	Cecil	26.0[a](26.4)[b]	16.2(20.5)	17.3(19.6)	14.4(13.0)	19.2 (ND)	15.5(18.7)
	Webster	47.6(53.8)	31.7(30.7)	28.3(22.4)	ND (28.6)	20.5(24.7)	18.6 (ND)
10	Cecil	24.9(29.9)	21.9(23.3)	20.1(19.2)	12.5(16.4)	13.3 (ND)	14.1(14.8)
	Webster	58.4(56.2)	33.6(32.2)	31.7(28.9)	ND (28.3)	22.1 (30.9)	24.3 (ND)
1,000	Cecil	30.1(30.6)	18.0(20.5)	18.0(24.9)	10.3(14.8)	10.9 (ND)	17.3(15.0)
	Webster	62.7(30.4)	33.8(38.2)	22.9(25.7)	ND (20.3)	22.6(34.8)	17.7 (ND)
20,000	Cecil	32.4(69.1)[d]	19.6(111.0)[d]	22.1[c](121.0)[d]	14.4(70.9)[d]	16.2 (ND)	18.5(51.3)[d]
	Webster	52.0(50.7)	29.9(70.7)[d]	22.6(59.3)[d]	ND (47.1)[d]	24.2(28.1)	16.1 (ND)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$

(continued)

TABLE 8. (continued)

Concentration of atrazine ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-6}) Time (Weeks) 6	7	8	9	10	11
0	Cecil	ND (15.7)	15.2(16.0)	13.9 (ND)	17.7(13.5)	16.3(13.7)	18.5(16.2)
	Webster	13.5(23.4)	18.2(22.8)	16.1(18.5)	19.2(20.0)	20.0(21.1)	19.5(25.2)
10	Cecil	ND (20.9)	12.1(14.7)	17.7 (ND)	10.9[c](11.4)	12.0(14.8)	13.7(13.9)
	Webster	18.5(33.8)	27.0(16.4)	20.0(19.8)	26.8(18.7)	24.4(21.6)	19.8(19.5)
1,000	Cecil	ND (11.6)	11.4(15.0)	17.6 (ND)	13.7(11.9)	11.9(16.9)	17.1(13.0)
	Webster	21.8(19.8)	19.0(19.2)	21.1(27.3)	13.8(23.1)	23.9(21.8)	19.2(27.0)
20,000	Cecil	ND (49.6)[d]	13.5(56.3)[d]	13.9 (ND)	19.8(52.0)[d]	16.0(36.3)[d]	19.2(57.2)[d]
	Webster	17.6(30.4)	18.7(28.9)	20.8(32.2)	15.3(23.4)	19.5(25.1)	17.4(23.1)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$

(continued)

TABLE 8. (continued)

Concentration of atrazine ($\mu g \cdot g^{-1}$)	cfu·g^{-1} soil (x 10^{-6}) Time (Weeks)	Average
0	Cecil	17.3(17.3)
	Webster	23.0(26.5)
10	Cecil	15.7(17.9)
	Webster	27.9(26.9)
1,000	Cecil	16.0(17.4)
	Webster	25.3(26.2)
20,000	Cecil	18.7(67.8)[d]
	Webster	23.1(38.1)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

TABLE 9. EFFECT OF TECHNICAL GRADE AND FORMULATED ATRAZINE ON FUNGAL POPULATIONS IN CECIL AND WEBSTER SOILS.

Concentration of atrazine ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks) 0.1	1	2	3	4	5
0	Cecil	8.0[a](8.6)[b]	8.1(9.1)	9.0(8.9)	9.0(8.8)	8.7 (ND)	8.9(8.5)
	Webster	15.2(15.2)	14.0(15.3)	8.7(12.1)	ND (13.3)	8.4(12.2)	7.0 (ND)
10	Cecil	8.9(8.6)	10.2(8.5)	9.5(8.9)	10.0(9.1)	9.6 (ND)	8.6(9.4)
	Webster	15.9(16.3)	15.3(12.7)	14.4[d](12.1)	ND (12.9)	9.8(15.0)	14.4[d](ND)
1,000	Cecil	9.4(7.9)	9.6(9.7)	8.4(8.4)	7.7(9.5)	8.8 (ND)	9.5(8.9)
	Webster	17.7(10.9)[d]	14.8(14.4)	14.2[d](13.3)	ND (14.7)	13.3[d](17.8)	12.7[d](ND)
20,000	Cecil	7.7(3.8)[d]	8.8(6.5)[d]	9.1(5.3)[d]	9.3(6.2)[d]	8.9 (ND)	9.7(6.5)[d]
	Webster	17.3(12.8)[c]	16.5(15.3)	11.4[c](14.0)	ND (14.8)	14.6[d](12.9)	14.6[d](ND)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 9. (continued)

Concentration of atrazine ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks) 6	7	8	9	10	11
0	Cecil	ND (9.1)	8.2(8.6)	8.5 (ND)	9.1(9.0)	8.6(8.0)	9.3(9.5)
	Webster	6.1(10.6)	6.9(13.1)	8.1(10.2)	6.5(11.6)	7.1(11.1)	6.5(12.7)
10	Cecil	ND (9.1)	8.4(9.1)	10.8 (ND)	8.8(9.6)	8.9(9.3)	8.8(8.6)
	Webster	9.9[d](10.8)	12.0[d](10.2)	10.8(11.9)	14.2[d](12.1)	13.3[d](11.0)	12.5[d](10.4)
1,000	Cecil	ND (9.7)	8.8(9.2)	9.4 (ND)	8.6(8.4)	7.9(8.6)	9.0(8.2)
	Webster	12.8[d](11.4)	13.3[d](14.7)	11.6[d](14.8)[d]	9.8[d](16.4)[d]	11.8[d](11.1)	10.6[d](14.6)
20,000	Cecil	ND (5.5)[d]	8.7(6.6)[d]	9.9 (ND)	7.2(9.4)	8.0(8.3)	7.6(7.5)
	Webster	13.8[d](12.4)	13.5[d](11.5)	11.9[c](14.3)[d]	13.7[d](13.1)	13.3[d](15.0)[d]	13.1[d](16.0)[c]

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 9. (continued)

Concentration of atrazine ($\mu g \cdot g^{-1}$)	cfu$\cdot g^{-1}$ soil (x 10^{-4}) Time (Weeks)	Average
0	Cecil	8.7(8.8)
	Webster	8.6(12.5)
10	Cecil	9.3(9.0)
	Webster	13.0[d](12.3)
1,000	Cecil	8.8(8.9)
	Webster	13.0[d](14.0)
20,000	Cecil	8.6(6.6)[d]
	Webster	14.0[d](13.8)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

TABLE 10. EFFECT OF TECHNICAL GRADE AND FORMULATED ATRAZINE ON ACTINOMYCETE POPULATIONS IN CECIL AND WEBSTER SOILS

Concentrations of atrazine ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-5}) Time (Weeks) 0.1	1	2	3	4	5
0	Cecil	4.6[a](1.8)[b]	2.3(3.4)	5.5(10.0)	6.6(10.0)	10.7 (ND)	5.9(6.2)
	Webster	14.6(17.7)	14.6(12.7)	8.8(7.5)	ND (12.7)	9.6(12.5)	14.0 (ND)
10	Cecil	5.2(3.0)	7.3(2.5)	9.8[c](4.3)[c]	9.4(7.5)	11.7 (ND)	3.7(7.3)
	Webster	17.4(16.6)	16.4(8.3)	11.2(8.1)	ND (13.0)	12.2(8.8)	12.5 (ND)
1,000	Cecil	6.0(1.6)	6.4(1.4)	7.5(3.9)[c]	6.4(5.2)[c]	7.4 (ND)	6.4(5.5)
	Webster	19.8(10.4)[c]	14.8(12.7)	8.8(10.1)	ND (11.4)	13.5(10.4)	8.6[c](ND)
20,000	Cecil	3.2(0.2)[d]	4.8(0.2)[d]	8.0(1.4)[d]	11.9[d](0.9)[d]	8.0 (ND)	7.3(0.5)[d]
	Webster	19.0(13.8)	13.8(10.4)	11.2(10.1)	ND (13.0)	13.5(7.5)[c]	10.7 (ND)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 10. (continued)

Concentration of atrazine ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-5}) Time (Weeks) 6	7	8	9	10	11
0	Cecil	ND (8.4)	1.8(5.5)	4.8 (ND)	1.4(2.7)	3.2(4.3)	1.4(2.1)
	Webster	ND(10.4)	12.7(8.5)	13.0 (ND)	9.9(10.4)	ND (11.2)	12.0(9.6)
10	Cecil	ND (7.8)	2.7(5.7)	5.2 (ND)	1.1(2.1)	1.4(4.8)	1.8(0.7)
	Webster	ND (10.4)	8.8(7.3)	9.1 (ND)	10.1(8.1)	ND (9.6)	14.3(11.4)
1,000	Cecil	ND (11.2)	2.1(3.0)	5.5 (ND)	2.1(2.3)	1.1(4.3)	1.4(0.9)
	Webster	ND (7.0)	13.3(6.5)	12.5 (ND)	14.8[c](13.8)	ND (11.4)	9.6(11.7)
20,000	Cecil	ND (0.7)[d]	3.0(1.4)[d]	8.4[c] (ND)	2.3(0.2)[d]	2.1(0.5)[d]	0.7(0.2)[c]
	Webster	ND (9.6)	15.6(6.8)	11.7 (ND)	12.2(9.9)	ND (9.1)	17.7(13.5)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 10. (continued)

Concentration of atrazine ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-5}) Time (Weeks) Average
0	Cecil	4.4(5.4)
	Webster	12.1(11.3)
10	Cecil	5.4(5.2)
	Webster	12.4(10.2)
1,000	Cecil	4.7(3.8)
	Webster	12.9(10.5)
20,000	Cecil	5.4(0.6)[d]
	Webster	13.9(10.4)

[a]First column, technical grade atrazine.

[b]Second column, formulated atrazine.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

TABLE 11. TOTAL CO_2 EVOLUTION FROM METHYL PARATHION TREATED WEBSTER SOIL

Time (day)	CO_2-C mg/100g soil/day				
	0 ppm	24.5 ppm		10,015 ppm	
		Technical	Formulated	Technical	Formulated
2	1.81	2.88	2.40	1.99	2.64
7	1.32	1.53	1.85	1.45	1.73
12.5	1.15	1.25	0.91	1.00	1.25
18.5	0.86	1.00	1.24	0.93	0.89
25.5	0.79	0.89	1.07	0.89	0.82
32.5	0.72	0.82	0.89	0.72	0.75
39.5	0.51	0.58	0.58	0.54	0.40
47.5	0.56	0.56	0.72	0.50	0.61
Total	45.65	54.94	58.18	47.74	52.79

TABLE 12. TOTAL CO_2 EVOLUTION FROM METHYL PARATHION TREATED CECIL SOIL

Time (day)	CO_2-C mg/100g soil/day				
	0 ppm	24.5 ppm		10,015 ppm	
		Technical	Formulated	Technical	Formulated
2	1.93	1.75	2.16	1.34	0.45
7	1.20	1.12	1.28	0.55	0.67
12.5	0.86	0.86	0.86	0.61	0.57
18.5	0.82	0.82	0.72	0.37	0.40
25.5	0.75	0.61	0.79	0.54	0.51
32.5	0.65	0.65	0.65	0.54	0.47
39.5	0.61	0.68	0.79	0.58	0.65
47.5	0.56	0.40	0.42	0.40	0.40
Total	44.10	40.95	45.04	29.04	26.74

TABLE 13. PERCENT OF ^{14}C-METHYL PARATHION EVOLVED AS $^{14}CO_2$ IN WEBSTER AND CECIL SOILS

Concentration (ppm)		% evolved as $^{14}CO_2$ Time (days)					
		4	10	15	29	43	52
		----------Webster soil----------					
24.5	Technical	45.9	67.0	73.3	80.6	83.8	85.0
	Formulated	44.8	64.5	69.7	76.2	79.2	80.3
10,015	Technical	0	0	0	~0	<0.1	<0.1
	Formulated	0	0	0	~0	<0.1	<0.1
		----------Cecil soil----------					
24.5	Technical	36.7	59.7	66.6	75.1	78.5	79.4
	Formulated	32.6	55.0	61.9	70.6	73.9	75.0
10,015	Technical	0	0	0	~0	~0	~0
	Formulated	0	0	0	~0	<0.1	<0.1

exhibited the characteristics of a bound residue after 28 days, and only 7% of the ^{14}C-activity was extractable.

For the 10,015 ppm concentrations, very little technical grade or formulated methyl parathion was degraded in Webster or Cecil soils during 52 days of incubation. Less than 0.1% of ^{14}C-methyl parathion was degraded to $^{14}CO_2$ at the 10,015 ppm concentration (technical grade and formulated). Total CO_2 evolution from the soils containing 10,015 ppm methyl parathion was in good agreement with $^{14}CO_2$ evolution. The total amount of methyl parathion-carbon added to 100 g of soil at 10,015 ppm was 365 mg. If extensive degradation occurred, a substantial amount of CO_2 would have evolved. For example, if 10% of the methyl parathion had mineralized, 36.6 mg of CO_2-carbon would have evolved. Total CO_2 evolution from the Cecil soil receiving 10,015 ppm of methyl parathion was less than the untreated soil; therefore, it would not be expected that extensive degradation occurred. Total CO_2 evolution for the Webster soil receiving 10,015 ppm of methyl parathion was not enhanced, and extensive degradation did not occur. Microbial populations have been reported to be inhibited five years after parathion application of 30,000 to 95,000 ppm to a soil (Wolfe, et al., 1973).

This project has shown that for low application rates, methyl parathion was nonpersistent in soils, but the insecticide persisted following applications of large quantities. Thus, using the results from the low application rates to predict the behavior of methyl parathion at high applications would lead to erroneous conclusions.

TRIFLURALIN

Soil respiration rates from Cecil and Webster soils receiving 10 ppm of technical grade and formulated trifluralin were not different from untreated soils except during the first week of incubation (Figures 18 and 19). Carbon dioxide evolution from the Webster soil receiving 1,000 and 20,000 ppm of technical grade trifluralin were not enhanced except during the initial incubation period (Figure 19). Soil respiration from the Cecil soil treated with 1,000 and 20,000 ppm at technical grade trifluralin was enhanced during the first two weeks of incubation. CO_2 evolution from the Cecil and Webster soil receiving 1,000 ppm of formulated trifluralin was also enhanced during the initial period of incubation, and the enhancement of CO_2 evolution was greatest for the Webster soil. CO_2 evolution in the Cecil and Webster soils treated with 20,000 ppm of formulated trifluralin was stimulated in the first 5 days of incubation. This stimulation was followed by a later increase in CO_2 production. Stimulation in CO_2 production in the Webster soil treated with 20,000 ppm of formulated trifluralin was much greater than that in the Cecil soil receiving the same treatment, and CO_2 production in the Webster soil remained 2 to 9 times higher than for the untreated Webster soil during the entire 83 days of incubation.

Less than 5% of the trifluralin applied to the Cecil and Webster soils was degraded to $^{14}CO_2$ after 83 days of incubation. Several metabolites from the trifluralin were detected and characterized. Information regarding metabolites will be presented in the metabolite section of this manuscript.

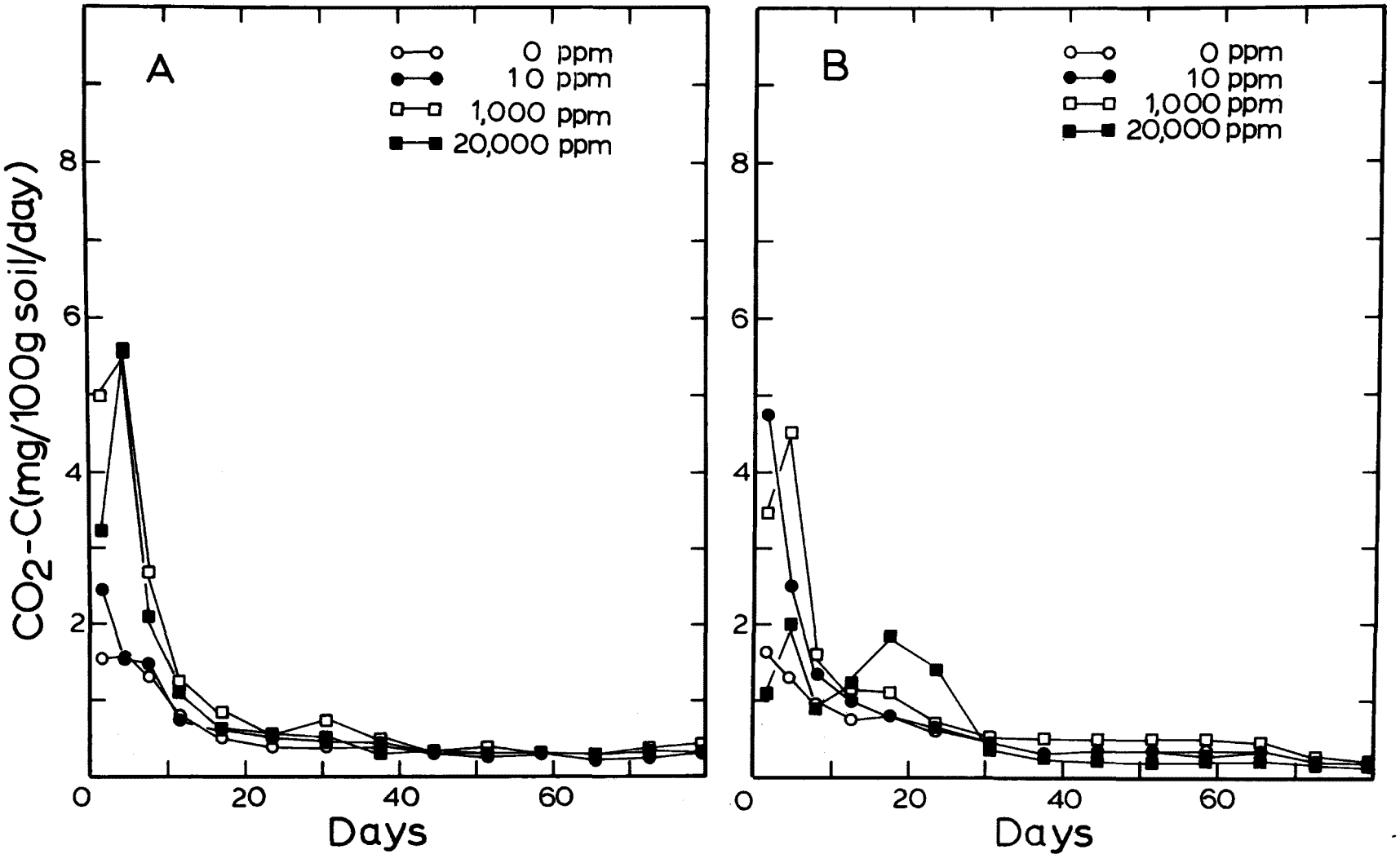

Figure 18. CO_2 evolution rate from the Cecil soil receiving various concentrations of trifluralin (A) Technical grade; (B) Formulated trifluralin.

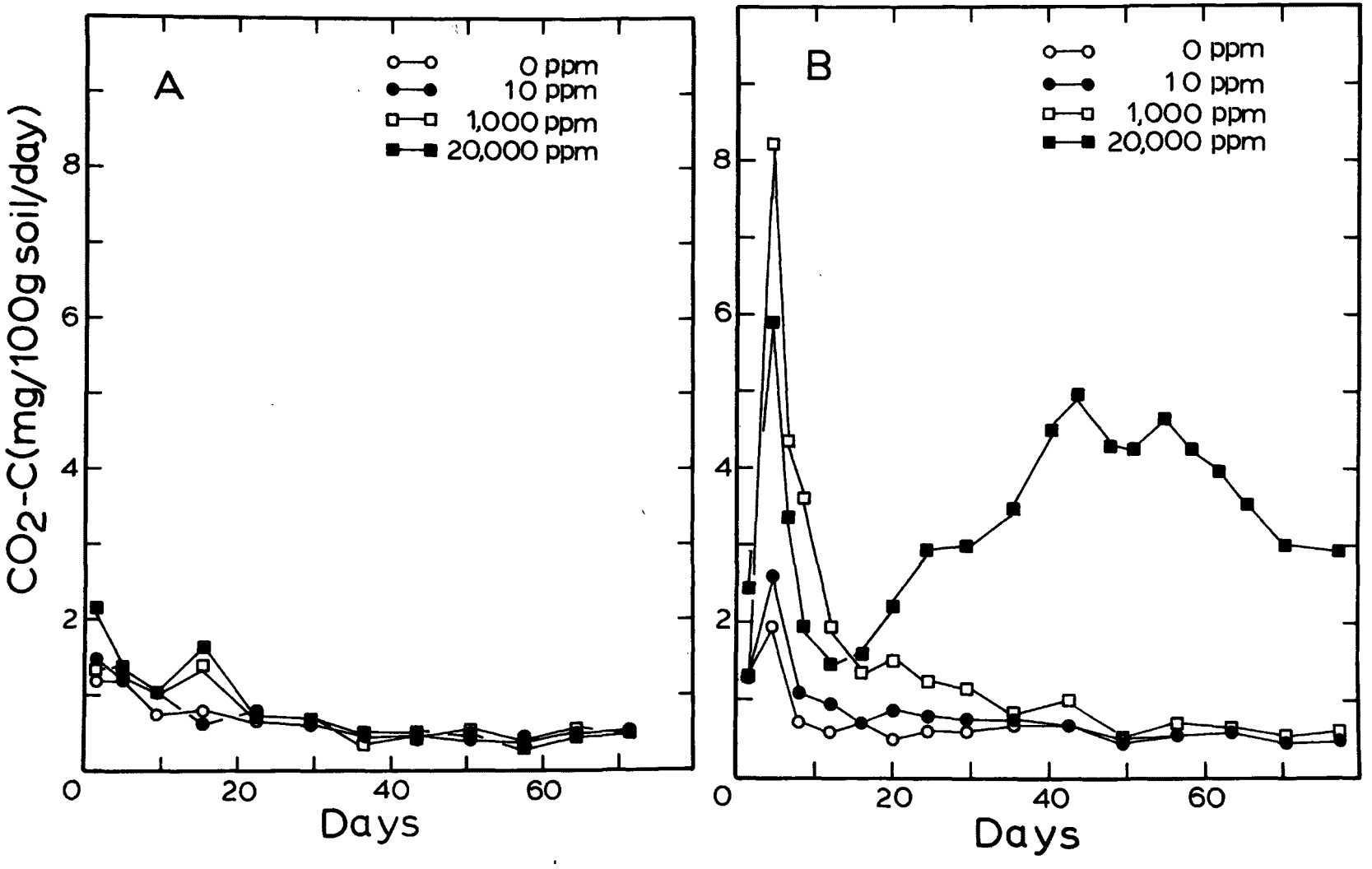

Figure 19. CO_2 evolution rate from the Webster soil receiving various concentrations of trifluralin (A) Technical grade; (B) Formulated trifluralin.

Bacterial populations in the Webster soil treated with 10 ppm trifluralin (technical grade and formulated) were not significantly different from the untreated soil (Table 14). However, bacterial populations in the Webster soil receiving 1,000 ppm of formulated trifluralin were consistently higher than the untreated soil with the greater stimulation occurring in the Cecil rather than the Webster soil (Table 14). For 20,000 ppm of technical grade trifluralin, bacterial populations in the Cecil soil were greater than those in the Webster soil. Bacterial populations in the Cecil soil receiving 20,000 ppm of formulated trifluralin were initially inhibited, but were enhanced significantly after two weeks of incubation; whereas bacterial populations in the Webster soil for the same treatment were stimulated during the first 18 hours and the stimulation was greatest during the third week of incubation.

Fungal populations in the Cecil and Webster soils treated with 10 ppm of technical grade and formulated trifluralin were generally not significantly different from the untreated soil (Table 15). For the 1,000 ppm treatments, fungal populations in the Cecil soil receiving technical grade and in the Webster soil receiving formulated trifluralin were not significantly affected, whereas the Cecil soil treated with the formulated material and the Webster soil with the technical grade material showed a significant effect at the 0.01 and 0.05 levels, respectively. Fungal populations were significantly reduced in both soils at 20,000 ppm of formulated trifluralin; whereas fungal populations in the Webster soil receiving the technical grade material were stimulated during the first four weeks.

Actinomycete populations in Cecil and Webster soils receiving 10, 1,000 and 20,000 ppm of trifluralin (technical grade or formulation) were not significantly different from the untreated soils (Table 16) except in the 20,000 ppm formulated trifluralin treatments. Actinomycete populations in both soils receiving 20,000 ppm of the formulated material were reduced significantly.

2,4-D

The rates of total CO_2 evolution from the Webster soil receiving various concentrations of 2,4-D are given in Figure 20. A common characteristic of the CO_2 evolution rates for 5,000 and 20,000 ppm was the presence of two response peaks. The initial increase in CO_2 evolution rate was followed by a decline and a second increase. This was observed for both forms of 2,4-D. The CO_2-carbon (CO_2-C) produced prior to the appearance of the second peak was not from the 2,4-D-carbon (2,4-C) because very little $^{14}CO_2$ was measured during this initial time period. For formulated 2,4-D, the CO_2-C in the first peak appeared to come from the oxidation of the formulation ingredients including dimethylamine; and for technical grade 2,4-D, the CO_2-C probably originated from impurities and soil organic matter. The appearance of the second peak coincided with the occurrence of 2,4-D degradation (^{14}C-CO_2 activity) (Figure 21). Assuming all CO_2-C was evolved from 2,4-D-carbon, the extent of degradation during the entire experimental period (80 days) and during the second peak period were calculated and are shown in Table 17. These results clearly illustrated that the majority of the CO_2-C evolved during the second peak period was

TABLE 14. EFFECT OF TECHNICAL GRADE AND FORMULATED TRIFLURALIN ON BACTERIAL POPULATIONS IN CECIL AND WEBSTER SOILS

Concentration of trifluralin ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-6}) Time (Weeks) 0.1	1	2	3	4	5
0	Cecil	17.2[a](17.0)[b]	8.7(19.9)	11.4(16.5)	ND (14.4)	16.2(14.9)	ND (12.8)
	Webster	39.4(25.2)	21.1(17.0)	18.9(15.9)	20.5(15.5)	15.3(14.4)	ND (13.1)
10	Cecil	20.1(16.4)	12.5(17.1)	12.8(14.9)	10.2(15.4)	11.4(16.0)	ND (13.3)
	Webster	46.8(46.5)[c]	40.0[d](28.3)[c]	31.5[d](20.8)	20.7(19.0)	17.6(14.6)	ND (15.0)
1,000	Cecil	20.7(40.7)[d]	11.5(259.0)[d]	10.7(238.0)[d]	11.1(331.0)[d]	9.1(288.0)[d]	ND(246.0)[d]
	Webster	49.1(38.2)[c]	29.6(298.0)[d]	26.4(107.0)[d]	23.9(42.8)[d]	17.9(41.3)[d]	ND (31.2)[d]
20,000	Cecil	27.9[d](3.6)[d]	18.5[d](70.3)[d]	33.3[d](173.0)[d]	21.0(120.0)[d]	21.1(74.6)[d]	ND (62.2)[d]
	Webster	39.9(63.2)[d]	28.3(352.0)[d]	27.0(559.0)[d]	19.0(2030.0)[d]	18.6(1140.0)[d]	ND(484.0)[d]

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 14. (continued)

Concentration of trifluralin ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-6}) Time (Weeks) 6	7	8	9	10	11
0	Cecil	8.6(16.7)	11.3 (ND)	12.5(12.3)	ND (18.1)	11.4 (ND)	12.4(14.4)
	Webster	15.7(13.9)	ND (17.9)	16.3(14.8)	15.3(12.7)	16.6(14.0)	ND (ND)
10	Cecil	8.3(14.1)	11.9 (ND)	10.6(14.0)	ND (15.0)	15.7 (ND)	14.1(11.5)
	Webster	18.3(14.4)	ND (20.3)	18.5(18.9)	17.4(15.3)	16.5(15.7)	ND (ND)
1,000	Cecil	11.0(284.0)[d]	10.5 (ND)	11.9(160.0)[d]	ND(141.0)[d]	11.3 (ND)	9.0(134.0)[d]
	Webster	18.9(36.7)[d]	ND(36.4)[d]	18.2(32.1)[d]	19.1(36.6)[d]	19.4(32.6)[d]	ND (ND)
20,000	Cecil	26.0[d](62.8)[d]	23.7[d](ND)	27.7[d](37.7)[d]	ND(55.1)[d]	30.6[d](ND)	31.0(13.1)
	Webster	17.0(204.0)[d]	ND(189.0)[d]	15.3(195.0)[d]	16.1(147.0)[d]	14.4(168.0)[d]	ND (ND)

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 14. (continued)

Concentration of trifluralin ($\mu g \cdot g^{-1}$)	cfu·g^{-1} soil (x 10^{-6}) Time (Weeks)	Average
0	Cecil	12.2(15.7)
	Webster	19.9(15.8)
10	Cecil	12.8(15.8)
	Webster	25.3(20.8)
1,000	Cecil	11.7(212.0)[d]
	Webster	25.5(66.6)[d]
20,000	Cecil	26.1[d](67.2)[d]
	Webster	21.7(503.0)[d]

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

TABLE 15. EFFECT OF TECHNICAL GRADE AND FORMULATED TRIFLURALIN ON FUNGAL POPULATIONS IN CECIL AND WEBSTER SOILS

Concentration of trifluralin ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks) 0.1	1	2	3	4	5
0	Cecil	12.2[a](14.3)[b]	9.1(12.7)	10.5(13.6)	11.4(11.7)	10.6(10.3)	ND (10.7)
	Webster	14.0(13.4)	9.3(11.7)	9.4(10.5)	10.8(12.0)	8.6(12.5)	ND (10.3)
10	Cecil	13.3(14.5)	13.1(10.1)	12.2(11.3)	10.7(12.4)	10.4(11.1)	ND (10.5)
	Webster	16.0(14.6)	16.1[d](12.7)	13.5[d](11.5)	13.9(13.8)	14.4[d](12.3)	ND (12.4)
1,000	Cecil	13.8(11.0)	11.4(6.9)[d]	10.9(13.1)	10.5(6.0)[d]	6.1[d](6.2)[d]	ND (7.9)[d]
	Webster	14.0(12.1)	14.0[d](12.3)	15.0[d](13.7)	13.8(13.6)	13.8[d](13.6)	ND (10.9)
20,000	Cecil	13.7(6.9)[d]	10.3(0.7)[d]	9.7(0.2)[d]	9.3(0.3)[d]	6.5[d](0.2)[d]	ND(<0.1)[d]
	Webster	13.7(12.6)	15.0[d](3.4)[d]	14.2[d](2.1)[d]	13.3(0.3)[d]	13.3[d](0.4)[d]	ND (0.3)[d]

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 15. (continued)

Concentration of trifluralin ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks) 6	7	8	9	10	11
0	Cecil	9.8(8.8)	11.2 (ND)	11.1(9.9)	ND (13.1)	9.9 (ND)	8.9(12.0)
	Webster	9.5(12.3)	ND (11.2)	9.6(10.0)	9.7(8.9)	9.2(10.7)	ND (ND)
10	Cecil	6.2[d](10.4)	11.5 (ND)	19.7[d](10.3)	ND (16.4)	11.4 (ND)	9.9(8.1)[d]
	Webster	13.7(9.6)	ND (15.1)	12.4(12.8)	11.3(10.3)	12.9(11.1)	ND (ND)
1,000	Cecil	11.9(6.8)[c]	11.7 (ND)	12.7(5.8)[d]	ND(6.3)[d]	8.9 (ND)	19.7(6.3)[d]
	Webster	14.3(13.8)	ND (13.4)	12.2(15.1)	12.7(15.0)[d]	14.0(12.9)[d]	ND (ND)
20,000	Cecil	9.7(0.2)[d]	9.2 (ND)	11.5(0.1)[d]	ND(<0.1)[d]	9.0 (ND)	9.3(0.0)[d]
	Webster	11.2(0.3)[d]	ND(0.3)[d]	10.3(0.2)[d]	10.9(<0.1)[d]	10.7(<0.1)[d]	ND (ND)

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 15. (continued)

Concentration of trifluralin ($\mu g \cdot g^{-1}$)	cfu·g^{-1} soil (x 10^{-4}) Time (Weeks)	Average
0	Cecil	10.5(11.7)
	Webster	10.0(11.2)
10	Cecil	11.8(11.5)
	Webster	13.8[c](12.4)
1,000	Cecil	11.8(7.6)[d]
	Webster	13.8[c](13.3)
20,000	Cecil	9.8(0.9)[d]
	Webster	12.5[c](1.8)[d]

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

TABLE 16. EFFECT OF TECHNICAL GRADE AND FORMULATED TRIFLURALIN ON ACTINOMYCETE POPULATIONS IN CECIL AND WEBSTER SOILS

Concentration of trifluralin ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-5}) Time (Weeks) 0.1	1	2	3	4	5
0	Cecil	5.2[a](11.4)[b]	6.8(9.8)	5.2(8.9)	ND (7.5)	4.6(5.0)	ND (ND)
	Webster	14.0(11.2)	12.0(13.3)	18.5(8.8)	16.4(18.2)	11.4(14.6)	ND (14.6)
10	Cecil	5.2(14.3)	5.7(6.8)	6.2(4.6)	ND (6.2)	5.5(4.8)	ND (ND)
	Webster	27.8[c](12.5)	13.5(14.3)	15.6(12.7)	15.1(15.6)	14.0(15.6)	ND (13.3)
1,000	Cecil	12.1[d](9.8)	4.6(3.2)[d]	7.5(6.2)	ND (3.4)	5.1(5.0)	ND (ND)
	Webster	16.9(13.0)	16.6(13.5)	13.3(13.3)	15.1(16.1)	13.3(16.6)	ND (14.0)
20,000	Cecil	7.1(15.3)	6.4(7.3)	5.2(1.9)[d]	ND (1.1)[d]	4.8(1.4)[d]	ND (ND)
	Webster	15.9(6.0)[c]	14.0(2.1)[d]	13.3(1.3)[d]	15.1(0.7)[d]	14.0(0.3)[d]	ND (0.2)[d]

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 16. (continued)

Concentration of trifluralin ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-5}) Time (Weeks) 6	7	8	9	10	11
0	Cecil	4.1(7.8)	4.1 (ND)	5.0(5.5)	ND (5.7)	5.9 (ND)	3.4(7.5)
	Webster	14.2(10.9)	ND (15.3)	16.9(9.1)	11.2(9.1)	12.2(10.9)	ND (ND)
10	Cecil	2.5(6.6)	3.4 (ND)	4.1(4.1)	ND (5.0)	4.6 (ND)	3.2(4.8)
	Webster	14.7(12.0)	ND (19.5)	15.9(18.2)[d]	10.7(10.9)	13.3(13.5)	ND (ND)
1,000	Cecil	3.9(6.6)	5.0 (ND)	6.2(5.2)	ND (7.1)	4.8 (ND)	3.7(4.6)
	Webster	14.0(16.1)	ND (18.2)	11.4(12.5)	15.1(10.9)	14.0(17.9)	ND (ND)
20,000	Cecil	5.2(1.8)[d]	3.9 (ND)	3.7(0.4)[d]	ND(<0.1)[d]	3.4 (ND)	4.6(0.0)[d]
	Webster	15.0(0.2)[d]	ND (0.2)[d]	14.6(0.2)[d]	10.4(0.0)[d]	19.2(0.0)[d]	ND (ND)

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

(continued)

TABLE 16. (continued)

Concentration of trifluralin ($\mu g \cdot g^{-1}$)	cfu·g^{-1} soil (x 10^{-5}) Time (Weeks)	Average
0	Cecil	4.9(7.7)
	Webster	14.1(12.4)
10	Cecil	3.2(6.4)
	Webster	15.6(14.4)
1,000	Cecil	3.7(5.7)
	Webster	14.4(14.7)
20,000	Cecil	4.9(3.2)[c]
	Webster	14.6(1.0)[d]

[a]First column, technical grade trifluralin.

[b]Second column, formulated trifluralin.

[c]Significant at $p < 0.05$.

[d]Significant at $p < 0.01$.

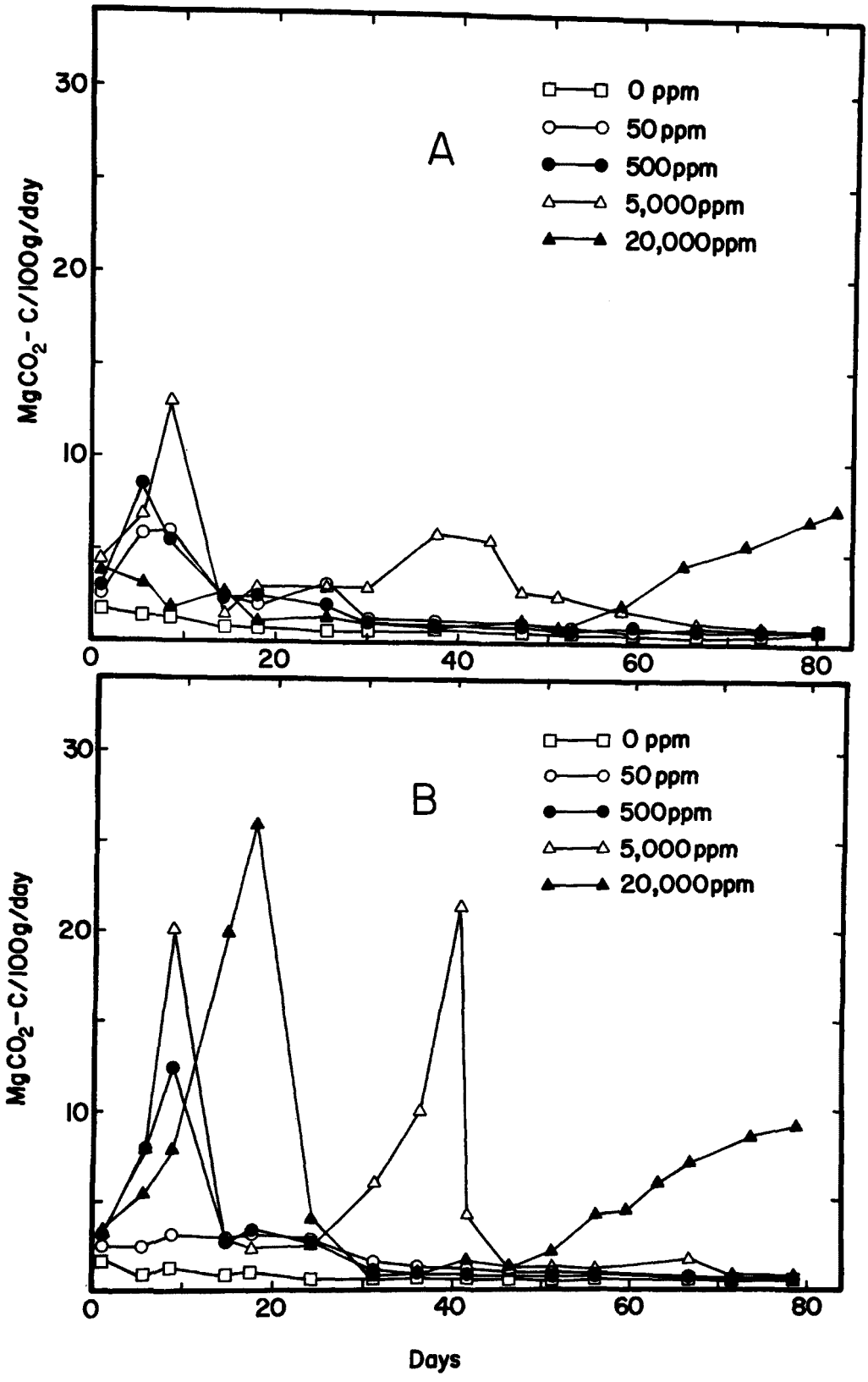

Figure 20. CO_2 evolution rate from the Webster soil receiving various concentrations of 2,4-D. (A) Technical grade; (B) Formulated 2,4-D.

from the carbon in the 2,4-D. The CO_2 evolution rates were generally higher from the formulated 2,4-D treated soil than from the technical grade treated soil. Therefore, microbial activity in the soil with formulated treatments was higher.

Unlike the Webster soil, total CO_2 evolution was inhibited in the Cecil soil which received 5,000 and 20,000 ppm of technical grade 2,4-D as well as 20,000 ppm of formulated 2,4-D (Figure 22). Small stimulations were noted in the total CO_2 evolution from the soil treated with 5,000 ppm of formulated 2,4-D. In contrast to the Webster soil, very little degradation was observed in the Cecil soil receiving 5,000 and 20,000 ppm (Figure 23). At a rate of 500 ppm, both forms of 2,4-D were degraded slowly. Only 10.5% and 6.3% of the technical and formulated material were degraded, respectively, in the Cecil soil after 80 days of incubation.

The CO_2 evolution rates from the Terra Ceia soil receiving 2,4-D are presented in Figure 24. The CO_2 evolution rate from the untreated organic soil was approximately four times higher than that from the Webster soil and 11 times higher than that from Cecil soil. Total CO_2 evolution from the organic soil treated with 5,000 and 20,000 ppm of formulated 2,4-D was high. For the technical grade material, CO_2 evolution was inhibited initially. The CO_2-C produced from 5,000 ppm of formulated 2,4-D after 7 days was at least partly from the 2,4-D-C because significant degradation occurred thereafter. For the organic soil treated with 20,000 ppm of formulated 2,4-D, total CO_2 evolution was enhanced after 36 days. This increase in CO_2 evolution was concurrent with the degradation of the herbicide. The CO_2 evolution rate for the organic soil treated with 5,000 ppm of the technical grade 2,4-D increased after 20 days of incubation. This increase coincided with the period of rapid 2,4-D degradation (Figure 25). Total CO_2 evolution was inhibited throughout the 80 days of incubation for the organic soil treated with 20,000 ppm of technical grade 2,4-D. Similar to the Webster soil, comparable degradation results were obtained for the organic soil when total CO_2 evolution during the second peak rather than the entire experimental period was used to calculate 2,4-D degradation.

Degradation rates for the formulated 2,4-D in the Webster and organic soil were greater than for the technical grade material when the application rate was 5,000 ppm or higher. Table 18 shows the rates of first order (exponential) degradation for the three soils receiving 5,000 ppm of 2,4-D. Exponential degradation was not observed for the Cecil soil.

Attempts were made to stimulate 2,4-D degradation in the Cecil soil receiving 5,000 ppm of 2,4-D. In addition to 2,4-D (technical grade or formulated) and ^{14}C-2,4-D, the Cecil soil was amended with various nutrient sources. Table 19 shows the amount of 2,4-D degradation during 60 days of incubation. Readily degradable nutrients such as yeast extract (1%) and glucose (1%) plus urea(0.5%) did not stimulate 2,4-D degradation. Only a small stimulation, if any, occurred with these treatments with the exception of the treatment with lime plus 2,4-D degrading bacterium. In this treatment 28.6 and 3.9% of the formulated and technical grade 2,4-D, respectively, were degraded in 60 days.

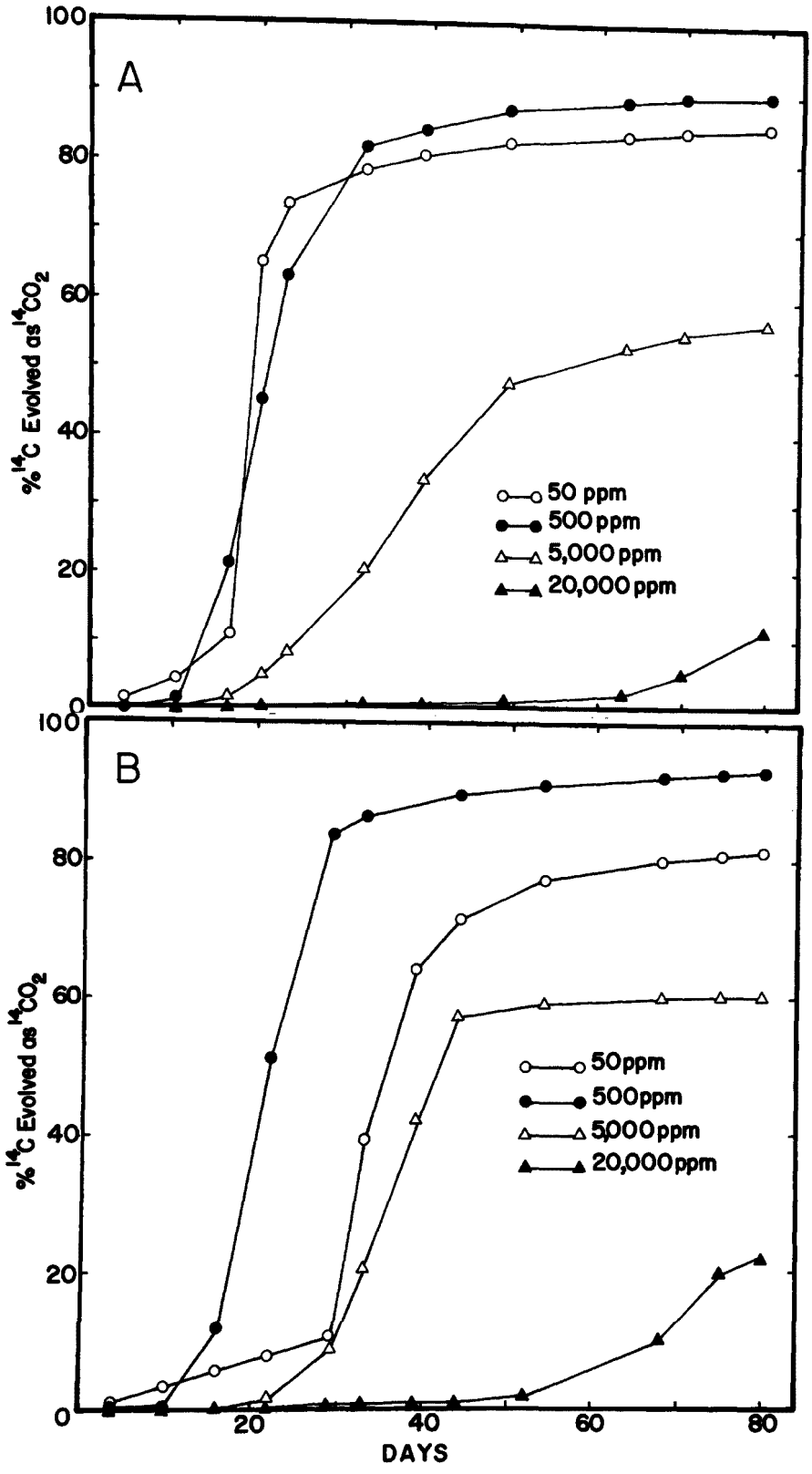

Figure 21. Percent $^{14}CO_2$ evolved from the Webster soil receiving various concentrations of 2,4-D. (A) Technical grade; (B) Formulated 2,4-D.

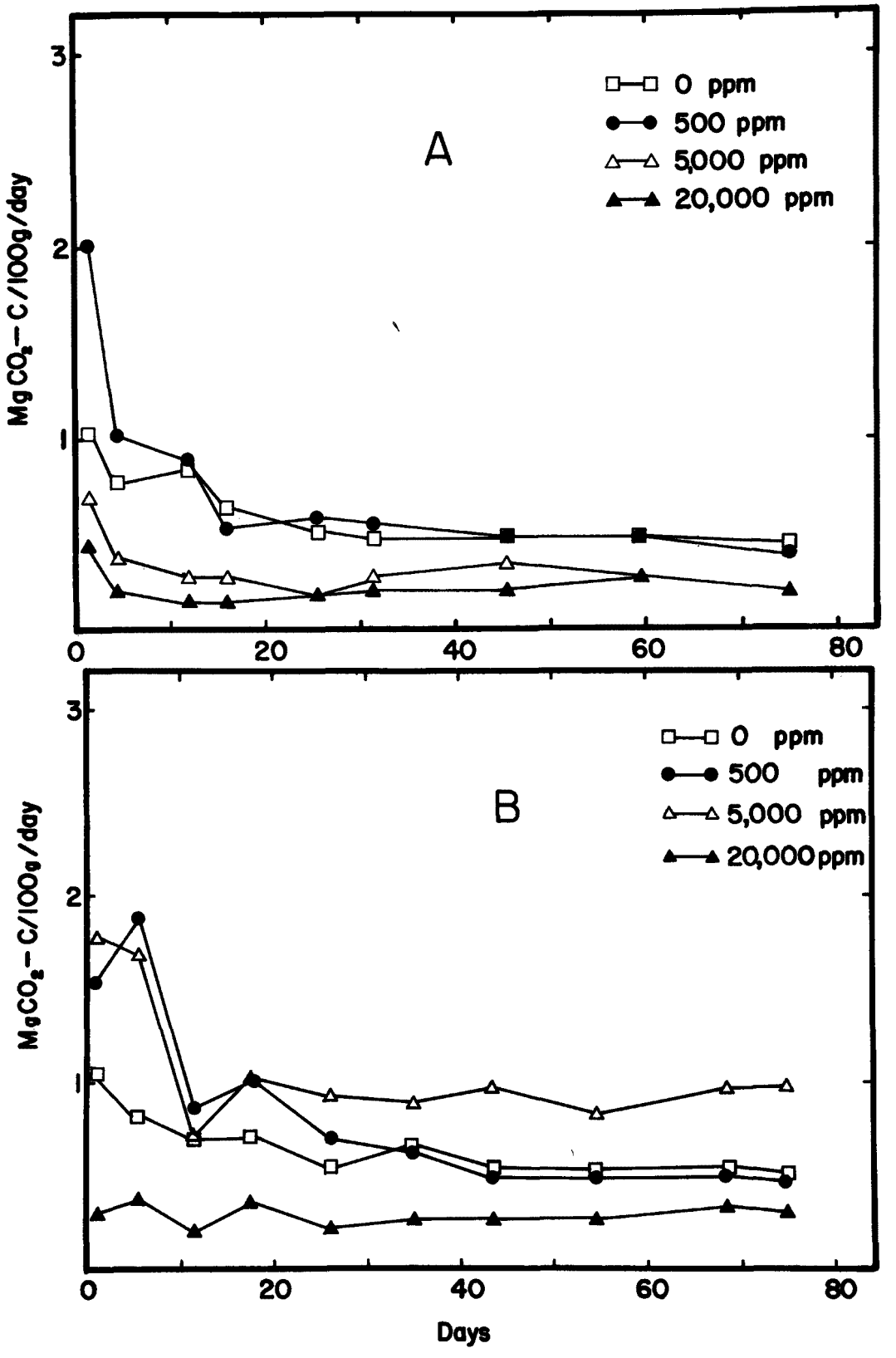

Figure 22. CO_2 evolution rate from the Cecil soil receiving various concentrations of 2,4-D. (A) Technical grade; (B) Formulated 2,4-D.

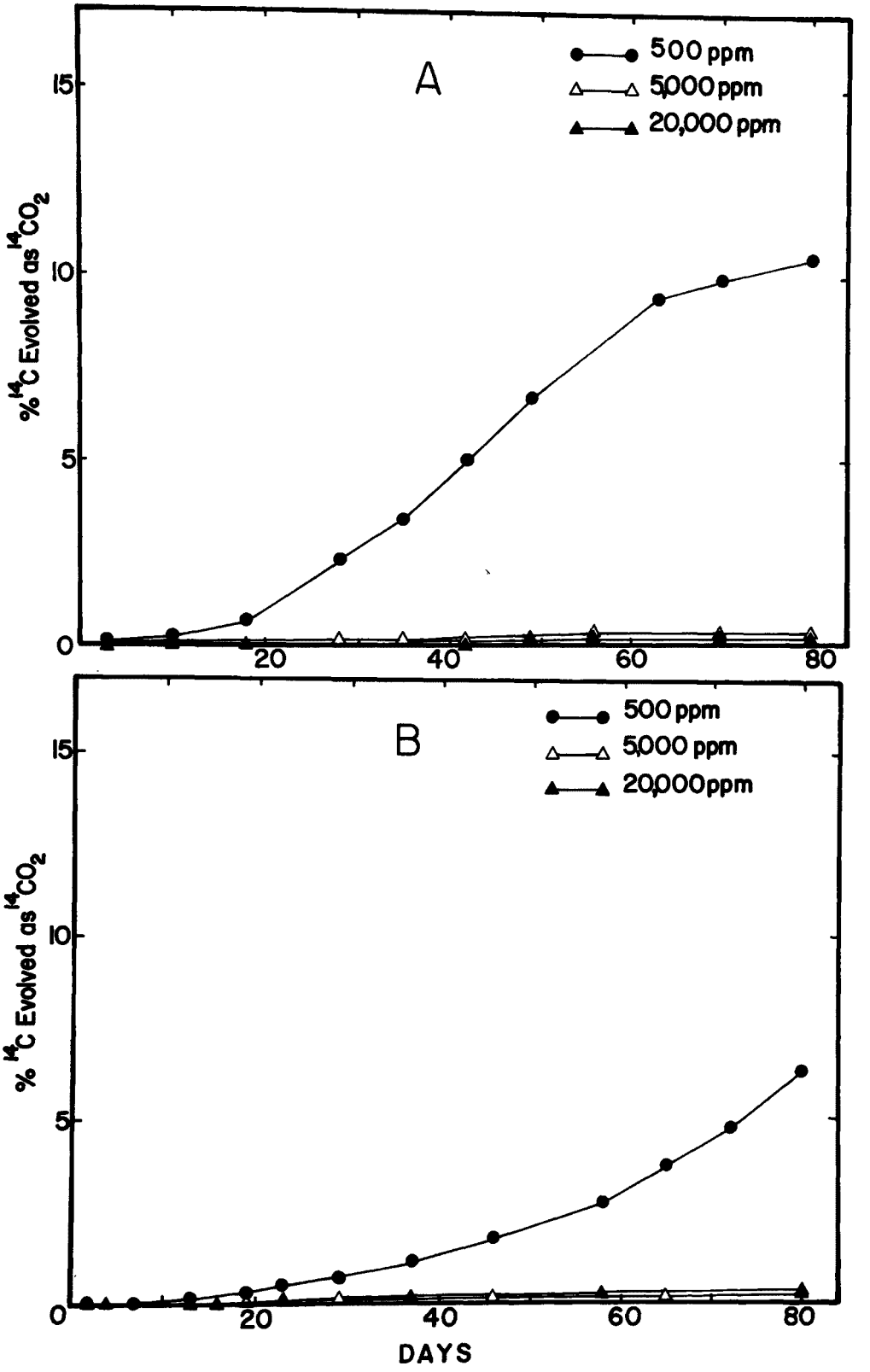

Figure 23. Percent $^{14}CO_2$ evolved from the Cecil soil receiving various concentrations of 2,4-D. (A) Technical grade; (B) Formulated 2,4-D.

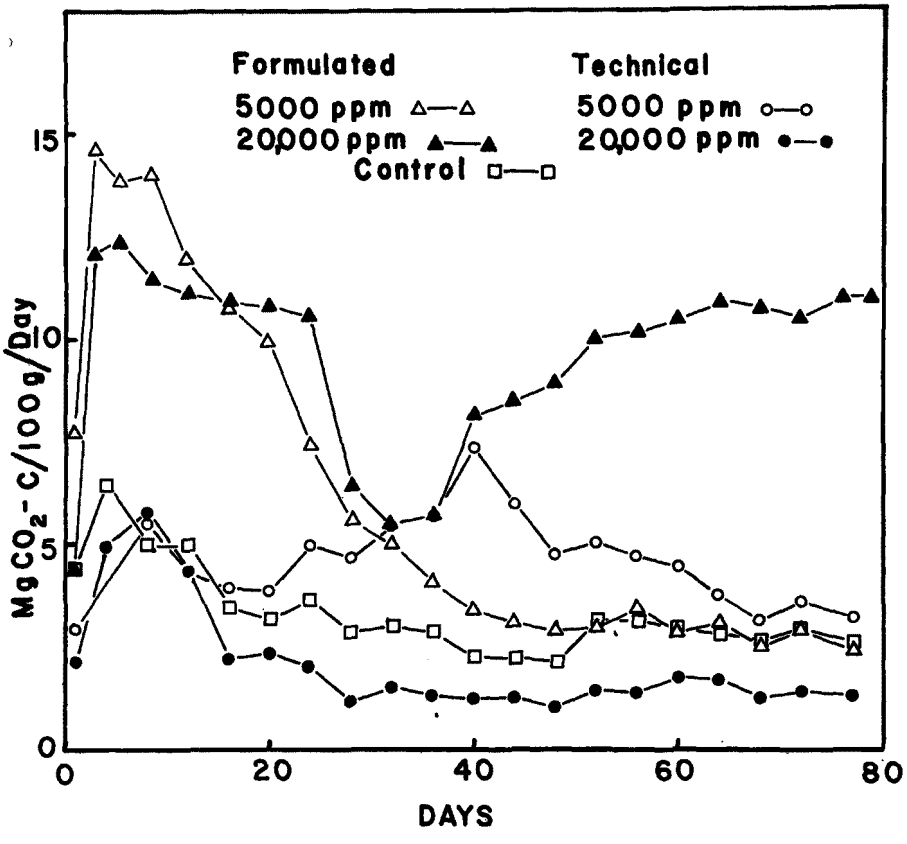

Figure 24. CO_2 evolution rate from the Terra Ceia soil receiving 5,000 and 20,000 ppm of technical grade and formulated 2,4-D.

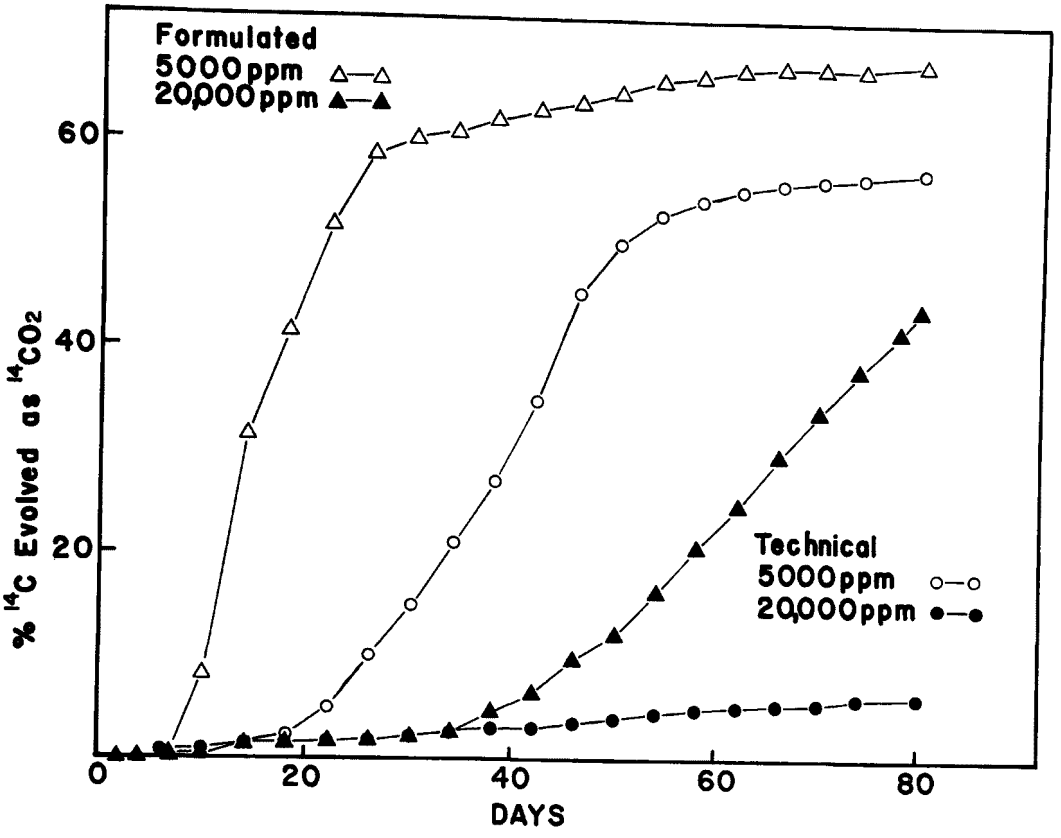

Figure 25. Percent $^{14}CO_2$ evolved from the Terra Ceia soil receiving 5,000 and 20,000 ppm of technical grade and formulated 2,4-D.

TABLE 17. COMPARISON OF THE PERCENTAGE OF 2,4-D DEGRADATION FROM THE WEBSTER SOIL DERIVED FROM $^{14}CO_2$ AND TOTAL CO_2 EVOLUTION DURING THE SECOND PEAK PERIOD AND THE TOTAL EXPERIMENTAL PERIOD

Form of 2,4-D	Concentration (ppm)	% degradation calculated from total CO_2 evolution	% degradation from % of ^{14}C-activity evolved as $^{14}CO_2$
Technical grade	5,000	32.7* (87.0)**	30.3* (56.9)**
	20,000	14.2 (18.2)	11.6 (12.9)
Formulated	5,000	77.3 (152.0)	55.5 (60.4)
	20,000	21.4 (52.1)	21.0 (22.7)

*The second peak period

**80-day period

TABLE 18. DEGRADATION RATES FOR THE THREE SOILS RECEIVING 5,000 ppm OF TECHNICAL GRADE AND FORMULATED 2,4-D DURING EXPONENTIAL DEGRADATION PERIOD

	Exponential degradation period (day)	%degradation (% of 2,4-D evolved as CO_2-C)	Rate of degradation during this period (% per day)
Webster soil + technical grade 2,4-D	10th-45th	43.1	1.23
Webster soil + formulated 2,4-D	19th-42nd	53.9	2.34
Organic soil + technical grade 2,4-D	18th-42nd	32.4	1.35
Organic soil + formulated 2,4-D	7th-26th	59.0	3.11
Cecil soil + technical grade 2,4-D	none	~0	~0
Cecil soil + formulated 2,4-D	none	~0	~0

The soil pH of the Webster and the Cecil soils receiving formulated 2,4-D were not changed appreciably during 11 weeks of incubation (Tables 20 and 21). However, the pH of the two soils decreased after receiving 5,000 and 20,000 ppm of technical grade 2,4-D, especially the Cecil soil. The pH of the Webster soil receiving 5,000 and 20,000 ppm of technical grade 2,4-D increased to 7.1 and to 6.7, respectively after the 11th week of incubation. pH changes were small in the Terra Ceia soil receiving the technical grade and formulated 2,4-D.

At application rates of 5,000 ppm or higher, if 2,4-D degradation occurred, total CO_2 evolution was generally enhanced. In this case, the pattern of the CO_2 evolution rate was generally a two peak response. The results from 2,4-D degradation indicated that the CO_2-C from the second peak appeared to be associated with the 2,4-D-C (oxidation of 2,4-D-C to CO_2-C) and the CO_2-C from the first peak was probably from formulation compounds, impurities and/or soil organic matter. Thus, using total CO_2 evolution for the entire experimental period to calculate the extent of 2,4-D degradation may lead to erroneous conclusions.

It was observed that if degradation occurred at high 2,4-D application rates, the degradation rate for formulated 2,4-D was generally higher than that for the technical material. This may be attributed to the additional carbon or nutrients present in the formulation material. The solubility of the dimethylamine salt of 2,4-D in water is 300 g per 100 g water, whereas, the solubility of 2,4-D is only 900 ppm (Weed Science Society of America, 1974). Therefore, formulated 2,4-D, even at 20,000 ppm, would remain in the soil aqueous phase, whereas the majority of technical grade 2,4-D at concentrations of 5,000 and 20,000 ppm would remain as a solid. Also the 2,4-D in the formulation was neutralized by dimethylamine; thus, the soil pH did not change appreciably. The pH in the soil receiving technical grade 2,4-D decreased up to 3 pH units, depending upon the soil type and 2,4-D concentration. This decrease in pH may have an inhibitory effect on soil microbial activity.

For low application rates, i.e., below 100 ppm, 2,4-D degradation has been shown to be favored by moisture and organic matter (Foster and McKercher, 1973; Loos, 1969). Based on the information presented in this manuscript, herbicide degradation in the presence of high concentrations was also higher in soils with large quantities of organic matter. Numerous other factors may also influence the rate of degradation. For example, 2,4-D concentration, concentration of formulation material, supplement of external nutrients, clay, soil pH, and temperature. Increasing the herbicide concentration may exhibit direct and indirect effects on microbial activity. For example, bacteria have been reported as being the major organisms responsible for 2,4-D degradation in soils (Loos, 1975), and the activity of bacteria will be significantly reduced by a low soil pH. The buffering capacity of the Webster soil and organic soil was greater than that for the Cecil soil. The pH of the Cecil soil dropped 1.9 and 2.7 units when application rates of technical grade 2,4-D were 5,000 and 20,000 ppm, respectively; whereas, the pH of the Webster soil declined only 0.6 and 1.2 units for 5,000 and 20,000 ppm, respectively. Only a small pH change was observed in the organic soil receiving 5,000 ppm of technical grade

TABLE 19. 2,4-D DEGRADATION IN THE CECIL SOIL RECEIVING 5,000 ppm OF THE HERBICIDE AND VARIOUS NUTRIENT TREATMENTS DURING 60 DAYS OF INCUBATION

Treatment	% Degradation	
	Technical	Formulated
None	0.2	0.2
Glucose (1%) + Urea (0.5%)	0.2	0.1
Yeast extract (1%)	0.2	0
Webster soil (2%)	0.6	0.4
Terra Ceia organic soil (2%)	0.3	0.4
Cow manure (2%)	0.4	0.5
2,4-D degrading bacterium (1 x 10^6 cells/g soil)*	0.4	0.4
Lime (pH 7.5)	0.9	0.6
Lime (pH 7.5) + Terra Ceia organic soil (2%)	1.1	0.4
Lime (pH 7.5) + 2,4-D degrading bacterium (1 x 10^6 cells/g soil)	3.9	28.6

*2,4-D degrading bacterium was isolated from the Webster soil treated with 5,000 ppm of technical 2,4-D. The bacterium was a gram-negative, motile rod.

TABLE 20. SOIL pH OF THE WEBSTER SOIL RECEIVING TECHNICAL GRADE AND FORMULATED 2,4-D

Weeks	pH			
	0 ppm	500 ppm	5,000 ppm	20,000 ppm
0	7.3	7.3* (7.3)**	6.7 (7.3)	5.1 (7.4)
6	7.3	7.3 (7.4)	7.0 (7.4)	6.2 (7.4)
11	7.2	7.3 (7.4)	7.1 (7.4)	6.7 (7.4)

*Technical grade 2,4-D

**Formulated 2,4-D

TABLE 21. SOIL pH OF THE CECIL SOIL RECEIVING TECHNICAL GRADE AND FORMULATED 2,4-D

Weeks	pH			
	0 ppm	500 ppm	5,000 ppm	20,000 ppm
0	5.6	5.3* (5.9)**	3.9 (5.9)	3.7 (6.2)
6	5.6	6.0 (6.2)	3.7 (6.1)	2.9 (5.9)
11	5.4	5.8 (5.9)	3.8 (5.9)	2.8 (5.8)

*Technical grade 2,4-D

**Formulated 2,4-D

2,4-D. The inability of the Cecil soil to degrade 2,4-D at a concentration of 5,000 ppm or higher appeared to be due to concentration effects of the herbicide and the formulation chemicals, low pH, low organic matter content, and low 2,4-D degrading microorganism populations.

The bacterial population in the 500 ppm technical grade 2,4-D treated Cecil soil was significantly lower than that in the untreated Cecil soil except during the 6th and 7th week (Table 22). During the 6th and 7th week there was no significant difference at the 0.05 level. The bacterial density in the 500 ppm formulated 2,4-D treated soil was also significantly lower than that of the control ($P < 0.05$ level), except during the 2nd week. The overall bacterial population in the 500 ppm technical grade treated soil during the entire experimental period was 7.99×10^6 cfu per g soil which was significantly lower (0.05 level) than the 1.11×10^7 cfu per g soil in the untreated soil. Also, the overall average bacterial density for 500 ppm formulation treated soil was significantly lower than the control, i.e., 6.1×10^6 vs 1.0×10^7. As the 2,4-D concentration was increased to 5,000 and 20,000 ppm, the bacterial populations declined profoundly even after three hours of incubation. Furthermore, the bacterial populations in the 5,000 and 20,000 ppm treated soil, for both technical grade and formulated, were all significantly lower ($P < 0.01$) than from the untreated soil. The 20,000 ppm treatments had a more detrimental effect than 5,000 ppm. The overall average bacterial populations for 5,000 and 20,000 ppm technical 2,4-D treated soil were 1.7×10^6 and 7.0×10^5, whereas the bacterial populations for 5,000 and 20,000 ppm formulated treated soil were 1.9×10^6 and 8.2×10^5, respectively.

Both forms of 2,4-D significantly stimulated fungal population ($P < 0.01$) when the application was at 500 ppm (Table 23). The stimulation was greater for the formulation treatment. At an application rate of 5,000 ppm, formulated 2,4-D did not stimulate or inhibit fungal population (not significant at 0.05 level), whereas technical 2,4-D profoundly inhibited fungal populations throughout the entire experimental period ($P < 0.01$). At 20,000 ppm, both forms of 2,4-D exhibited inhibition on fungal populations. Fungal populations were reduced drastically after 3 hours of incubation, and completely destroyed in 7 and 6 weeks after incubation with technical and formulated 2,4-D, respectively.

Actinomycete populations in the 500 ppm technical 2,4-D treated soil were significantly reduced ($P < 0.01$), except during the 5th week of incubation (Table 24). Whereas, for formulated 2,4-D at the same application rate, actinomycete populations were significantly lower than in the untreated soil ($P < 0.01$) after the 5th week. At application rates of 5,000 and 20,000 ppm, both forms of 2,4-D caused sharp declines in actinomycete populations. At these concentrations, technical grade 2,4-D appeared to have a greater inhibitory effect on actinomycetes in Cecil soil. Actinomycetes were not detected in the SC agar after 2 weeks of incubation; whereas, actonomycetes were not detected after 4 and 5 weeks in soils treated with 5,000 and 20,000 ppm of formulated 2,4-D.

Generally, technical grade 2,4-D had a greater inhibitory effect on the bacteria, fungi and actinomycetes in the Cecil soil for applications

TABLE 22. EFFECT OF 2,4-D ON BACTERIAL POPULATIONS IN CECIL SOIL

Concentration of 2,4-D ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-6}) Time (Weeks) 0(3h)	1	2	3	4	5
0	Technical	12.5	10.6	11.9	10.3	11.4	14.0
	Formulated	12.3	15.0	8.1	11.2	9.0	12.7
500	Technical	11.0	7.6†	7.3†	4.4*	8.1†	n.d.
	Formulated	5.0*	7.6*	7.8	8.7†	5.6†	7.6†
5,000	Technical	3.2*	1.1*	2.5*	2.9*	1.3*	n.d.
	Formulated	2.1*	1.4*	1.0*	1.7*	1.0*	3.1*
20,000	Technical	0.7*	1.1*	1.1*	0.7*	0.5*	n.d.
	Formulated	1.3*	0.8*	1.1*	0.5*	0.8*	0.7*

*Significant at $p < 0.01$.

†Significant at $p < 0.05$.

(continued)

TABLE 22. (continued)

Concentration of 2,4-D ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-6}) Time (Weeks) 6	7	8	9	10	11	Average
0	Technical	10.9	8.6	8.1	12.9	10.9	n.d.	11.1
	Formulated	10.0	11.5	n.d.	8.9	10.8	9.4	10.8
500	Technical	10.9	9.5	6.9†	7.0†	7.3†	n.d.	8.0†
	Formulated	4.6*	6.5*	n.d.	3.2*	4.1*	6.3†	6.1*
5,000	Technical	1.6*	0.7*	1.4*	1.0*	1.5*	n.d.	1.7*
	Formulated	1.1*	3.4*	n.d.	2.6*	1.3*	2.1*	1.9*
20,000	Technical	0.3*	0.6*	0.8*	0.5*	0.5*	n.d.	0.7*
	Formulated	0.7*	n.d.	n.d.	0.9*	0.8*	0.7*	0.8*

*Significant at $p < 0.01$.

†Significant at $p < 0.05$.

TABLE 23. EFFECT OF 2,4-D ON FUNGAL POPULATIONS IN CECIL SOIL

Concentration of 2,4-D ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks) 0(3h)	1	2	3	4	5
0	Technical	25.7	10.5	9.1	10.2	n.d.	12.8
	Formulated	16.3	6.6	10.8	10.8	12.5	13.2
500	Technical	25.9	24.4†	48.5*	57.9*	n.d.	70.9*
	Formulated	14.8	71.8*	124*	103*	133*	144*
5,000	Technical	1.9*	0.2*	0.2*	0.9*	n.d.	0.8*
	Formulated	4.0*	3.2*	12.3	10.3	11.4	13.6
20,000	Technical	0.2*	0.2*	0.4*	0.2*	n.d.	0.1*
	Formulated	1.6*	<0.1*	<0.1*	0.4*	<0.1*	0.1*

*Significant at $p < 0.01$.

†Significant at $p < 0.05$.

(continued)

TABLE 23. (continued)

Concentration of 2,4-D ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks) 6	7	8	9	10	11	Average
0	Technical	9.1	5.7	9.3	3.4	5.2	n.d.	10.1
	Formulated	10.9	9.7	9.8	8.8	7.1	10.5	10.6
500	Technical	70.9*	69.0*	77.1*	33.7*	74.3*	n.d.	55.3*
	Formulated	132*	324*	310*	196*	204*	192*	162*
5,000	Technical	0.2*	<0.1*	0.1*	<0.1*	0.2*	n.d.	0.4*
	Formulated	31.0*	13.1	13.0	12.5	6.0	7.9	13.8
20,000	Technical	<0.1*	0*	0*	0*	0*	n.d.	0.1*
	Formulated	<0.1*	<0.1*	0.1*	0*	0*	0*	0.2*

*Significant at $p < 0.01$.

†Significant at $p < 0.05$.

TABLE 24. EFFECT OF 2,4-D ON ACTINOMYCETE POPULATIONS IN CECIL SOIL

Concentration of 2,4-D ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks)					
		0(3h)	1	2	3	4	5
0	Technical	15.4	14.8	n.d.	8.9	n.d.	1.2
	Formulated	2.4	1.2	2.4	2.3	2.1	5.0
500	Technical	14.1	2.5*	n.d.	1.3*	n.d.	1.9
	Formulated	2.4	1.1	1.1	3.0	2.3	0.5*
5,000	Technical	8.4*	<0.1*	n.d.	0*	n.d.	0*
	Formulated	0.3*	0.2*	0.2*	<0.1*	<0.1*	0*
20,000	Technical	0.1*	<0.1*	n.d.	0*	n.d.	0*
	Formulated	0.4*	0.1*	<0.1*	<0.1*	0*	0*

*Significant at $p < 0.01$.

(continued)

TABLE 24. (continued)

Concentration of 2,4-D ($\mu g \cdot g^{-1}$)		cfu·g^{-1} soil (x 10^{-4}) Time (Weeks) 6	7	8	9	10	11	Average
0	Technical	1.7	1.7	1.4	n.d.	1.7	n.d.	5.9
	Formulated	1.1	1.3	n.d.	2.6	1.7	2.0	2.2
500	Technical	0.2*	0.2*	0.2*	n.d.	<0.1*	n.d.	2.6*
	Formulated	0.2*	0.2*	0.2*	0.2*	0.5*	0.2*	1.1*
5,000	Technical	0*	0*	0*	n.d.	0*	n.d.	1.1*
	Formulated	0*	0*	n.d.	0*	0*	0*	0.1*
20,000	Technical	0*	0*	0*	n.d.	0*	n.d.	0.02*
	Formulated	0*	0*	n.d.	0*	0*	0*	0.1*

*Significant at $p < 0.01$.

of 5,000 ppm and higher. This may be attributed to the fact that the soil pH dropped from 5.6 to 3.7 and 2.9 in the soil treated with 5,000 and 20,000 ppm of technical grade 2,4-D. The pH in the formulated treated soils remained unchanged. Also, formulation compounds in the formulated 2,4-D may reduce or buffer 2,4-D toxicity to the microorganisms. Among the three groups of microorganisms considered, bacteria were the least sensitive to high 2,4-D concentrations (5,000 ppm and higher) and actinomycetes were the most sensitive for the soils considered. However, for the soils that degraded 2,4-D at high concentrations, for example, Webster silty clay loam and Terra Ceia muck (Ou et al., 1978), the response of the soil microflora to high 2,4-D concentrations may be different. Microorganisms in the 20,000 ppm treated Webster soil after 70 days of incubation were nearly all bacteria, and the number of bacteria was more than 100 times higher than that in the untreated soil.

METABOLITES

Atrazine

Only tentative indentifications of atrazine metabolites were made. Structures are based on thin layer and gas chromatographic behavior. Mass spectral analyses are currently incomplete. In the Webster soil treated with 10 or 1,000 ppm, 4 to 8 percent of the radioactivity was associated with a compound or compounds having a relative R_f similar to that of 2-chloro-4-amino-6-isopropylamino-s-triazine (0.80) and/or 2-chloro-4-ethylamino-6-amino-s-triazine (0.88). One to four percent of the activity was associated with a component having a relative R_f indistinguishable from that of 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (0.48; hydroxyatrazine). Less than 2 percent of the radioactivity was detected at a relative R_f similar to that of 2-hydroxy-4-amino-6-isopropyl-amino-s-triazine (0.10) and 2-hydroxy-4-ethylamino-6-amino-s-triazine (0.10). In the Cecil soil, all the radioactivity not associated with atrazine had a relative R_f corresponding to hydroxy-atrazine (0.48). Percentages of metabolites increased with time and corresponded to a reduction in the level of the parent compound.

The percentage of unextractable radioactivity was generally higher at 10 and 1,000 ppm for the Cecil soil than for the Webster soil; this difference was not observed at the 20,000 ppm treatment. There was no apparent difference in bound residues between the technical and formulated applications at any of the three concentrations studied (Figure 26). The percentage of bound ^{14}C-activity increased with time and as much as 30% of the ^{14}C detected in the soil was unextractable.

Trifluralin

Trifluralin degradation in the Webster and Cecil soils measured by $^{14}CO_2$ evolution from the ^{14}C-labeled trifluralin decreased on a percentage basis with an increase in herbicide concentration during the 83 days of aerobic incubation (Table 25). Degradation was greater in the Webster soil for all concentrations (10, 1,000 and 20,000 ppm) than in the Cecil soil. The percentage volatilized (^{14}C-material trapped in ethylene glycol) was

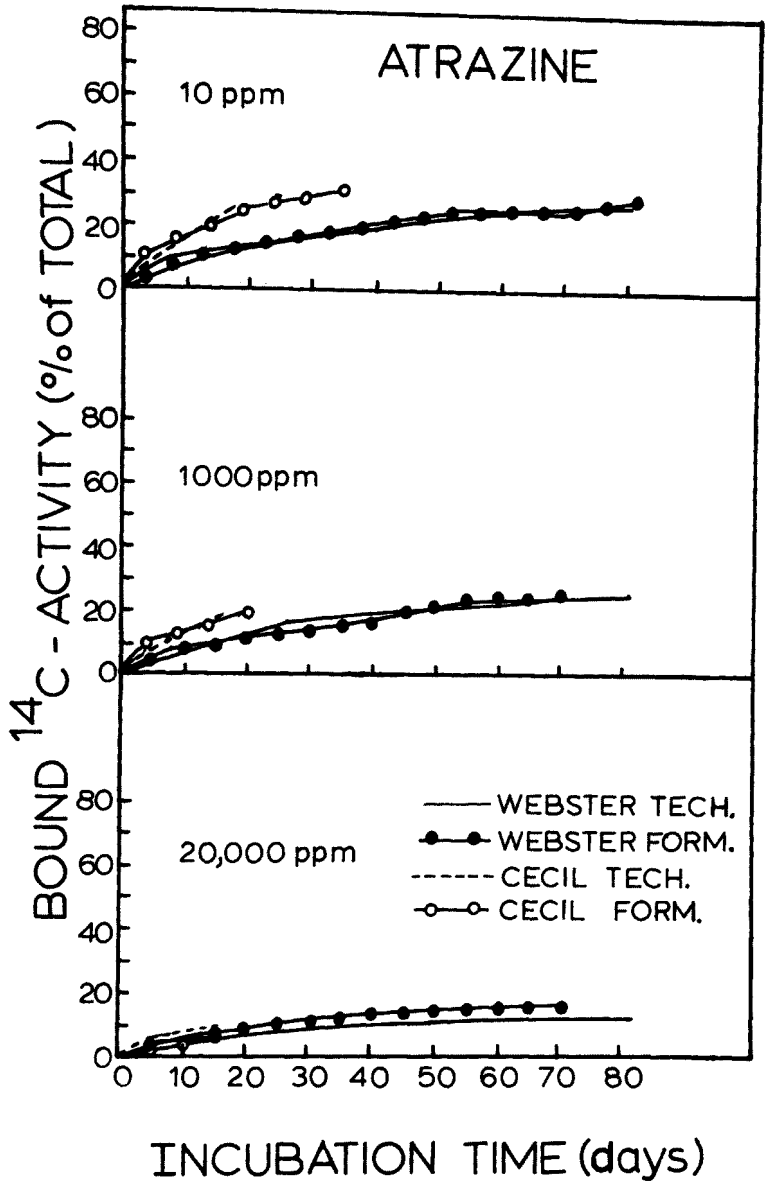

Figure 26. Percent of total ^{14}C-activity bound to Webster and Cecil soil after receiving 10, 1,000 and 20,000 ppm of technical grade and formulated atrazine.

negligible for all treatments except for the 10 ppm formulated application. In this treatment, 0.1% of the total ^{14}C-activity was trapped in the ethylene glycol in the first three weeks of incubation, but no ^{14}C-activity was detected thereafter. It was apparent, however, that volatilization occurred to a certain extent based on the orange color observed on the tygon tubing connecting the soil incubation flask to the ethylene glycol test tube. The tygon tubing was extracted with acetone and the amount of ^{14}C-activity associated with the orange color determined. The percentage of the total amount of trifluralin evaporated decreased with an increase in herbicide concentration, although a greater quantity was volatilized at the higher concentrations (Table 25).

The chromatographic and mass spectral characteristics of the metabolites detected are presented in Tables 26 and 27. Table 27 presents the GC and TLC behavior and mass spectral fragmentation pattern for each material isolated. In addition to the trifluralin, four compounds were identified: (1), α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine (2), α,α,α-trifluoro-2,6-dinitro-p-toluidine (3), 2-ethyl-7-nitro-1-propyl-5-trifluoromethyl benzimidazole (4) and 2-ethyl-7-nitro-5-trifluoromethyl benzimidazole (5). Each compound identified was identical to authentic standards in chromatographic behavior and mass spectral fragmentation patterns. It is interesting to note that methane chemical ionization mass spectrometry (CI/MS) gave rise to four distinctive fragments. These were the molecular ion minus 19 (m-19) due to a loss of hydrogen fluoride from the protonated parent molecule and the m+1, m+9, and M+41 fragments. The last three components result from the addition of H^+, $C_2H_5^+$ to the molecular ion and are characteristic of methane CI/MS. All of the authentic standards received from Eli Lilly and Co. were subjected to GC/CI/MS and each gave rise to these four characteristic fragments.

In addition to the four metabolites described above, two other components designated unknowns A and B were also detected (Table 27). The GLC retention time and mass spectrum data for unknown A is indistinguishable from mono-dealkylated, 2. Thin-layer chromatography, however, revealed that product A possessed a relative R_f of 0.56 while compound 2 has a relative R_f of 0.82. This material could be some derivative of 2 which yields 2 when subjected to elevated temperatures in the GC or GC/MS. The other unknown component, B, had a relative R_f of approximately 0.1 to 0.2, a GC retention time of 9.75 minutes and a mass spectrum different, but typical of the other dinitro aniline derivatives. This material has an apparent molecular weight of 223 and had the m-19, m+29 and m+41 fragments. A tentative structure has not been identified.

No differences in metabolic rates or pathways could be detected between the Webster or Cecil soils or between the formulated or technical trifluralin. The quantity of "bound" residues of trifluralin is illustrated in Figure 27. The percentage bound was calculated by measuring the organic solvent extractable $^{14}Carbon$ and the unextractable amount as determined by combustion of the soil after extraction. For the 10 ppm concentration, a greater percentage of technical trifluralin was bound to Webster soil than to Cecil. Ten days after application, 10% was bound and by 35 days it had risen to 30% and after 63 days of incubation, 72% was unextractable.

TABLE 25. PERCENTAGE OF APPLIED TRIFLURALIN MINERALIZED AND VOLATILIZED AFTER 83 DAYS OF INCUBATION

		10 ppm			1,000 ppm		
	Soil	Mineralized	Volatilized	On Tygon Tubing	Mineralized	Volatilized	On Tygon Tubing
Webster	Technical	2.5* (0.04)**	0.01 (.0015)	7.9 (.12)	0.4 (0.4)	0.0 (0.0)	1.1 (1.1)
	Formulated	3.1 (0.05)	0.0 (0.0)	9.8 (0.4)	0.5 (0.5)	0.0 (0.0)	1.2 (1.2)
Cecil	Technical	2.0 (0.03)	0.0 (0.0)	8.2 (0.12)	0.3 (0.3)	0.0 (0.0)	1.2 (1.2)
	Formulated	1.4 (0.02)	0.0 (0.0)	8.7 (0.13)	0.3 (0.3)	0.0 (0.0)	1.3 (1.3)

*percent

**milligrams

(continued)

TABLE 25. (continued)

		20,000 ppm		
	Soil	Mineralized	Volatilized	On Tygon Tubing
Webster	Technical	0.1 (2.0)	0.0 (0.0)	0.1 (2.0)
	Formulated	0.1 (2.0)	0.0 (0.0)	0.1 (2.0)
Cecil	Technical	0.1 (2.0)	0.0 (0.0)	0.1 (2.0)
	Formulated	0.1 (2.0)	0.0 (0.0)	0.1 (2.0)

*percent

**milligrams

TABLE 26. R_f VALUES FOR TRIFLURALIN AND METABOLITE REFERENCES

Number		R_f
1	Trifluralin (α,α,α-Trifluoro-2,6-dinitro-N, N-dipropyl-p-toluidine	1.00
2	α,α,α-Trifluoro-2,6-dinitro-N-propyl-p-toluidine	0.82
3	α,α,α-Trifluoro-2,6-dinitro-p-toluidine	0.25
4	2-Ethyl-7-nitro-1-propyl-5-trifluoromethyl benzimidazole	0.25
5	2-Ethyl-7-nitro-5-trifluoromethyl bezimidazole	0
6	α,α,α-Trifluoro-N,N-dipropyl-5-nitrotoluene-3,4-diamine	0.60
7	α,α,α-Trifluoro-5-nitro-N-propyltoluene-3,4-diamine	0.22
8	α,α,α-Trifluoro-5-nitrotoluene-3,4-diamine	0
9	α,α,α-Trifluoro-N,N,dipropyltoluene-3,4,5-triamine	0.44
10	α,α,α-Trifluoromethyl-5-nitrotoluene-3,4-diamine	--
11	α,α,α-Trifluorotoluene-3,4,5-triamine	0

TABLE 27. CHROMATOGRAPHIC AND MASS SPECTRAL PARAMETERS OF PRODUCTS ISOLATED FROM TRIFLURALIN TREATED SOIL

Compound	Code	TLC[a] R_f	GLC[b] R_t	Mass[c] Spec M-19	M+1	M+29	M+41
Trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine)	1	1.00	19.6	316	336	364	376
α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine	2	0.82	24.6	275	295	323	335
Unknown A	--	0.56	24.6	275	295	323	335
α,α,α-trifluoro-2,6-dinitro-p-toluidine	3	0.25	13.2	234	254	282	294
2-ethyl-7-nitro-1-propyl-5-trifluoromethyl benzimidazole	4	0.25	30.1	281	301	329	341
2-ethyl-7-nitro-5-trifluoromethyl benzimidazole	--	0.00	22.7	240	260	288	300
Unknown B	--	0.1-0.2	9.75	204	224	252	264

[a]See text for TLC parameters; values given are relative R_f's.

[b]See text for GLC parameters.

[c]The four characteristic molecular ions are given. See text for mass spec parameters.

The quantity of formulated trifluralin bound in the Webster soil was only measured after 68 and 84 days incubation, but showed a similar but somewhat lesser (45 and 51%) amount of bound residue than that measured for the technical material.

There was less bound trifluralin material in the Cecil soil. Approximately 8% of the technical trifluralin was bound after 7 days. The percentage remained relatively constant throughout the sampling period. The formulated material was somewhat slower in binding, but reached approximately the same level.

For the 1,000 ppm concentration, the Webster soil also bound more trifluralin than did the Cecil soil and the technical material appeared to be bound to a greater extent than did the formulated material. Twenty to 35% of the ^{14}C was bound in the Webster soil at 1,000 ppm.

At the 20,000 ppm level, relatively low percentages of trifluralin were bound; however, these still represent considerable quantities of the pesticide. Again it appears that the Webster soil binds more than Cecil soil.

Recent reports by Katan et al. (1976) and Katan and Lichtenstein (1977) show rapid binding of the parathion amine analogue which suggests that a similar phenomenon may have occurred with trifluralin in the Webster soil. The parent compound represented 90% or more of the extractable ^{14}C while considerable radioactivity was not extracted. Thus, it is possible that some metabolic products were formed and a substantial portion of them were bound. This would explain why certain previously reported metabolites were not detected in the extract or were only found in small quantities. In an effort to examine this possibility, trifluralin, mono-dealkylated, and di-dealkylated derivatives were incubated in sterilized Webster soil for four hours. Percentages of each compound extractable after four hours were 89, 75 and 57 for the above compounds, respectively. Thus, in the Webster soil there was a clear relationship between the amount of non-extractable material and the substitution on the amino nitrogen. This is consistent with the findings of Katan and Lichtenstein (1977) with amino analogs of parathion. If one fortifies Webster soil with either trifluralin or the di-dealkylated derivative and immediately perform an extraction, 93-95% of both compounds were recoverable. Substantial binding did not occur for the di-dealkylated derivative in the sandy Cecil soil. Thus, it is possible in the case of the Webster soil, that metabolites containing secondary or primary amino functional groups became a part of the "bound" portion of the residue. The absence of the same magnitude of binding in Cecil soil could be the result of different kinds and numbers of microbial populations, etc. This could also influence the formation of microbially induced amino metabolites in the Cecil soil.

The metabolites detected were isolated from both soils treated at all three application rates and are characteristic of the aerobic degradation pathway described by Probst et al. (1975) and shown in Figure 28. Trifluralin 1 underwent dealkylation to mono-dealdylated and subsequently

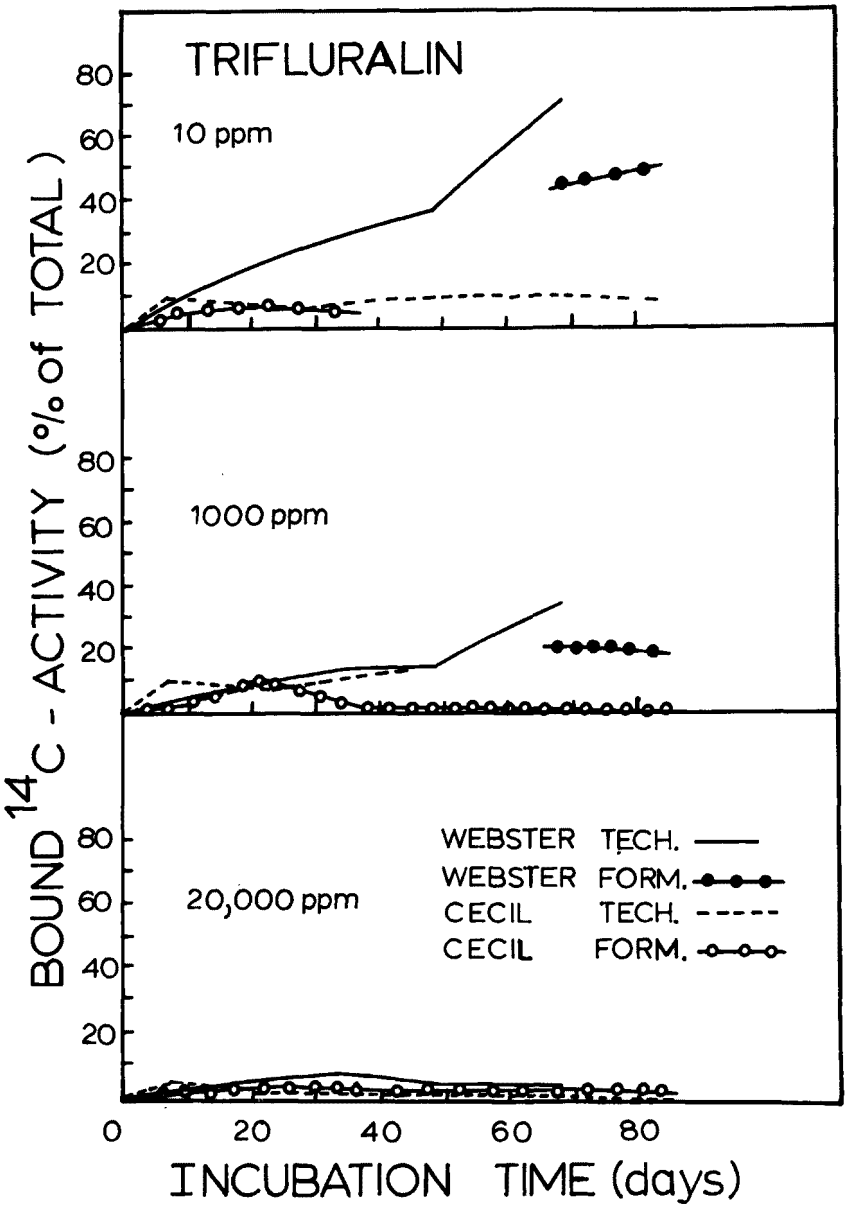

Figure 27. Percent of total ^{14}C-activity bound to Webster and Cecil soil after receiving 10, 1,000 and 20,000 ppm of technical grade and formulated trifluralin.

to the di-dealkylated product. Two benzimidazoles, 4 (2-ethyl-7-nitro-1-propyl-5-trifluoromethyl benzimidazole) and 5 (2-ethyl-7-nitro-5-triflouromethyl bezimidazole) were also identified. Thus, very high application rates of trifluralin resulted in the same degradation pathways that have been previously reported.

The GC/MS data system also performed limited mass searches (LMS) for ions characteristic of 6 (α,α,α-trifluoro-methyl-N,N-dipropyl-5-nitrotoluene-3,4-deamine), 7 (α,α,α-trifluoro-5-nitro-N-propyltoluene-3,4-diamine) and 9 (α,α,α-Trifluoro-N,N-dipropyltoluene-3,4,5-triamine) in soil extracts from both soils (Figure 28). All LMS's were negative for these compounds. These materials represent the transitions between postulated aerobic and anaerobic pathway. Thus, there was no detectable reduction of ring nitro groups. In the Webster soil, the possibility exists that the amino metabolites, 6, 7, 8 (α,α,α-trifluoro-5-nitro-toluene-3,4-diamine) and 9, may have been hidden in the "bound" portion of the residue and should not be overlooked.

2,4-D

In the majority of cases, parent 2,4-D was the only radioactive component isolated from the soil. In a few instances, 2,4-dichlorophenol (based upon thin-layer chromatography) was detected. It appeared that more 2,4-dichlorophenol accumulated at the 500 ppm treatment after 7 to 10 days of incubation than for other treatments and was present to a greater extent in the Webster than in the Cecil soil. Only the parent 2,4-D, however, was detected after 29 days of incubation.

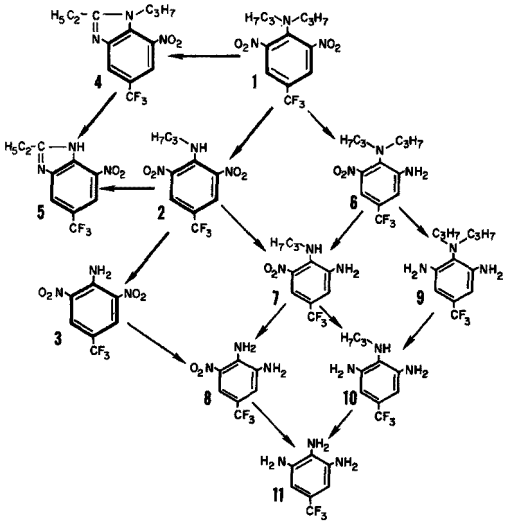

Figure 28. Metabolic pathways for trifluralin metabolism: Code numbers correspond with those in Tables 26 and 27.

SECTION 6

IMPLICATIONS OF PROJECT RESULTS WITH REGARDS TO PESTICIDE DISPOSAL

Pesticide applications to control pests associated with agricultural, industrial and urban environments, in general, have not had an adverse effect on soil microorganisms or groundwater quality. Because applications to these environments have involved primarily low concentrations (0.5 to 10 kg/ha), the suitability of these data for designing and managing pesticide waste disposal sites has been questioned. Therefore, the objectives of this project were to: 1) Measure the adsorption-desorption and mobility characteristics of various pesticides in different soil-water systems receiving high pesticide concentrations; 2) Quantify and describe microbial degradation rates of various pesticides in soils containing large pesticide concentrations, and 3) Measure the influence of large pesticide concentrations on soil microbial activity and respiration rates as well as to identify specific microorganisms which degrade a given pesticide at both low and high pesticide concentrations.

Two significant conclusions can be made regarding the adsorption results obtained during this project. First, the Freundlich adsorption equation described all pesticide adsorption isotherms considered for solution concentrations up to the aqueous solubility of the pesticide. Thus, the pesticide adsorption sites for all soils investigated were apparently not saturated at any concentration considered in this study. Second, contrary to a frequent assumption, pesticide adsorption isotherms were not linear, that is, N in the Freundlich equation was generally less than one. The nonlinearity of the pesticide adsorption isotherm is an important observation because it explicitly points out that pesticides will be more mobile in soils containing pesticide concentrations similar to those associated with pesticide waste disposal sites. This is especially true for pesticides that are very soluble in water (e.g., 2,4-D amine).

The increased pesticide mobility at high pesticide concentrations limits the usefulness of the available low concentration data base for developing "safe" management practices for pesticide disposal procedures in soils. If a linear adsorption isotherm is assumed on the basis of the low pesticide concentration data, one underestimates the soil depth to which a pesticide will leach or move for a given water input. The seriousness of the failure of the low concentration data base to describe the true mobility of a pesticide as it moves toward the groundwater from a waste disposal site depends upon the water solubility of the pesticide and nonlinearity of the adsorption isotherm. For example, the adsorption isotherms for atrazine and 2,4-D and a Eustis soil were similar (see Table 5); however, 2,4-D

moved similar to an unadsorbed chemical as it moved away from a simulated waste disposal site, while the mobility of the atrazine through the same soil was about 2.5 times less (Figure 14). To have assumed that the adsorption isotherms were linear would have resulted in a serious underestimation of the depth to which each pesticide would have moved for a given water input.

Many of the pesticides available on the market today are biodegradable in soils when applied at low concentrations (0.5 to 10 kg/ha). However, many of these same organic chemicals become persistant when applied to soils at high concentrations. It has been observed that some soils are able to biologically mineralize one pesticide (e.g., 2,4-D in Webster soil), but the same pesticide may be persistant in another soil (e.g., Cecil). This study clearly points out that the soil respiration rate of a soil receiving high pesticide concentrations is not, in general, a reasonable procedure for measuring pesticide degradation potential. Also, the apparent persistance of some pesticides may be further confounded by the formation of metabolites which are "bound" (not extractable by recommended procedures) to the soil and suggest a greater apparent loss of the original chemical than what actually occurred.

The contrast between the behavior of soil environments containing large and small pesticide concentrations illustrates the importance and potential for management of pesticide waste disposal sites. Many soils frequently can be altered chemically and/or biologically to enhance their potential for biologically degrading pesticides. Also, microorganisms capable of degrading specific chemicals at high concentrations have been identified and isolated which could be added to a waste disposal site to enhance the degradation and mineralization of a given chemical. Because of increased pesticide mobility at high concentrations, the chemical may not, however, remain in the vicinity of desired biological environment for degradation; thus, it is important to manage both the water leaching rate and biological environment for optimum inactivation and efficiency of a pesticide waste disposal site.

A major limitation in using the results of this project is that only one chemical was applied to a soil at a time. Combination or mixtures of pesticides would be the common situation for a pesticide waste disposal site. Waste disposal sites receiving several pesticides may fail to function as designed for a specific pesticide because of interactions between chemicals and their environment. The behavior of a pesticide mixture may or may not be independent or additive, but rather based upon the influence of one pesticide and/or the formulation associated with a given pesticide. Problems which may arise owing to the mixing of pesticide in a waste disposal site should be considered before site selection and management protocols are defined by the United States Environmental Protection Agency. This work should include the evaluation of the major surfactants used with pesticides and various formulation chemicals.

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APPENDIX

LIST OF PUBLICATIONS RESULTING FROM THIS PROJECT

1. Davidson, J. M., L.-T. Ou, and P. S. C. Rao. 1976. Behavior of high pesticide concentrations in soil-water systems. In: Residual Management by Land Disposal: Proc. of the Hazardous Waste Research Symp. (ed. W. H. Fuller). EPA-600/9-76-015, July 1976. p. 206-212.

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3. Ou, L.-T., D. F. Rothwell, W. B. Wheeler, and J. M. Davidson. 1978. The effect of high 2,4-D concentrations on degradation and carbon dioxide evolution in soils. J. Environ. Quality. 7, 241-246.

4. Davidson, J. M., L.-T. Ou, and P. S. C. Rao. 1978. Adsorption, movement, and biological degradation of high concentrations of selected pesticide in soils. In: Fourth Annual Hazardous Waste Management Symp. (ed. D. Shultz). EPA-600/9-78-016, March 1978.

5. Ou, L.-T., J. M. Davidson, and D. F. Rothwell. 1978. Response of soil microflora to high 2,4-D applications. Soil Biol. Biochem. 10;443-445, 1978.

6. Rao, P. S. C., and J. M. Davidson. 1978. Adsorption and movement of selected pesticides at high concentrations in soils. Water Res. (in press).

7. Rao, P. S. C., J. M. Davidson, R. E. Jessup, and H. M. Selim. 1978. Evaluation of conceptual models for describing nonequilibrium adsorption-desorption of pesticides during steady-flow in soils. Soil Sci. Soc. Amer. J. Vol. 43(1), 1979.

8. Ou, L.-T., and J. M. Davidson. High concentration effect of methyl-parathion on degradation and carbon dioxide evolution in soils. J. Environ. Quality. (submitted).

9. Ou, L.-T., J. M. Davidson, and D. F. Rothwell. High concentration effect of herbicides trifluralin and atrazine on microbiota and soil respiration. Soil Biol. Biochem. (submitted).

10. Wheeler, W. B., G. D. Stratton, R. P. Twilley, L.-T. Ou, D. A. Carlson, and J. M. Davidson. 1979. Trifluralin degradation and binding in soils at high concentrations. J. Agr. Food Chem. (submitted).

11. Rao, P. S. C. and J. M. Davidson. Non-equilibrium conditions for solute transport in soils: Flow interuption experiments. Soil Sci. (in preparation).

12. Wheeler, W. B., G. D. Stratton, R. P. Twilley, L.-T. Ou, and J. M. Davidson. Atrazine degradation and binding in soils at high applications. (in preparation).

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16. ABSTRACT
Because of the importance of soil in biologically reducing the quantity and retarding the rate of pollutant movement into groundwater, this laboratory study was initiated to evaluate the adsorption, mobility, and degradation of large concentrations of the pesticides atrazine, methyl parathion, terbacil, trifluralin, and 2, 4-D in soils representing four major soil orders in the United States.

Solution concentrations ranged from zero to the aqueous solubility limit for each pesticide. The mobility of each pesticide increased as its concentration in the soil solution phase increased. These results were in agreement with the adsorption isotherm data. Pesticide degradation rates and soil microbial populations generally declined as the pesticide concentration in soil increased; however, some soils were able to degrade a pesticide at all concentrations studied, while others remained essentially sterile throughout the incubation period (50 to 80 days). As shown by measurements of $^{14}CO_2$ evolution, total CO_2 evolution was not always a good indication of pesticide degradation. Several pesticide metabolites were formed and identified. Bound residues of trifluralin and atrazine at the end of the incubation period appeared to be related to types of metabolites formed.

The observed increase in pesticide mobility for large pesticide concentrations in the soil invalidates, in many cases, the usefulness of the existing low concentration data base for designing pesticide waste disposal sites.

17. KEY WORDS AND DOCUMENT ANALYSIS

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