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DEVELOPMENT OF MANAGEMENT GUIDELINES TO PREVENT POLLUTION BY IRRIGATION RETURN FLOW FROM RICE FIELDS



Robert S. Kerr Environmental Research Laboratory
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DEVELOPMENT OF MANAGEMENT GUIDELINES TO PREVENT POLLUTION
BY IRRIGATION RETURN FLOW FROM RICE FIELDS

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is responsible for the management of programs to: (a) investigate the nature, transport, fate and management of pollutants in groundwater; (b) develop and demonstrate methods for treating wastewaters with soil and other natural systems; (c) develop and demonstrate pollution control technologies for irrigation return flows; (d) develop and demonstrate pollution control technologies for animal production wastes; (e) develop and demonstrate technologies to prevent, control or abate pollution from the petroleum refining and petrochemical industries; and (f) develop and demonstrate technologies to manage pollution resulting from combinations of industrial wastewaters or industrial/municipal wastewaters.

This report contributes to the knowledge essential if the EPA is to meet the requirements of environmental laws that it establish and enforce pollution control standards which are reasonable, cost effective and provide adequate protection for the American public.

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ABSTRACT

A three year field and laboratory study was conducted to determine the influence of management practices on the quantity and quality of irrigation return flow from rice paddies. Continuous and intermittent irrigation techniques were used on replanted field plots which received either recommended or excessive applications of fertilizer and four selected pesticides. Water quality was evaluated with respect to fertilizer amendments, pesticides, pH and total salt load. Pesticides monitored included propanil, molinate, carbofuran, carbaryl and their respective metabolites.

Present water management practices result in large return flow volumes. Occasionally concentrations of NH_4 exceeded drinking water standards. Losses as nitrate were below such limits and the total nitrogen losses were a small fraction of the fertilizer applied. A model was developed to simulate the ionic constituency of the return flow.

Propanil was washed from the foliage into the flood water and dissipated within 24 hours. Evidence is given that carbaryl is washed from the leaves by rainfall, thus providing available source to contaminate return flow. As long as 8 days were required to dissipate residue resulting from recommended applications. Retention times to assure low concentrations in the irrigation return flow for carbofuran are of the order of 16 days. Granular applied molinate necessitates a retention time of 4 days to assure concentrations are within 10% of the TLM to fish. Laboratory studies were conducted to assess the primary modes of dissipation of the above pesticides.

It is suggested that through improved water management and knowledge of dissipation rates, the quantity of irrigation return flow can be reduced and the quality can be improved.

This report was submitted in fulfillment of Grant No. S-802008 by Texas A&M University, Soil and Crop Sciences Department under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period January 1, 1973 to January 17, 1976.

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SECTION 1

INTRODUCTION

As a result of technical advancements, particularly the sophistication of methodology and new instrumentation, the distribution and levels of hazardous chemicals in our environment are being revealed. The simplest, most expedient solution to chemicals in the environment would be to ban the use of all potential pollutants. This would include virtually all soil amendments and chemicals employed in agricultural production, without which production would be seriously curtailed.

A more logical approach is to determine the longevity and mobility of the chemicals used for agricultural production and to select those chemicals and management practices which minimize pollution hazards. This project is one such endeavor.

Rice is presently the third largest cash crop in Texas with approximately 578,000 acres irrigated rice grown yearly. Louisiana has approximately 588,000 acres in rice cultivation, Arkansas about 787,000 acres, and California approximately 395,000 acres. The Texas Water Development Board has predicted that by 2020, the acreage in rice will have doubled in Texas alone. Fertilizer amendments and pesticides are essential for the production of rice. However, fresh water supplies for urban use and the estuaries along the coastal regions are relatively unbuffered geographically from the rice growing areas. Some of the chemicals used are known to be toxic to animals, fish and plants in low concentrations. Fish kills have been found on several occasions in streams which flow through the rice growing areas. Although no direct cause and effect relationship has been established, it has been suggested that the fish were killed by pesticides released from the rice fields.

A good body of research has been done on the persistence and movement of nutrients and pesticides in soils (see Lichtenstein, 1970; and Biggar and Nielsen, 1967 for review). However, much of this work has been done on upland soils under laboratory conditions. The results provide some understanding of extrinsic factors involved, but cannot generally be extrapolated to field conditions due to unknown or unduplicated intrinsic soil factors. We therefore, undertook a comprehensive field experiment to determine the effects of different management regimes on the pesticide, nutrient and corresponding water and salt balances under a flooded rice culture. Particular emphasis was placed on monitoring potentially harmful constituents of the irrigation return flow.

The specific objectives of the project were: a) to conduct field scale

experiments on the nutrient, pesticide and water balance of rice fields with particular emphasis on measurements of deep percolation and released water; b) to sample and analyze the water entering and leaving the fields by the various pathways for persistent and toxic pesticides and nutrients; c) to determine the effect of recommended and excessive application rates of nutrients and pesticides on the pollution hazard from rice production; d) to use the data obtained to develop management practices which will minimize or eliminate the pollution hazard; and e) to evaluate fish toxicity levels of the pesticides employed.

SECTION 2

CONCLUSIONS

1. Maintaining the flood depth to the top of the lowest level encourages run-off and provides for inefficient use of the rainfall, which in some cases could supply all the water required by the crop.

2. Continuous flow irrigation wastes much water and increases the probability that chemicals in the water will be lost in the irrigation return flow.

3. Salts in the irrigation return flow were generally lower than in the irrigation supply. A fact attributed to the high adsorption capacity of the clay soil, relatively low initial soluble salt in the irrigation water, nutrient uptake by rice plants, and dilution of the flood water by significant amounts of rainfall.

4. Salts or pesticides did not leach to any appreciable extent due to the low saturated conductivities of the flooded clay soil. The water table remained perched throughout the entire period of flooding.

5. Occasionally, the NH_4 concentration in the irrigation return flow exceeded the drinking water standards. The total amounts of NH_4 lost were, however, a very small fraction of that applied as fertilizer.

6. Nitrate-nitrogen concentrations in the flood water were consistently below the 10ppm $\text{NO}_3\text{-N}$ upper limit for drinking water throughout the growing season.

7. Nutrient levels were temporarily increased in the irrigation return flow following fertilizer applications. Fertilizer applied in the flood water had a greater influence on the salt load of the return flow than similar amounts either applied to dry soil just before flooding, or incorporated in soil before planting.

8. Propanil found in the plot water was directly proportional to that which was washed from the foliage by the flood; the flood being normally applied 24 hours following the propanil application. DCA was proportionate to the propanil dissipated, but the average concentration was less than 200 ppb at the recommended 3.4 kg/ha recommended propanil application. Concentrations in irrigation return flow could exceed 10% of the 96 hours TLM to fish if a rainfall large enough to cause overflow occurs within a few hours following the establishment of the permanent flood.

9. Best fit analysis of field data to the first order biological decay equation and laboratory studies under flooded soil conditions suggested that biological degradation was the principal mode by which molinate was dissipated in the field experiment. Persistence at statistically significant levels ranged from 96 to 384 hours following application, and generally was a function of the application rate and flood water depth. Half-life values averaged 96 hours in impounded plots and 54 hours in continuous flow plots over the 3-year experiment.

10. The 3-year field experiment indicated that carbofuran was chemically altered to something other than the toxic metabolites: 3-keto or 3-hydroxy carbofuran and was rapidly dissipated from the plot water. However, persistence of this chemical was extended due to a variable entry into the flood water from a significant fraction of the broadcast application intercepted by the rice foliage. Correspondence of residual carbofuran levels to rainfall events indicated that some of the material lodged at the leaf-stem junction of the rice plant was dissolved and washed into the plots by rain.

11. Concentrations of carbaryl in the paddy water corresponded to rainfall distribution. Once flushed from the leaf canopy, carbaryl was dissipated within 48 hours by an adsorptive mechanism interacting with both biological degradation and chemical alteration. Amounts of 1-naphthol, a toxic metabolite of carbaryl, reflected the rate of carbaryl applied, but was more the result of contamination of the commercial material rather than a degradation product. 1-Naphthol was rapidly dissipated in the paddy water and there was no evidence that it would extend the residual life of carbaryl under the conditions associated with flooded rice cultivation.

12. Releasing floodwater from a rice field 10 days before harvesting is a common water management practice which serves to dry the soil and thereby facilitate harvesting. The desirable dry soil conditions can be obtained by withholding additional irrigations and allowing all flood water to evapotranspire prior to harvest. Rice yields were not affected by allowing the soil to dry in this manner prior to harvest. Since very little salt is leached through this type of soil, run-off during the winter is needed to remove the salt that would otherwise accumulate.

SECTION 3

RECOMMENDATIONS

1. The practice of continuous flow irrigation should be eliminated.
2. Practices should be initiated to maintain the maximum amount of free-board possible to take advantage of natural rainfall and to minimize overflow. These should include the use of higher levees and careful control of irrigation water to prevent flooding to depths deeper than needed.
3. Fertilizers should be applied to dry soil rather than to flood water whenever possible to reduce the nutrient levels now attained in the return flow and to increase efficiency of nitrogen fertilizer.
4. To minimize concentrations of propanil in the irrigation return flow, no water should be released for at least 24 hours after flooding. This is now the general practice, but efforts should be made to assure that it is adhered to.
5. Irrigation water management and application of fertilizers or pesticides should be coordinated so that applications are made when the flood water depths are minimal. This will allow sufficient free board to retain rainwater, thus minimizing contaminated return flow.
6. Flood water should be retained a minimum of 4 days following the recommended 3.4 kg molinate/ha application to insure that molinate concentrations in the irrigation return flow are within an acceptable 3 ppm, or 10% of the TLM to fish.
7. Although carbofuran was rapidly dissipated from flood waters, there should not be a release from flooded rice fields for 16 days following a normal broadcast application of 0.56 kg/ha to insure that the fraction intercepted by the rice foliage does not adversely affect the quality of irrigation return flow.
8. Carbaryl applied as a foliar spray may be washed from the leaves by a rain; this results in a variable source to the paddy water. Paddy water should not be released for 8 days following an application of 1.12 kg/ha carbaryl to the rice, or within 48 hours following a heavy rain prior to the eighth day.
9. The wide range of retention times needed to assure low levels of the various pesticides tested in the irrigation return flow indicates the need

to establish such data on each pesticide in the aquatic rice environment.

10. Rice fields should be allowed to evapotranspire to desirable dry conditions to facilitate harvesting rather than maintaining flood levels until harvest. This simple procedure has merit from a conservation point of view, but also would minimize the movement of potential pollutants from the fields.

SECTION 4

EXPERIMENTAL DESIGN

A series of experiments to determine the impact of fertilizer and pesticide application on the quality of irrigation return flow were conducted in both the field and the laboratory. The experiments were also designed to elucidate the mechanisms influencing the quality of irrigation return flow.

The field studies were conducted on a group of 12 small rice paddies which were sealed to prevent lateral water movement between plots. Weirs, water stage recorders and rain gauges were utilized to monitor the water balance throughout each of the three cropping seasons. Insofar as possible, all cultural practices and their scheduling were done the same way they would be under normal field production. Pesticides were selected which were in wide use at the time of the experiment and are representative of several families of pesticides. Both recommended and excessive rates of both fertilizers and pesticides were utilized in the experiments. Two irrigation schemes, continuous flow and impounded, were utilized. Three replications of two application rates and two irrigation practices were applied to randomly selected plots.

The pesticides were applied at the time they would normally be needed whether or not the target organisms were present in sufficient numbers to warrant application. It is suggested that the presence or absence of the target organism should not effect the rate of dissipation of the pesticide or its toxic metabolites.

Water samples were collected from all plots and from the adjacent feeder canal throughout the season to be analyzed for salt and nutrient load in the flood water. The sampling schedule was adjusted to provide more frequent samples following significant events such as fertilizer applications or heavy rainfall. Water samples were collected for analysis on a geometric time scale following application of pesticides.

Special field tests including the use of an artificial rainfall simulator to wash the pesticides from the foliage, foliage harvesting, variable flood depths and withholding irrigation water as a means to reduce the volume of return flow were implemented throughout the study as their need was determined.

Laboratory studies consisted of testing various mechanisms of dissipation of pesticides from the flood water, chemical equilibrium studies to determine equilibrium rate constants, and fish toxicity studies to determine

lethal dose levels of the pesticides. Insofar as possible, all data was subjected to statistical analysis. A computer model was developed to allow the equilibrium of salts between the soil and the flood water and to further elucidate extrapolation of present data to other soils, irrigation water, and climates.

SECTION 5

EXPERIMENTAL PROCEDURES

DESCRIPTION OF FIELD AND SOIL

Twelve field plots were used at the Texas A&M Agricultural Research and Extension Center near Beaumont, Texas. Plots were laid out on a rather homogeneous Beaumont clay soil (Typic pelludert). One location was used for the plots during 1973, and another location was selected for use during 1974 and 1975. The texture analyses for the surface and subsoil of composited samples from the two locations are shown in Table 1. When the clay was further fractionated, it was found that approximately 70% was less than 0.2μ . The CEC of the surface sample was 35 meq/100g. The pH ranged between 5.7 and 6.1 at a 1:2 soil-water ratio. Carson and Dixon (1972) reported that the clay fraction of the Beaumont soil is montmorillonitic and greater than 50% of the isomorphous substitution is in the tetrahedral sheet. The area chosen for the experimental plots had not been cropped for three years.

TABLE 1. SOIL TEXTURE OF COMPOSITED SAMPLES
FOR THE 12 RESEARCH PLOTS

Year	Depth cm	Sand %	Silt %	Clay %	Texture USDA
1973	0-15	31.5	16.8	51.7	Clay
1973	15-28	27.9	14.6	57.5	Clay
1974 & 1975	0-15	33.3	14.7	47.0	Clay
1974 & 1975	15-28	32.7	19.2	48.1	Clay

FIELD PROCEDURES

Source of Irrigation Water

The Neches River was the source of the irrigation water used on the plots. The water is taken from the river by the irrigation district and travels

approximately 25 km through a series of canals before it reaches the experimental area. The suspended load of the source varies from time-to-time with a typical value of 0.2 g/l.

Management of Irrigation Water

Earthen levees were constructed along the boundaries of the plots, and plastic barriers were interred to a depth of 90 cm within the dikes to retard water from moving horizontally between plots. Views of the field plots are shown in Figures 1, 2 and 3. The flooded surface area of the plots averaged 300 m².

Two prepermanent flood irrigations, applied after planting and two weeks later, were accomplished using 5 cm diameter plastic tubes to siphon water from a feeder canal. The irrigations required to bring the plots up to full flood and subsequent irrigations required to replenish the flood water were also accomplished by siphoning. Only infrequently was it necessary to siphon water into the continuous flow plots. Such irrigation was necessary when the continuous flow system lagged behind the losses. Intentional irrigation of the plots was continued until the flood water reached the bottom of the 10° weir described below.

Plots for irrigation treatment were randomly selected. The continual flow plots were supplied with water through an aluminum irrigation pipe connected to a gate on the district canal. The water flowed through a float valve into a stilling chamber behind a 10° weir. The level of the float valve was adjusted to control the flow rate through the weir (Figure 4).

Two weirs and a water stage recorder were used to measure the outflow water. A 45° weir was installed so that the bottom on the V was at the level of the bottom of the plots. It was used to release the water from the two prepermanent flood irrigations, as necessary to rapidly release water from exceedingly heavy rainfall during the permanent flood, and to release the final flood. At other times during the permanent flood, it was sealed. A 10° outflow weir was placed such that the bottom of the V was nominally 10 cm above the mean bottom of the plot. Excess water from both continuous and intermittent plots was released through the weir. A Stevens Model 68 water stage recorder with special pulleys to increase the sensitivity to 0.05 cm of depth was used to measure the water depth inside a stilling well made of a 30 cm diameter, 120 cm long concrete tile. See Figure 5 for details. A hole was drilled in the side of the tile below the water level. To further damp oscillations in the water level which resulted from the influence of wind, it was necessary to connect under water a 100 cm section of 2 cm diameter hose to the hole in the side of the tile.

In 1973, the levees were constructed of soil and covered with black plastic. It was apparent from the fluctuating water depths and the seeps around the edges of the plots that water was leaking both between plots and from the edges of the plots. In 1974, the plot location was moved some 100 meters from the location used in 1973. Before the new levees were constructed, a ditch digger was utilized to dig a 90 cm deep trench around each of the 12 plots. A 150 cm wide piece of black plastic (Griffon No. 45) was



Figure 1. View of the field before planting showing levees, stand pipes ready for the installation of water stage recorders and a lysimeter box behind the stand pipe located to the left of the photograph.



Figure 2. View of field plots showing outflow weirs and the boardwalks used for access to plots. A water stage recorder can be seen in the upper right quadrant of the photograph.

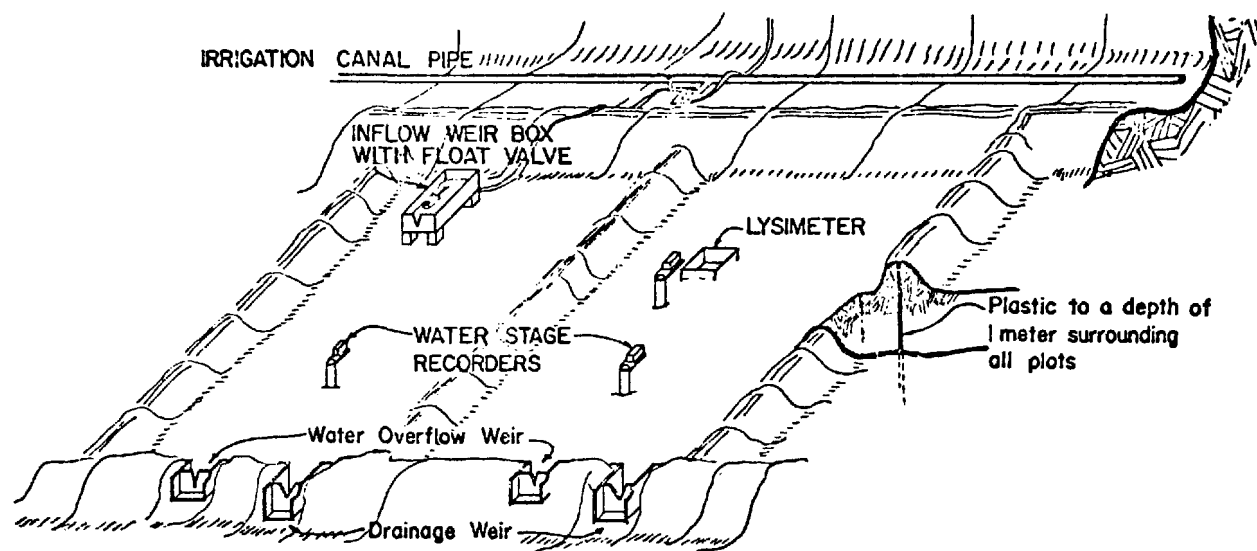


Figure 3. Schematic diagram of two of the research plots showing water control devices.



Figure 4. A water flow regulating float valve, stilling chamber and weir used to maintain continuous flow plots.

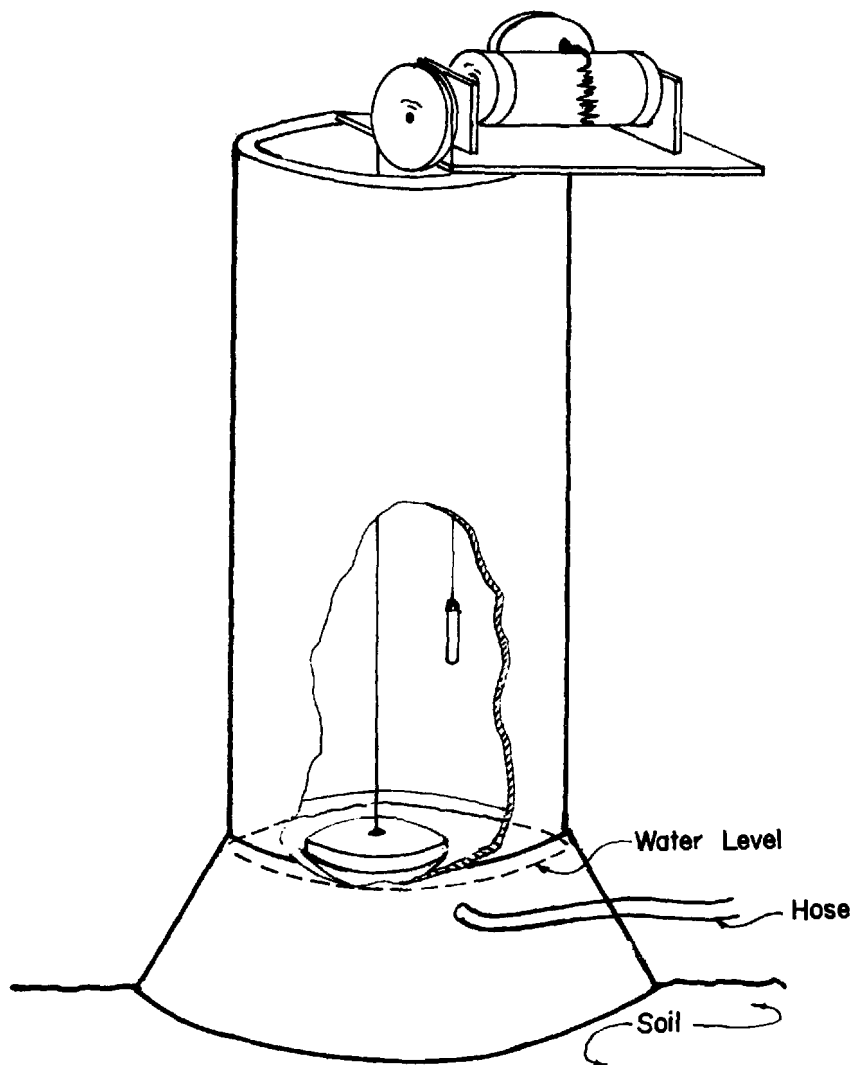


Figure 5. Schematic diagram of water stage recorder mounting and stilling well.

placed in the ditch and the soil was replaced. The levees were constructed on either side of the strip of plastic which protruded from the ditch. During the process, vibrating compactors and a pneumatic tamper were used to pack the soil to insure a water-proof barrier. Subsequent tests conducted by irrigating alternate plots indicated that the barriers were effective in preventing leaks. The same plots were utilized during the 1975 season.

Several methods were used to measure the movement of water into the profile. A water balance comparing the lysimeter data and the water loss from the plots, was used to determine infiltration during the period the paddy was flooded. Additionally, measurements of infiltration were made on small plots isolated with metal frames and surrounded by water. Measurements were made of the amount of water required to refill the covered isolated plot to the original level. During 1975, three sets of piezometer tubes were placed in the plots at a series of depths. Observations of water level in these were recorded throughout the season.

Lysimeters

Lysimeters were installed each year near the center of each of the impounded plots. They consisted of galvanized sheet metal boxes 30 cm tall and 100 cm square. They were installed by digging a square hole 10 cm deep. After the bottom of the hole was smoothed, the lysimeter boxes were set in place and the excavated soil was placed inside and packed back to nearly the same volume. Because of the late start in 1973, the rice was hand transplanted into the lysimeters. Direct seeding was employed in 1974 and 1975. In all seasons, the foliar canopy developed in the lysimeters was similar to that in the adjacent field. A series of holes at different depths was located in one side of each lysimeter box. These holes were fitted with stoppers which remained in place except when one or more was removed for a brief time to allow the flood water from the plot to resupply the water in the lysimeter.

A hose fitting was sealed into the lysimeter below the water level. The other end of the hose was fitted into the bell end of a sealed 30 cm diameter, 120 cm long tube which served as a stilling well and as a stand to hold the water stage recorder.

Application of Nutrients and Pesticides

The plots were randomized with respect to application rates of the nutrients and pesticides. Excessive rates of both were applied to the same plots. The actual rates employed for the pesticides and fertilizers are given in Table 2. Applications of nitrogen were split with 40% being applied at planting time, 40% just before permanent flood, and 20% at panicle differentiation. The excessive rates were employed in an attempt to increase the sensitivity limits for the detection of metabolites. Structural chemical formulas for the pesticides and their metabolites analyzed are given in Table 3.

TABLE 2. RATE OF FERTILIZERS AND PESTICIDES APPLIED
GIVEN IN KG/HA ACTIVE INGREDIENTS

Fertilizers and Pesticides	Recommended	Excessive
Nitrogen as N	134.40	179.20
Phosphate as P_2O_5	44.80	112.00
Potassium as K_2O	22.40	89.60
Propanil	3.36	6.72
Molinate	3.36	11.20
Carbofuran	0.56	3.36
Carbaryl	1.12	5.60

Sampling

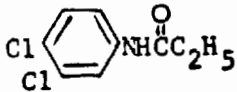
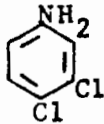
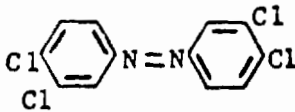
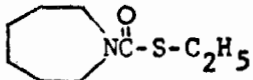
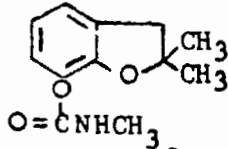
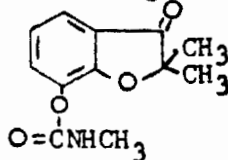
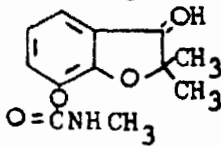
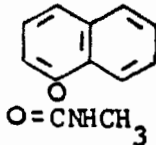
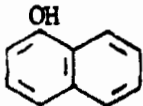
Water--

The irrigation water and the flood water in the plots were sampled on a schedule designed to provide detailed information about changes following events such as irrigation, heavy rainfall, and applications.

Samples were collected for salt and nutrient analyses from the two floods applied early in each season just before the water was released. In addition, samples were collected from the water ponded in the plots after significant rainfall events prior to the permanent flood. Water samples were taken after the permanent flood was established by dipping a fraction of a 100 ml plastic sample bottle into the flood water at three or four locations along the boardwalk which was located down the center of the plot. Samples were collected of the irrigation water more frequently during the early part of the season particularly after fertilizer applications. The samples were transported directly to the laboratory where they were analyzed or in some cases, frozen and stored for later analysis.

Water samples for pesticide analyses were taken as soon after application as possible and assigned a relative time of 0 hours. Subsequent samples were generally taken 24, 48, 96, 192, 384, and 768 hours. Time 0 for propanil was approximately 24 hours following the application because

TABLE 3. STRUCTURAL CHEMICAL FORMULAS OF THE PESTICIDES
AND THEIR TOXIC METABOLITES.

Pesticide	Structural formula
Propanil	
DCA	
TCAB	
Molinate	
Carbofuran	
3-Keto carbofuran	
3-Hydroxy carbofuran	
Carbaryl	
1-Naphthol	

that was when the rice plots were flooded. Then sampling proceeded according to the above schedule. Plots were already under permanent flood at the time of application of the other chemicals.

The sampling technique entailed dipping a 1.85 l wide-mouthed jar into the plot at random points along the boardwalk until full. Care was taken not to disturb the bottom sediment when collecting samples.

Water samples were taken to the laboratory, deaerated with N_2 , and adjusted between pH 5 and 6 with concentrated HCl, sealed with a teflon liner, then packed in cartons for shipment by bus to the pesticide laboratory. Water samples spiked with each of the pesticides were carried through the above procedure to determine the losses that may have occurred in the delay between sampling and final analysis. Upon arrival at the pesticide laboratory at College Station, the samples were placed under refrigeration until they were extracted. Samples were normally extracted into their respective solvents on the day of receipt. In some cases, when sampling schedules were intensive, the samples were extracted in the laboratory at Beaumont, and the refrigerated extracts were transported directly to College Station.

Soil Solution Sampling--

The original plan was to sample the solution of the soil profile by using 76 cm long, 16 cm diameter aluminum access tubes. These were forced vertically into the soil, the inner soil was removed, and the sides of the aluminum tube was fitted with porous sampling filters at 5, 15.4, 30, and 61 cm below the soil surface as described by Hossner and Phillips (1973). This approach to sampling the soil solution was not reliable because very little or no water could be withdrawn from the tight, fine-textured, very slowly permeable soil. In the few cases where adequate replicated samples of soil solution were obtained, analysis for certain ions showed excessive variability. Thus, the lack of sample, sample volume, and the excessive variation within replications called for another sampling method.

Since water percolation studies showed that the movement of water through the soil profile was very small, during 1974 the effort to characterize the soil below 15 cm was abandoned and a concentrated effort was made to collect soil solution samples from the top 15 cm of soil. At the beginning of the 1974 season, rigid PVC tubes (1.5 cm in I.D.) were fitted with plastic porous filters (4 cm long and 1.1 cm O.D.) and forced into the soil to a depth of 10 to 15 cm. Again, difficulty was experienced in obtaining adequate volume and with excessive variations between replications. Therefore, during the end of 1974 and throughout the 1975 season when the flood water was on the field, a dialysis tube method of sample collection was used. Dialysis tubing (1.7 cm diameter by 15 cm long) was filled with distilled water. These were placed in the plots and covered with approximately 1 cm of soil. After 24 hours of contact with soil solution, equilibrium had been attained and the dialysis tubing was removed from the plots and analyzed for NH_4^+ and NO_3^- .

Soil Sampling--

At the beginning of the experiment, soil samples were taken for ion and nutrient analysis with a soil core sampler from 0 to 15, 15 to 30, 30 to

45, 45 to 60, 60 to 76, and 76 to 91 cm depths in each plot to establish the background ionic constituency. Additional soil-surface samples were taken during the growing seasons. During the 1974 and 1975 seasons, only samples of the soil surface were obtained because it became evident that water percolation was very slow and that the top 15 cm of soil was most important.

Soil samples were also collected with a split tube from each plot in biweekly intervals at 2.5 to 5.0 and 17.5 to 20.0 cm depths to determine if any of the applied pesticide moved down through the soil profile. An aggregate of several small cores from each depth was placed in a 450 ml jar and stored in a freezer. The samples were packed in dry ice and transferred to the pesticide laboratory for subsequent screening of the primary pesticides and/or metabolites. The samples were always kept frozen prior to extraction.

Special Field Experiments and Measurements

Propanil Foliar Study--

After reviewing the 1973 propanil data, it was decided to initiate a special study to ascertain the source of propanil in the plot water following the flood. A border plot adjacent to the regular plots was seeded with rice. Ten metal frames 1.3 m^2 were driven 5 cm into the soil in the border plot. The entire border plot was sprayed with the excessive rate of propanil. The areas within the frames were protected from rainfall with removable plastic covers. These allowed air passage over the plots but were broad enough to prevent rainfall from reaching them.

Two metal frames were chosen at random 0, 24, 48, 72, and 120 hours following the spray application. Foliage samples were taken by completely removing all the vegetation within a 0.2 m^2 area in each frame. The foliage samples were placed into 1.85 liter jars and rinsed with 1 liter canal water. A 200 ml aliquot of the rinse was extracted for propanil by the procedure previously discussed. Following the foliage sampling, the area within the frames was flooded to a depth of 10 cm. A water sample was collected approximately one hour following the flood and analyzed for propanil.

Prior to the spray application, nine petri dishes with 50 g soil in each were placed on the soil surface between the foliage in the border plot to determine the amount of the spray reaching the soil surface. To increase sensitivity, the soils in three petri dishes were aggregated to give one sample.

Foliage samples were also collected from all of the regular plots immediately following the spray application and 24 hours later just prior to the flood. Sampling entailed exfoliation within a 0.2 m^2 area within each plot. This gave a measure of the actual amount of propanil remaining on the plants after spraying and just prior to flooding.

Simulated Rainfall Washoff--

Data collected during the first season indicated the possibility that carbaryl was washed off from the foliage by rainfall, resulting in an increase in concentration in the flood water, rather than a decrease

as might be expected due to dilution effects. An experiment was thus designed to determine the amount of carbaryl which could be washed from the foliage by rains of different intensities and durations which occurred at 0, 1, 2, 4, and 7 days after pesticide application.

A rainfall simulator similar to that described by Morin et al. (1967) was used to generate controlled rainfall events in the field. Briefly, the simulator consists of a rotating nozzle which delivers the equivalent of 150 cm of rainfall per hour. A slit disk rotating at 200 rpm intercepts the majority of the rain so that only specified amounts reach the plots. By varying the slit width, the intensity can be adjusted from 0.5 to 24 cm per hour. The rainfall simulator closely approximates the characteristics of natural rainfall including drop size, distribution and impact energy. In the field, canvas curtains were used to prevent the wind from shifting the rainfall pattern which is uniform over a square area 1.3 m on a side. The well water used in the rainfall simulator was free of compounds which would interfere with detection of the pesticide.

Since the simulator could only cover a small area at one time, 25 cm tall plot frames made of galvanized steel were driven 5 cm into the soil. They surrounded a plot 1.3 m on a side and extended about 10 cm above the flood level. During 1974 and 1975, the subplots were established in the border plots not used in the main experiment. Carbaryl was sprayed on the plots within a few days of the time it was sprayed on the main experiment. Applications were scheduled so that the long rainfall simulations could be accomplished within a one or two day period. To prevent natural rainfall from reaching the plots between application and simulated rainfall, plastic tents were suspended above the plots. These were 2.5 m square and allowed air and light to reach the plots but did not allow even wind-driven rain to reach the plots. Measurements were made on three replications of all treatments.

Samples of flood water in the plots were collected by dipping a 1.85 liter wide-mouth jar into the plots just prior to the simulated rainstorm and again at 2, 4, 8, 16, and 30 minutes after the initiation of the storm.

Withholding Irrigation Water--

One management practice which would reduce the quantity of irrigation water would be to stop adding irrigation water to the permanent flood late in the season so that the water already present would be lost by evapotranspiration before the end of the season. The soil moisture reserve should be sufficient during this period to insure a yield without the flood. By this time in the season, competition from weeds which are normally kept down by the flood should be minimal. An additional advantage is dryer soil during harvesting.

Therefore, in the 1975 season, irrigation of selected impounded plots was stopped August 1. This date was selected to provide enough time for the flood present to evaporate by the time the flood would normally be released.

Bulk Density--

A pit was opened in the soil to a depth of 150 cm. Natural peds were collected from a series of depths. These were preserved at field moisture until the bulk density could be measured. Volume measurements were made by water displacement after the peds were coated with wax as described by Black (1965) in the Methods of Soil Analysis, Monograph No. 9 of the American Society of Agronomy.

Root Distribution--

To achieve some idea of the distribution of roots in the rice paddy before and during flooding, samples were collected by forcing 30 cm diameter, 30 cm long sleeves into the soil. These were sliced into layers. The roots were separated from the soil by the use of both water spray, sieve shakers, soil dispersants, and hand picking. Dry weight measurements were made. Length to weight ratios were determined on selected samples.

Organic Load--

At the end of each year, 1.85 liter water samples were collected from the plots just before the permanent flood was released. A sample was also collected from the feeder canal at this time. These were analyzed for BOD, TOC, and COD according to the methods outlined in Standard Methods for the Examination of Water and Wastewater, 13th edition (1971).

Sediment Load--

The sediment load was determined on the water samples collected for pesticide analysis. For each collection, three plots were selected at random, the sediment in the sample bottles was resuspended by vigorous shaking, and a 50 ml sample was withdrawn. This was dried in an oven at 98°C, and the residue was determined gravimetrically.

Meteorological Measurements

A standard set of meteorological data from a weather station located 1000 m from the field plots is given in Appendix B. It consists of minimum and maximum air temperature, relative humidity, air passage, precipitation, and evaporation from a class A pan and a sunken 60 cm diameter pan. Radiation measurements from the Port Arthur Station were extrapolated where necessary.

Because of the spacial variability of some storms, an additional weighing rain gauge was located at the site of the field plots. The water temperature and soil temperature were recorded continuously in selected plots during the time they were flooded.

ANALYTICAL PROCEDURES

Soil Extraction and Analyses

Soil cores for the respective depths were air dried, ground, and thoroughly mixed. Ten gram subsamples were then placed in centrifuge tubes followed by one of the three extractants: 1) water to extract $\text{SO}_4^{=}$ and Cl^- ; 2) 1 N KCl to extract NH_4^+ , NO_3^- and NO_2^- ; or 3) 1.4 N KCl adjusted to pH 4.2

to extract $\text{PO}_4^{=}$, Ca^{++} , Mg^{++} , Na^+ , and K^+ . The procedures employed were according to Methods of Soil Analysis Monograph No. 9 of the American Society of Agronomy (Black, 1965). Tubes were stoppered and placed on a reciprocating shaker for at least five minutes. Suspensions were then centrifuged for four minutes at 1200 RPM. The extract was decanted through Whatman No. 1 filter paper for analysis. Analyses were performed within two days after extraction. Corrections were made for moisture content and final data was reported on an oven-dry basis.

All cations except NH_4^+ were measured by atomic absorption or by flame emission on a Jarrell-Ash spectrophotometer. Sample readings were compared to corresponding values on standard curves prepared from serial dilutions of commercially available "Flame" standards. All dilutions involving either standards or samples were made with the respective sample extractant. Ammonium and all anion concentrations were determined colorimetrically employing a "Technicon Auto-Analyzer" (Model II) and accompanying strip chart recorder. To ensure reliability of the chemical analyses, routine control programs were used as described in the "Handbook for Analytical Quality Control in Water and Waste Water Laboratories". The "Technicon" automated procedures employed are detailed in Appendix C. The pH and E. C. were determined on the water extracts. Conductivity was measured using a wheatstone bridge, and pH using a pH meter.

Analysis of Water Samples

Analytical procedures for soil solutions were essentially the same as those employed for the soil analyses, with the exception that distilled, de-ionized H_2O was employed as the diluent, in the samples and standard preparations. Aliquots of suitable volume were taken for the respective elemental analyses. Samples were treated with two drops chloroform/100 ml and frozen to preserve the samples. Water samples were thawed and filtered just prior to the elemental analyses. Aliquots of the bulk water sample were employed for NH_4 and each anion. Cation concentrations were determined on the bulk water sample. Nitrogen as NH_4^+ , NO_3^- , and NO_2^- was analyzed first to prevent errors due to nitrification/denitrification. This was just a precautionary sequence since chloroform had been added to the water samples upon collection. The analyses of plot water were performed according to the same procedures used for soil samples.

Propanil and TCAB--

The procedure used for screening of propanil and TCAB was basically that developed by Kearney et al. (1970) for rice soils. It was assumed that an extractant adequate for soils would also be adequate for water.

Five hundred ml of a water sample were placed in a 1 liter separatory funnel, followed by 200 ml of 1:1 acetone:benzene solution. The mixture was shaken for one minute. The aqueous phase was removed by washing with three, 40 ml volumes of 0.1 N NaOH, followed by three, 40 ml volumes of 2 N HCl. The benzene layer was dried into a 10 cm bed of anhydrous Na_2SO_4 and transferred to 250 ml round bottom flask. Samples were reduced in volume on a Rinco flash evaporator, then taken to dryness with a gentle stream of clean, dry air. Five ml of hexane were pipetted into the flask, transferred to a

stoppered test tube, and injected directly into the gas chromatograph (GC) if no clean-up was indicated.

When indicated, samples were cleaned up on Florisil columns. These were prepared by adding the following to glass columns: glass wool plug, 10 g deactivated Florisil, 1 cm anhydrous Na_2SO_4 and another glass wool plug. Florisil, 100/200 mesh, was deactivated at 25°C for 24 hours in an atmosphere of 30% relative humidity. This environment is established by placing a saturated solution of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in the bottom of a desiccator. Columns were prerinsed with 50 ml n-hexane. Just as the last of the rinse penetrated the column, the sample was added followed immediately with the first of two, 10 ml rinses of the flask. The columns were first eluted with 150 ml hexane at a rate of 5 ml/min. This fraction contained the TCAB. Columns were eluted with 100 ml 12% diethyl ether/petroleum ether which was discarded. Finally, propanil was eluted with 200 ml 5% dichloromethane in benzene. This was reduced in volume to near dryness, then readjusted to a suitable volume and injected into the GC.

Soil samples were handled in much the same manner as the water samples with the only difference being an initial filtration of the acetone:benzene before the washes. Also the sediment on the filter paper was washed with two, 25 ml portions of the extracted solution. Soil samples and the 1974 and 1975 water samples did not require column clean-up since precautions were taken in keeping the plastic used to provide the water barrier isolated from the plot water.

All analyses were performed on a Barber Coleman GC model 5360 equipped with a tritium source EC detector. The instrument column contained one part 5% DC 710 and two parts 15% QF-1 on Chromosorb W (80/100 mesh). The pyrex glass column was 4 mm in diameter and 6 ft long. Inlet, column, and detector temperatures were 225, 185, and 200°C , respectively. The carrier gas (N_2) flow rate was 90 ml/min.

Standards were added to water samples and carried through the above procedure to determine percent recoveries. Standard recoveries for propanil and TCAB were generally around 90%.

Limits of detection were calculated by taking the corresponding amounts equivalent to twice the reagent blank at the appropriate retention time. These values were $0.4\mu\text{g}/\text{l}$ for propanil, and $0.2\mu\text{g}/\text{l}$ for TCAB in the water samples. Corresponding limits of detection for the soil samples were $0.01\mu\text{g}/\text{g}$ and $0.003\mu\text{g}/\text{g}$ for propanil and TCAB, respectively.

Molinate--

Molinate was extracted from water samples using three, 50 ml portions of n-hexane. This was followed by drying with Na_2SO_4 and reducing the extract to approximately 2 ml. The sample was quantitatively transferred to graduated test tube and reduced to a suitable volume with a gentle stream of dry air. The basic procedure employed was that developed by the Stauffer Chemical Co. research staff (Knarr, 1970; Schwab and Patchett, 1967).

Soil samples were extracted with 100 ml 20% diethyl ether in dichloro-

methane. The extracts were filtered and dried with anhydrous Na_2SO_4 prior to being taken just to dryness. Samples were taken up in exactly 2 ml n-hexane and injected into the GC.

All analyses were made on a Barber Coleman GC model 5360 equipped with a flame thermionic detector. The platinum-iridium wire was coated with rubidium and potassium sulfate. The column contained equal portions of 10% DC 200 and 15% QF-1 on Gas Chrom Q (80/100 mesh). Inlet, column, and detector temperatures were 225, 185, and 230°C, respectively. The carrier gas (N_2) flow rate was 90 ml/min. Air pressure was set at 30 psi. Hydrogen was adjusted to give maximum sensitivity.

The detection limit was 0.3 $\mu\text{g}/\text{l}$ for molinate in water and 0.02 $\mu\text{g}/\text{g}$ in soil samples. Percent recoveries were near 100% for fortified water samples and near 90% for spiked soil samples.

Carbofuran, 3-keto Carbofuran, and 3-hydroxy Carbofuran--

The derivatization procedure developed by Butler and McDonough (1971) was used to determine carbofuran and its metabolites. Five hundred ml of water was extracted with three, 50 ml portions of dichloromethane. The dichloromethane was dried by passing it through a bed of anhydrous Na_2SO_4 and evaporated to approximately 2 ml in a Rinco flash evaporator set at 40°C. The procedure called for the addition of 0.1 ml keeper solution (1 ml white mineral oil in 100 ml CH_2Cl_2) prior to reduction in volume. Following the volume reduction step, the extract was quantitatively transferred to 15 ml graduated test tubes for the derivatization described in the procedural paper. Derivatization entailed reaction of the esterified pesticide with trichloro-acetyl-chloride. This resulted in halogenation of the pesticide for EC detection.

Soil samples were extracted with 100 ml of 20% diethyl ether in dichloromethane on a rotation shaking device for approximately two hours. Samples were filtered on a buchner funnel, passed through anhydrous Na_2SO_4 , reduced in volume, and then carried through the derivatization procedure.

Instrumentation was the same as previously described for propanil. Recoveries of carbofuran, 3-keto carbofuran, and 3-hydroxy carbofuran from fortified soil and water samples were greater than 80% and generally greater than 90% in the water samples. Detection limits for carbofuran, 3-keto carbofuran, and 3-hydroxy carbofuran in water were 0.2 $\mu\text{g}/\text{l}$, 0.2 $\mu\text{g}/\text{l}$, and 0.5 $\mu\text{g}/\text{l}$, respectively. Corresponding limits for fortified soil samples were 0.01 $\mu\text{g}/\text{g}$ for carbofuran, 0.02 $\mu\text{g}/\text{g}$ for 3-keto carbofuran, and 0.04 $\mu\text{g}/\text{g}$ for 3-hydroxy carbofuran.

Carbaryl and 1-Naphthol--

The extraction procedure was essentially the same for carbaryl and 1-naphthol as that described for carbofuran. The technique utilized to separate carbaryl and 1-naphthol was that reported by Butler and McDonough (1970). The 1-naphthol is partitioned into 0.1 N NaOH, following the dichloromethane extraction. The NaOH layer containing the 1-naphthol was neutralized with 10 ml 6 N HCl and re-extracted with dichloromethane. The separate extracts were then carried through the derivatization procedure as previously mentioned.

in the carbofuran discussion.

The procedure for extraction of carbaryl and 1-naphthol from the soil samples was exactly the same as that used for carbofuran. However, no attempt was made to separate carbaryl and 1-naphthol because it was found that the procedure employed adversely affected the recovery of carbofuran from spiked water samples. There was too little material collected for separate extractions, so it was decided to forego differentiation between carbaryl and 1-naphthol.

Standard recoveries for carbaryl and 1-naphthol from water were approximately 100 and 90%, respectively. Recovery from soil fortification was found to be near 90% for carbaryl and near 80% for 1-naphthol.

Detection limits were about the same for carbaryl and 1-naphthol. The detection limit in water was 0.2 μ g/l, and in soil was 0.01 μ g/g.

Instrumentation and instrument parameters were the same as for carbofuran.

LABORATORY EXPERIMENTS

Pesticide Dissipation

Volatilization--

The volatility of the four pesticides used in the field experiment was determined in the laboratory using the procedure developed by Farmer et al. (1972). The method entailed passing air over a known water surface into a series of traps (Figure 6). The traps contained the appropriate extraction solvent and were kept at a lower temperature than the volatilization chamber to minimize losses from the traps.

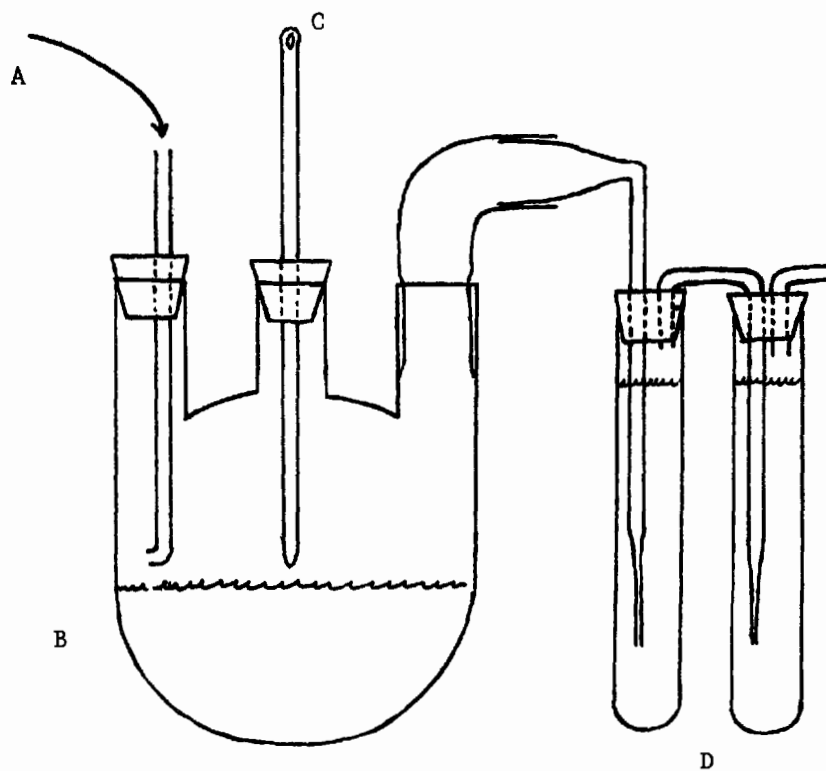
Air passed over the water surface was dry at first then saturated with water vapor to ascertain to what extent co-distillation with water occurred. If co-distillation was a factor, then the vapor flux would be greater with the dry air. The flow rates employed were 2 and 8 ml/sec. The vapor flux was determined initially at 42°C. If duplicate determinations using the highest flow rate showed no flux, no further assessments were made on the pesticide with respect to volatility.

If the results were positive, volatilization indicated, then a series of experiments were conducted to determine concentration effects and adsorption effects when soil was added to the water. These experiments were done at room temperature over an extended period of time.

Photodecomposition--

This mode was evaluated by exposing 300 ml distilled water containing 100 μ g of the specific pesticide to full sunlight. Duplicate samples were placed in the laboratory for comparison. After four days exposure, the water samples were extracted and analyzed for the appropriate pesticide.

It was surmised that distilled water would tend to maximize light



- A Air inlet from source
- B Volatilization chamber
- C Thermometer
- D Vapor traps

Figure 6. Schematic of apparatus used to determine volatilization potentials.

effects since the plot was somewhat turbid.

Adsorption--

Adsorption coefficients were determined for each of the pesticides and their respective metabolites. They were determined at various sediment loads and concentrations. The pesticide was put into a 250 ml centrifuge tube, and the carrier solvent was allowed to evaporate. Soil amounting to .5, 1, 2, 5, 10, 20, and 30 g was added to separate centrifuge tubes. This was followed by 200 ml water. The tubes were stoppered and the contents agitated on a reciprocating shaker for 30 minutes. Samples were centrifuged until the water was clear.

The water was transferred to separatory funnels and extracted for the appropriate pesticide. The percent recovered in the water was calculated from standards carried through the same procedure but in the absence of soil. Amounts adsorbed to the soil were determined by difference. Adsorption coefficients were calculated from the data. The resultant adsorption coefficient (K_d) was correlated to the percent pesticide in solution to assign some relativity to the values.

Biological and Chemical Degradation--

Soil samples from the field plots were placed in flasks and saturated with water to simulate the flooded rice paddies in the field (Figure 7). Some of the flasks were steam sterilized and then spiked with the appropriate pesticide to estimate non-biological degradation.

The effects of the quality of the reduced environment attained were determined for carbofuran, 3-keto carbofuran, molinate, carbaryl, and 1-naphthol. Carbofuran, molinate, and carbaryl were applied after the permanent flood under field conditions. The quality of the reduced environment was varied by adding different amounts of sugar to the soil sample and aided with different length air convection tubes. After equilibrating the flasks for one week, pesticide was injected into the flasks with a syringe through a rubber septum so that the equilibria would not be disturbed. The contents of the flasks were extracted with appropriate solvent after an additional equilibrium period of the pesticide with the reduced environment. Redox potentials were measured in the soil and in the flood water prior to pesticide extraction. Potentials were measured with a pH meter using a saturated calomel electrode and a shiny platinum electrode in combination.

Toxicity of Pesticides to Fish

The bioassays were conducted in an air conditioned laboratory at the Texas A&M University Research Annex near Bryan, Texas. The test animals, channel catfish (*Ictalurus punctatus*), were obtained from the Texas Agricultural Experiment Station's Aquaculture Center. The average weight of the six week old fish was .3 grams. The catfish were acclimated for a period of at least seven days in aquariums at the test lab. The fish were treated with actiflavine and 2% terramycin food as a general disease preventative five days before the tests began. The fish were fasted for 48 hours prior to the initiation of tests. Tests were conducted using tap water and rice paddy water. The tap water originated from a well at the Texas A&M Research Annex

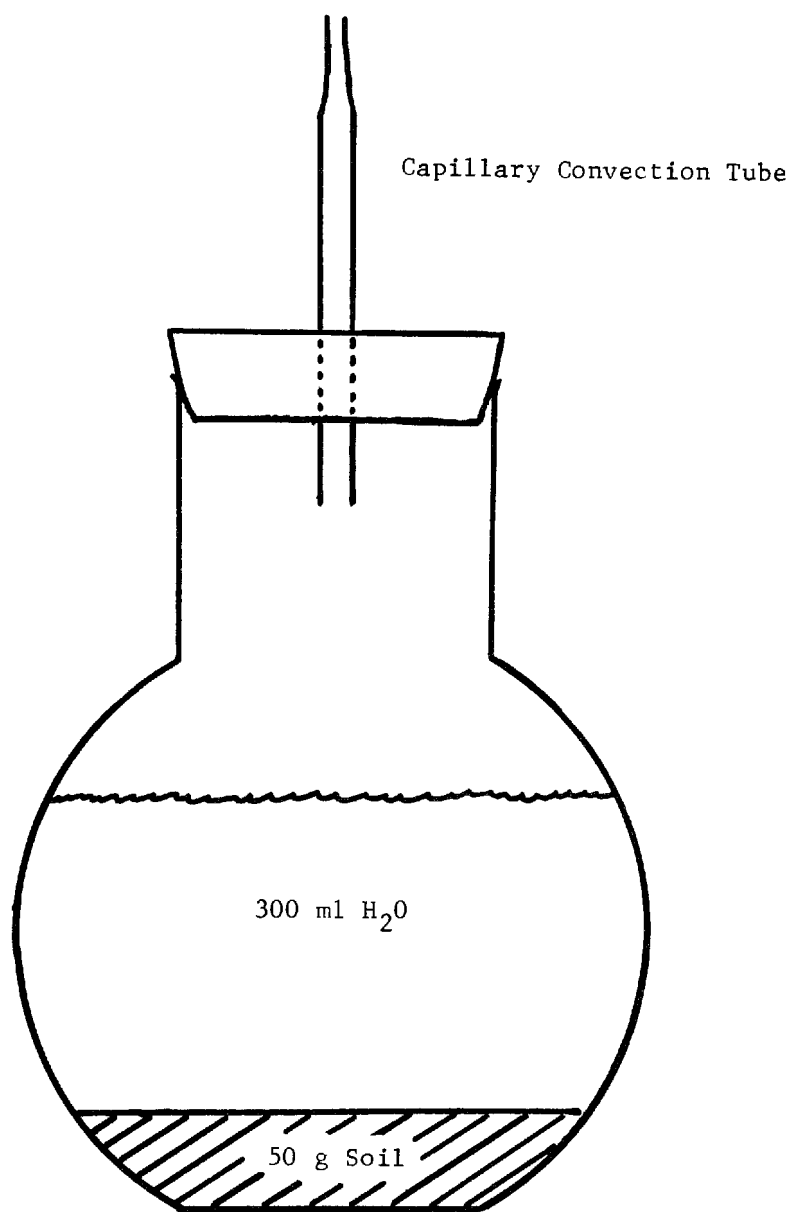


Figure 7. Apparatus for obtaining simulated flood water conditions.

and was passed through one cubic foot of activated charcoal to remove chlorine. Rice paddy water was collected from the Texas Agricultural Experiment Station at Beaumont, Texas, by means of a gasoline powered submersible pump. It was then transported to the test site in a 4800 liter epoxy coated steel tank trailer. The paddy water was held out of doors in a 12,000 liter tank for a period averaging one week before it was used in the tests. Water samples collected on July 29 and 30 are designated paddy water II.

Water quality parameters for the three test waters are given in Table 4. General values are given for paddy water. Pesticide and fertilizer treatments applied to the paddies from which the waters were taken are given in Table 5. Static bioassays were conducted with the four pesticides used in this study in the filtered tap and both paddy waters. The source and purity of the compounds used are given in Table 6. In addition, an intermittent flow bioassay was conducted for carbofuran only using the filtered tap water and water from paddy II.

TABLE 4. WATER QUALITY PARAMETERS FOR FILTERED TAP WATER AND PADDY WATER USED IN THE BIOASSAYS

	Filtered Tap Water	Paddy Water
pH	8.5	6.4
Total salts	597.0 ppm	-
Electrical conductivity	963.0 mhos	250.0 mhos
Calcium	2.0 ppm	2.0 ppm
Magnesium	1.2 ppm	2.0 ppm
Potassium	0.8 ppm	2.0 ppm
Sodium	237.0 ppm	10.0 ppm
Carbonate	22.0 ppm	-
Bicarbonate	461.0 ppm	120.0 ppm
Sulfate	39.0 ppm	10.0 ppm
Chloride	72.0 ppm	40.0 ppm

TABLE 5. FERTILIZER AND PESTICIDE APPLICATIONS TO THE PADDIES
FROM WHICH WATER WAS COLLECTED FOR THE BIOASSAYS

Paddy Water	Paddy Water II
5/4 Propanil 4/48 kg/ha	4/23 (16-20-0) 224 kg/ha
5/13 16-20-0 112 kg/ha	(21-0-0) 112 kg/ha
5/20 Propanil 3.36 kg/ha	5/19 Propanil 4.48 kg/ha
Molinate 3.36 kg/ha	5/25 21-0-0 224 kg/ha
5/25 (16-20-0) 112 kg/ha	5/29 Carbofuran 3.36 kg/ha
(21-0-0) 112 kg/ha	7/29 4800 liters collected
6/14 (21-0-0) 224 kg/ha	7/30 4800 liters collected
7/2 Benlate .56 kg/ha	
7/7 4800 liters collected	
7/12 4800 liters collected	

TABLE 6. SOURCE AND PURITY OF PESTICIDES USED IN THE BIOASSAY

Common Name	Trade Name	Manufacturer	% Purity
Propanil	Stam	Rohm Haas	88.0%
Molinate	Ordram	Stauffer Chem. Co.	93.3%
Carbofuran	Furadan	FMC Corp.	99.0%
Carbaryl	Sevin	Union Carbide	100.0%

Static Bioassays--

Static bioassays were conducted in accordance with the procedures described in Standard Methods for the Examination of Water and Waste Water. Four liter wide-mouth glass jars each containing three liters of water were used as test vessels. The pesticide, administered as a single dose, was dissolved in 3 mls of acetone before being introduced to the test water. Ten parts per billion of Triton X-100, a surfactant, was added to the carbaryl treatment to promote its dissolution. Ten test animals were introduced within 10 minutes after the addition of the toxicant. The test vessels were aerated throughout each test. Aeration was maintained at between 30 and 80 bubbles per minute. Mortalities were recorded every 24 hours, and dead fish were removed as soon as they were observed. Water temperature during the test was maintained at 23°C (+1°C) by the room air conditioner. Treatments were replicated and the data were analyzed by means of a probit procedure given by Barr et al. (1976).

Intermittent Flow Bioassays--

Bioassays were conducted on carbofuran with filtered tap water and paddy water II only. A system was used which added a dose of 250 ml of water containing toxicant at the proper concentration to each test vessel every five minutes.

For the sake of simplicity, the intermittent flow apparatus may be subdivided into the toxicant delivery system, the water delivery system, and the mixing and separation system. Overall schematics are shown in Figures 8a and b; the individual components will be discussed in detail.

Toxicant delivery system--The level of the concentrated solution of toxicant in the toxicant head tank was maintained by means of a pump (Chem Tech Series 100 Model 015). Excess toxicant was returned to the reservoir tank via an overflow stand pipe (Figure 9). The toxicant is delivered to the five toxicant metering devices by means of a manifold made of 5 mm capillary glass tubing. The toxicant metering device, which is similar to that described by Chandler et al. (1974), consisted of 15 ml conical centrifuge tube that was fitted with two siphons and a capillary tube. The toxicant entered the metering device through the capillary tube manifold from the toxicant head tank. The toxicant rose to a level in the toxicant metering device determined by the position of the toxicant metering device in relation to the level in the toxicant head tank.

Water delivery system--The water head tank was made from a 20 liter plastic bucket equipped with a floatless toilet fill valve (Figure 10). Water pressure from the faucet was adequate to deliver the filtered tap water to the water head tank. Rice paddy water was delivered to the water head tank by means of a small roller type pump that was adjusted to maintain a pressure of 1.7 bars. The test water was distributed to the six dosing units, via PVC pipe and 10 mm glass tube (Figure 11). The flow to each of the water metering devices was adjusted with a stopcock to approximately one liter per five minutes. The water metering device was constructed from a one liter Erlenmeyer flask equipped with a U-shaped siphon tube and a siphon break-tube. The volume delivered was determined by the height of the U-shaped siphon tube. The water metering device (Figure 12) is similar to part of the automatic dosing apparatus described by Abram (1960). The water in the metering device

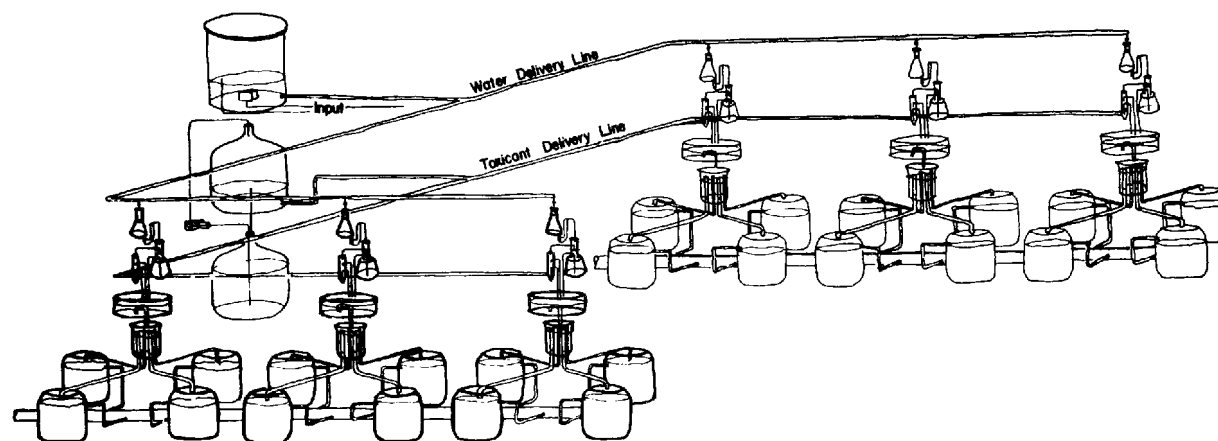


Figure 8a. A composite overall diagram of the intermittent flow apparatus.

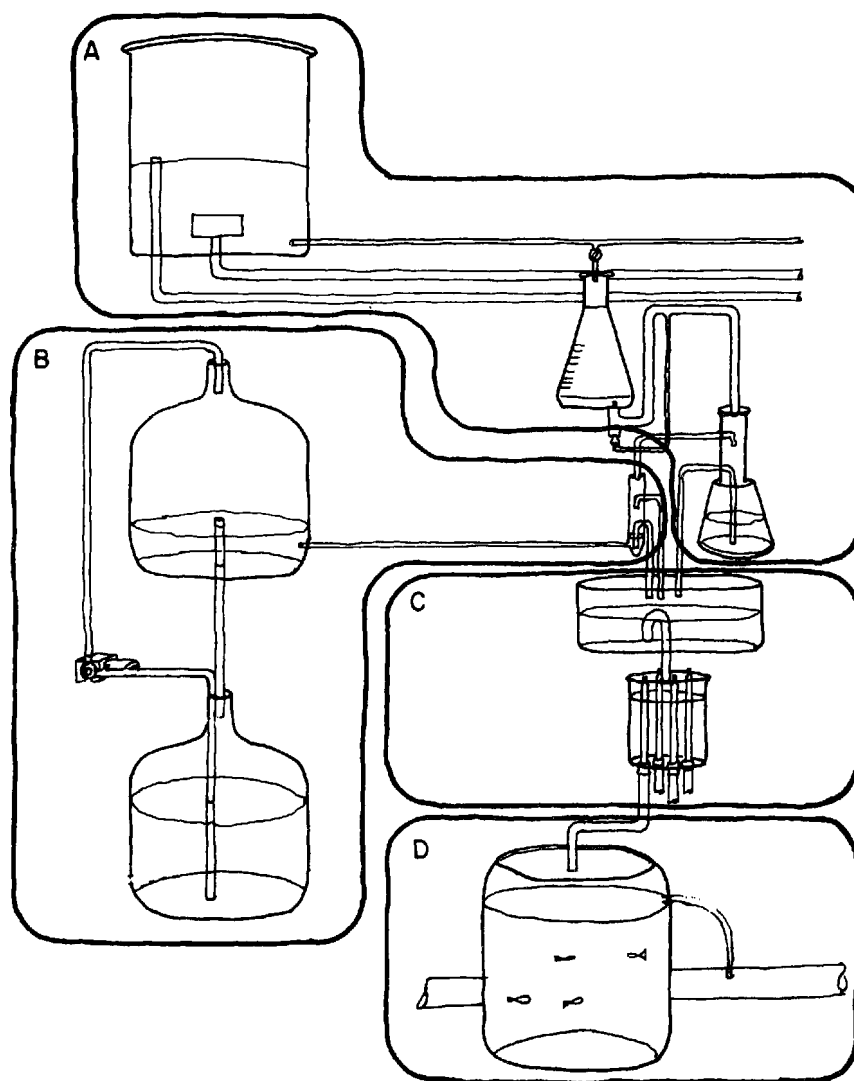


Figure 8b. Schematic diagram of the intermittent flow system showing (A) the water delivery system, (B) the toxicant delivery system, (C) the mixing and splitting apparatus and (D) the exposure chamber and overflow tube.

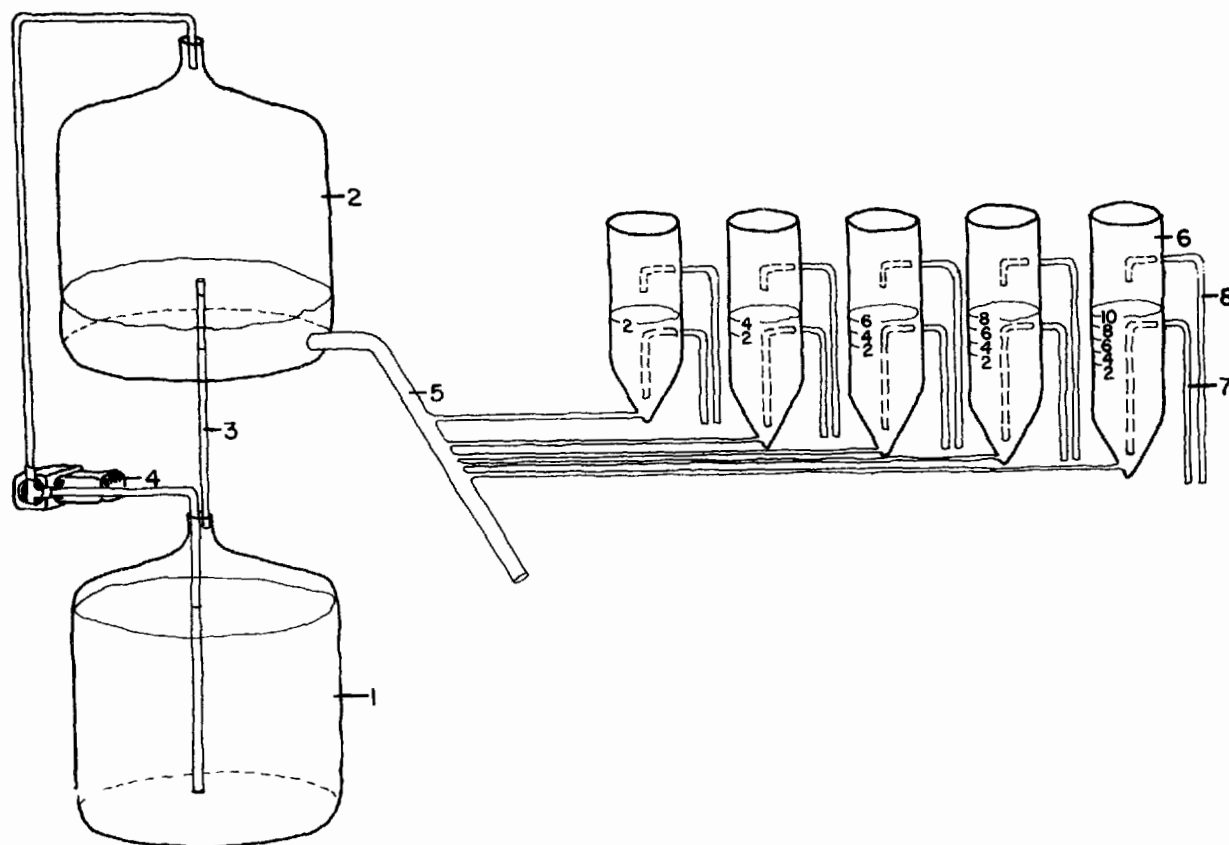


Figure 9. A schematic diagram of the toxicant delivery system and metering device where:
 (1) is the toxicant reservoir tank (20 l glass bottle), (2) is the toxicant head tank,
 (3) is the toxicant overflow standpipe, (4) is the chemical pump, (5) is the toxicant
 delivery tube manifold, (6) is the toxicant metering device, (7) is a siphon (5mm glass
 tube), and (8) is a siphon.

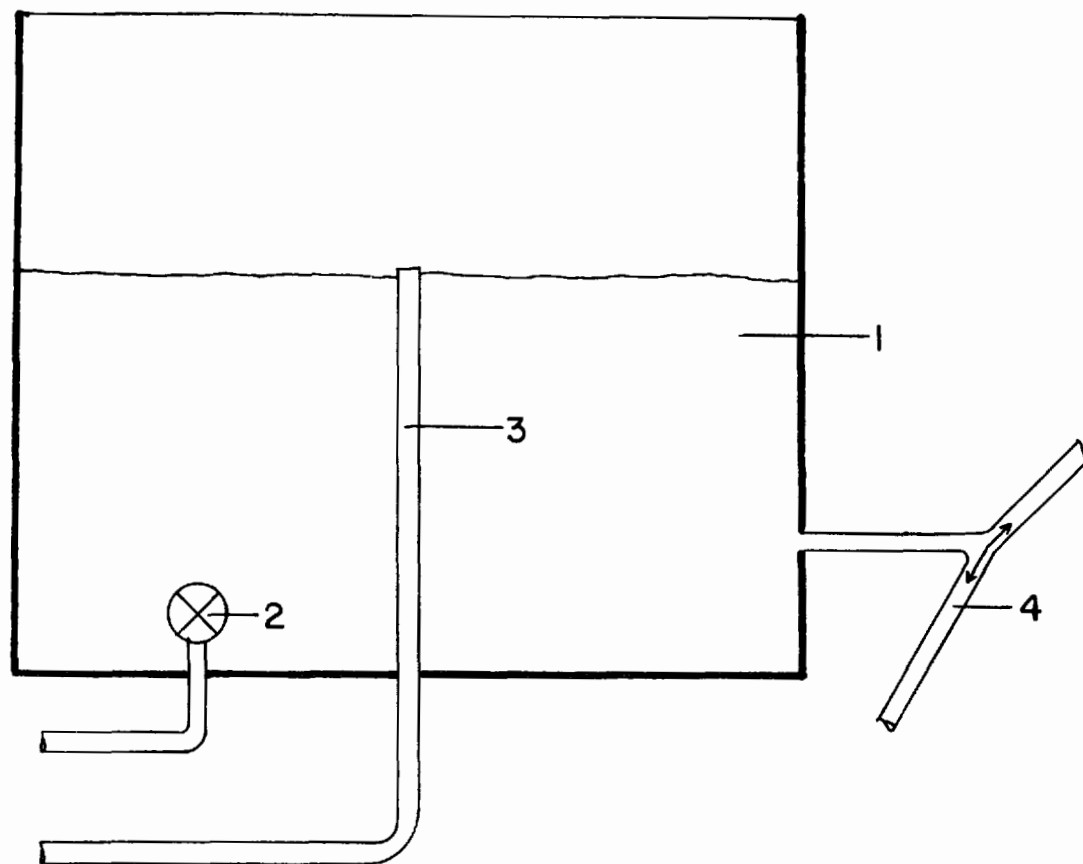


Figure 10. A schematic diagram of the water head tank where: (1) is the water head tank, (2) is the floatless toilet fill valve, (3) is the overflow standpipe, and (4) is the water delivery tube to water metering devices.

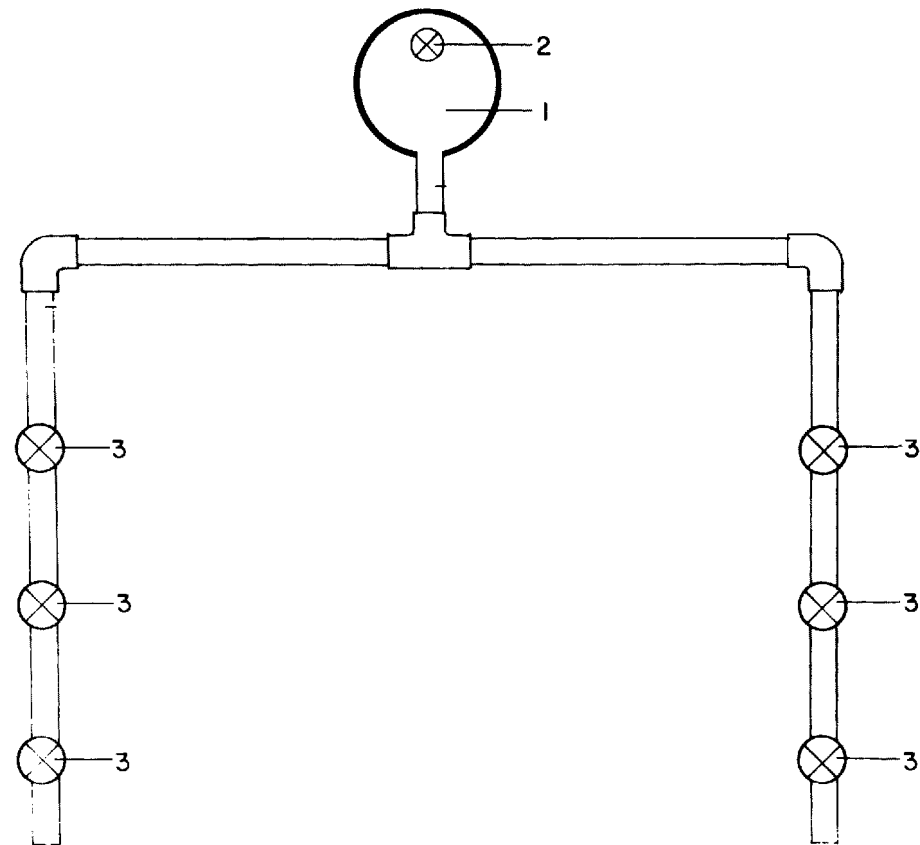


Figure 11. A schematic diagram of water delivery system from the water head tank to the six water metering devices where: (1) is the water head tank, (2) is the floatless toilet fill valve and (3) represents stopcocks.

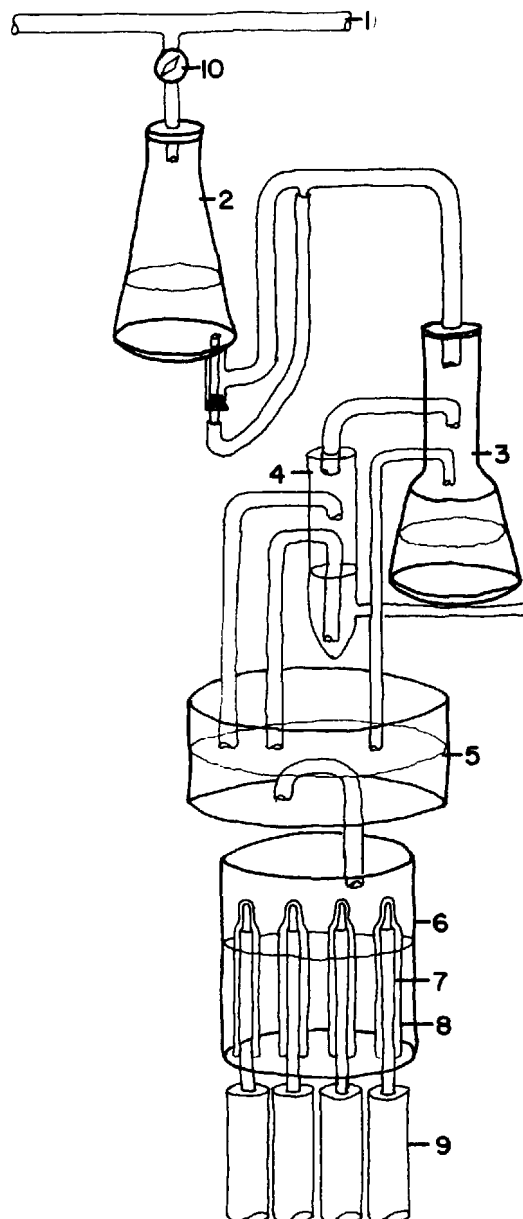


Figure 12. Schematic diagram of a dosing unit where: (1) is the water delivery tube, (2) is the water metering device, (3) is the water delivery device, (4) is the toxicant metering device, (5) is the mixing chamber, (6) is the flow splitting chamber, (7) is the standpipe, (8) is a sleeve, (9) is the flow splitting chamber to exposure tank delivery tube, and (10) is a stopcock.

is siphoned into the water delivery device. The water delivery device consisted of a 750 ml round bottom flask equipped with two siphon tubes (Figure 12). The function of the water delivery device was to divert a small portion of water to the toxicant metering device. This small portion of water causes the toxicant metering device to empty via its two siphon tubes and results in the appropriate amount of toxicant being delivered to the mixing chamber. The major portion of water from the water delivery device is siphoned directly into the mixing chambers.

Mixing and separation system--The mixing and separation system consisted of two major parts, the mixing chamber and the flow splitting chamber.

The mixing chamber (Figure 13) was made from a 2.5 liter crystallizing dish equipped with a U-shaped siphon tube similar to the mixing cells described by Mount and Warner (1965).

The mixing chamber was designed to siphon on half cycles, two liters of test solution, in order to facilitate better mixing of the toxicant and diluent water.

The test solution (toxicant mixed with diluent water) siphons from the mixing chamber to the flow splitting chamber. The flow splitting chamber, similar to that described by Benoit and Puglisi (1973) consists of a two liter beaker with four flow splitting siphons (Figure 13).

As the test solution rises slightly above the top of the sleeves in each chamber, water is forced through the notches and down the standpipe. This action creates a siphon which empties the flow splitting chamber and delivers the test solution to each of four exposure tanks via the exposure tank delivery tubes (Figure 13).

The test vessels, or exposure tanks, were 20 liter glass bottles with the tops cut off. Ten mm drain tubes were installed at the 16 liter level. The end of the drain tube in the exposure tanks was constricted to prevent fish from entering the drain. The drain tubes were connected with rubber hose to the central drain manifold that delivers the spent test solution to a tank trailer for disposal.

The intermittent flow apparatus was adjusted to deliver different dilutions of the toxicant. The dilutions used are given in Table 7.

The actual dilution factors were determined by operating the apparatus for 24 hours using a fluorescent dye (Rhodamine B) in the toxicant delivery system. The concentration of dye in the exposure tanks was determined with a fluorometer. The dye test showed the concentrations to be identical in each of the four exposure tanks within each dosing unit. These dilution factors were used to calculate the toxicant concentrations used in the actual test treatments.

The intermittent flow bioassays were conducted with 10 catfish (Ictalurus punctatus) in each 16 liter exposure tank. Mortalities were recorded every 12 hours and dead fish were removed as soon as they were observed. Tempera-

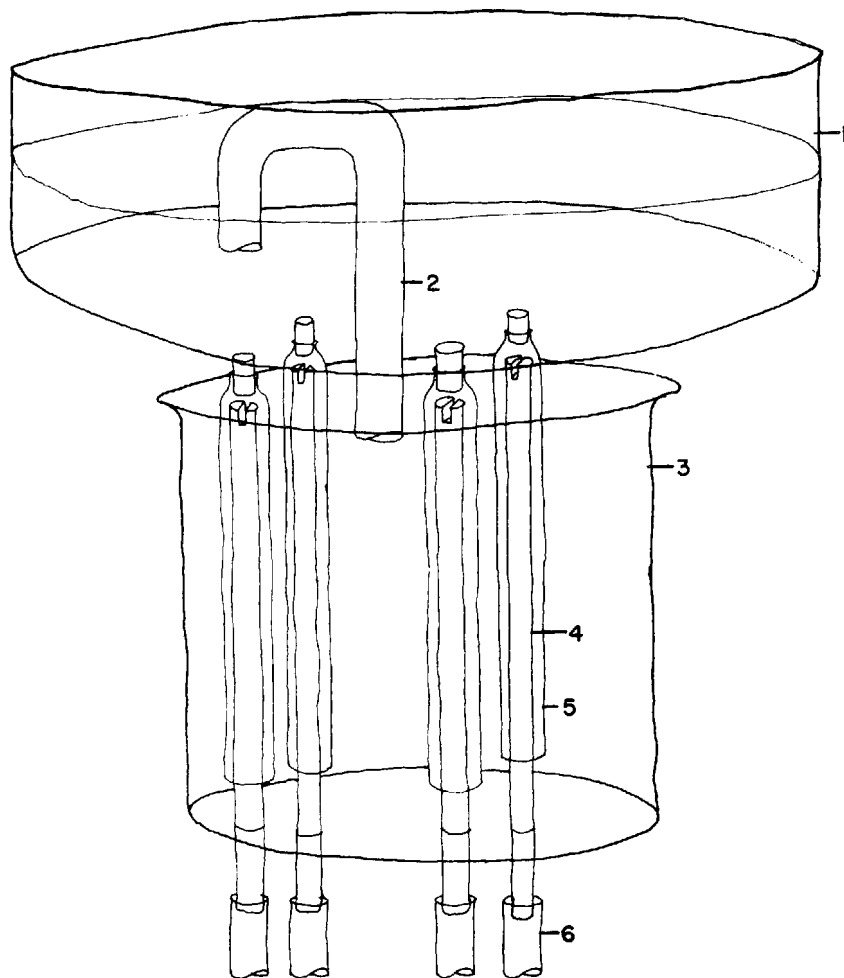


Figure 13. A diagram of the mixing and separation system where: (1) is the mixing chamber, (2) is the U shaped siphon tube, (3) is the flow splitting chamber, (4) is the standpipe, (5) is the sleeve, (6) is the flow splitting chamber to exposure tank delivery tube.

TABLE 7. ADJUSTED INTERMITTENT FLOW DILUTION RATES
USED IN THE BIOASSAY

Unit Number	Volume of Toxicant	Volume of Diluent Water
1	10 ml	990 ml
2	8 ml	992 ml
3 (control)	0	1000 ml
4	6 ml	994 ml
5	4 ml	996 ml
6	2 ml	998 ml

tures during the tests were 23°C ($\pm 2^{\circ}\text{C}$). Aeration was not needed since dissolved oxygen concentrations in the flowing systems were great enough. TLM values were calculated for 24, 48, and 96 hour periods. The results were subjected to the same analysis used for the data from the static bioassay.

Ion Equilibrium Studies

The primary objectives of the chemical equilibrium studies were to obtain values of the exchange coefficients for Na^+ , K^+ , Ca^{++} , and Mg^{++} in a Beaumont clay soil, and to determine the effect of concentration of various cations on the exchange coefficients.

One normal stock solutions of K^+ , Na^+ , Ca^{++} , Mg^{++} , Ba^{++} , and NH_4^+ were prepared from their respective Cl^- salt. These were standardized against commercially available flame standards.

A preliminary experiment was conducted to ascertain the interference levels between cations exchanged and the Ba^{++} exchanger in the subsequent flame and atomic absorption spectrophotometric analyses. Calcium and magnesium were determined by atomic absorption. Sodium and potassium were determined by flame emission. Barium was the exchange ion of choice since it does not normally occur on soil clay exchange sites. To evaluate possible antagonisms by Ba^{++} , standard dilution series were prepared for each cation employing distilled, deionized water as the diluent, and another using 1 N BaCl_2 . Instrument settings (slit width, wave length, etc.) were optimized for the standards in H_2O and were maintained the same for the standards in BaCl_2 .

Another preliminary experiment was conducted to determine optimum shaking times for the equilibrium studies. Twenty gram samples of a Beaumont clay soil were equilibrated for 0.5, 1.5, 3, 6, and 12 hours with 200 ml of distilled H₂O and a (50 + 50) ppm (K + Mg) solution on a reciprocating shaker. Resultant suspensions were centrifuged at 1500 rpm for 10 minutes, then an aliquot was collected to determine equilibrium solution concentrations of Na⁺, K⁺, Ca⁺⁺, and Mg⁺⁺. Analyses of the supernatant solution showed no difference in the concentration of Na⁺, K⁺, Ca⁺⁺, or Mg⁺⁺ with respect to time, suggesting that equilibrium was attained within 30 minutes at the dilution employed.

An equilibrium experiment was conducted on a soil classified as a Beaumont clay but was not collected within the plots. The experiment was not replicated but included all possible combinations for a two to four cation system. A 20-g subsample was weighed into a 250 ml centrifuge tube, followed by the respective cation treatments, and adjusted to give a final volume of 200 ml. Salts for the amendments were prepared in distilled, deionized H₂O. Samples were shaken 30 minutes on a reciprocating shaker, then centrifuged 10 minutes at 1500 rpm. An aliquot of the supernatant was collected and analyzed for Na⁺, K⁺, Ca⁺⁺, and Mg⁺⁺. These data were reported in m moles/liter based on a saturated soil solution. Percent water at saturation was assumed to be 45%. Taking into account initial moisture, a 20-g soil sample would, therefore, contain 0.00835 liters of solution at saturation. The sediments were rinsed with two, 100 ml volumes of distilled water prior to being extracted with 100 ml 1 N BaCl₂. The volume was adjusted for the H₂O remaining following the rinses. Dilutions, when necessary, were made with 1 N BaCl₂. Cation concentrations were reported in meq/100g on an oven dry soil basis.

A second equilibrium study was performed on Beaumont clay soil samples collected from the field study plot site. Duplicate 10 g soil samples were amended with the various treatments and adjusted to a 100 ml final volume. Handling from this point was the same as in the previous experiment. Solution concentrations were reported in m moles/liter of saturated soil solution. Corresponding soil values were reported in meq/100 g oven dry soil.

SECTION 6

RESULTS AND DISCUSSION

WATER BALANCE

Introduction

Several methods of managing flood water for rice cultivation are presently in use. In one, a flood may be maintained continuously from the time of seeding to just prior to harvesting. The primary purposes of the continuous flood is to control weeds and irrigate the crop. The availability of herbicides now allows procedures to use short floods (typically only 24 hours) early in the season to water the crop. In this system a permanent flood is established only after the crop has developed to a height such that approximately half of the foliage will protrude above the water level. During the period of permanent flood, water may be applied intermittently to resupply the losses or a continuous small flow may be used to maintain the water level and in some cases, maintain a continuously flowing stream through the paddy. Irrigation return flow from rice fields may thus occur during release of water when the fields are flooded and drained early in the season before permanent flood. In addition to planned releases, heavy rainfall may wash over the levees or necessitate a deliberate release to prevent erosion of the levees.

Most of the measurements of water balance in rice paddies have been made during the permanent flood. Several approaches have been utilized. Lysimeters were used by Kung (1965) and many of the earlier researchers he cites. Evans (1971) also used lysimeters to determine the evapotranspiration losses of water. Micrometeorological measurements of the energy balance have been made by Kumai and Chiba (1953), the scientists of the Research Group of Evapotranspiration of Japan's National Institute of Agricultural Services (1967) and Lourence and Pruitt (1971). Kato et al. (1965) utilized a leaf chamber to compare the transpiration rates of upland and flooded rice.

The water balance of a rice field over a season may be written as:

$$P + I = E + T + R + L_p$$

where P = amount of precipitation

I = depth of irrigation

E = amount of water lost due to evaporation from the water surface and, to a lesser extent, from wet foliage

T_p = the loss due to transpiration

R = the loss by runoff

L = the percolation loss

As indicated by Kung (1965), L may be a combination of losses which occur vertically below the root zone, or losses which result from lateral movement through the soil or through earthen levees. The latter can result in misleading results particularly where measurements are made on isolated field plots.

Evaporation and transpiration rates will depend on canopy cover and meteorological conditions, while L will depend on the properties of the soil. Thus, the contribution of each of these will vary from one location to another and even from one field to another. Many of the studies in the literature have reported on several of the parts of the water balance, but none report on all of the components in a controlled experiment.

Average seasonal transpirational losses (Kung, 1965) range from 0.12 to 9.8 mm per day, while losses to percolation range from 0.2 to 15.6 mm per day. For individual days, Evans (1971) reported evapotranspirational losses as great as 12.4 mm/day.

The piezometer data indicated that the wetting front had reached a depth of 10 cm in six hours after flooding. The soil in the lysimeter boxes was 10 cm deep, therefore, after the day on which irrigation was applied, no water was required to fill the pores in the soil in the lysimeters and since downward and lateral movement was prevented, subsequent losses in water were taken to be ET.

Irrigation and Rainfall

The amount of water used to irrigate the field just after seeding, that required to irrigate the crop between seeding and the permanent flood, and that required to establish the permanent flood were calculated from the amount of water required to saturate the surface soil plus the depth of water when irrigation was completed. Water was applied to all plots by the use of siphon tubes when the level dropped too low. When the level of water in the lysimeters became too low, the one or more stoppers were temporarily removed from the wall allowing water to flow from the flooded plots into the lysimeter. The rate of water delivery was rapid, generally requiring only a few minutes to a few hours to return the levels in the plots to the bottom of the 10⁰ out-flow weir or reestablish a 10 cm flood in the lysimeters. The supply of water to the continuous flow plots varied from time to time because of difficulty with material obstructing the float valve. The valves were checked and cleaned twice a week and the depth of water flowing through each weir was recorded at these times. Linear extrapolations between these data were used to calculate the rate of continuous flow irrigations for each plot.

Precipitation was measured in the recording rain gauge immediately adjacent to the plots, but for certain storms, the amount of water received by

different plots as shown by the depth records varied widely. For these occasions attempts were made to utilize the best average. The detailed rainfall data are shown in Appendix A for all three years.

Several extreme events required special attention. The 7.9 cm rain on July 6 and the 8.3 cm rain on July 31, 1974, and the 21.6 cm rain on June 9, 1975, fell too rapidly to allow all the water to flow through the 10° weir. The rainfall threatened to overtop the levees. This would have resulted in water flowing from one plot to another and could have washed out some of the levees making repair necessary and making later water control difficult. During each of these storms, the 45° weirs were opened to allow the excess water to drain off. Weirs were closed again soon after the storms were over. These storms resulted in large losses from the fields but are not unlike what occurs in large fields when large amounts of rain fall in a short period of time. The lysimeters were also overtopped during this period, and in some cases, a day or two passed before the level of water in the plots dropped below the level of the top of the lysimeters. During these periods, the data were adjusted as necessary.

During 1973, the rainfall was great enough and was well enough distributed so that very little supplemental irrigation was needed in the intermittent plots. During both 1974 and 1975, the rainfall during June and the first half of July was spaced, necessitating several irrigations. During both years the rainfall in late July and August was greater than evapotranspiration, eliminating the need for irrigation.

Water Depth Data

The depths of irrigation water calculated from the water stage recorders for all plots during 1974 and 1975 are shown in Appendix D, Tables D1 through D6.

The water stage recorders provided resolution of 0.05 cm of water depth or better so that the daily pattern of water loss from each plot was traced. Detailed data for a several day period from one plot are shown in Figure 14. This was an intermittently irrigated plot and during this time, no water was flowing out of the weir. The line at 9.4 cm represents the level of the bottom of the 10° weir.

Two problems occurred with the water data the first year which made it impossible to calculate an accurate water balance. Despite our efforts to compact and cover the earth levees with plastic, leaks occurred into, out of, and between the plots. Although vertical infiltration in these clay soils is very slow, apparently considerable movement occurred between the peds that were scraped from the surface to make the levees. The second problem was the lack of sensitivity of the water stage recorder. Steps were taken to correct both of these problems before the second year of research. As a result of the difficulties, a majority of the effort in interpreting the water balance and its subsequent use to calculate the salt balance, was concentrated on the 1974 and 1975 data.

During the night, the water losses due to infiltration or evapotrans-

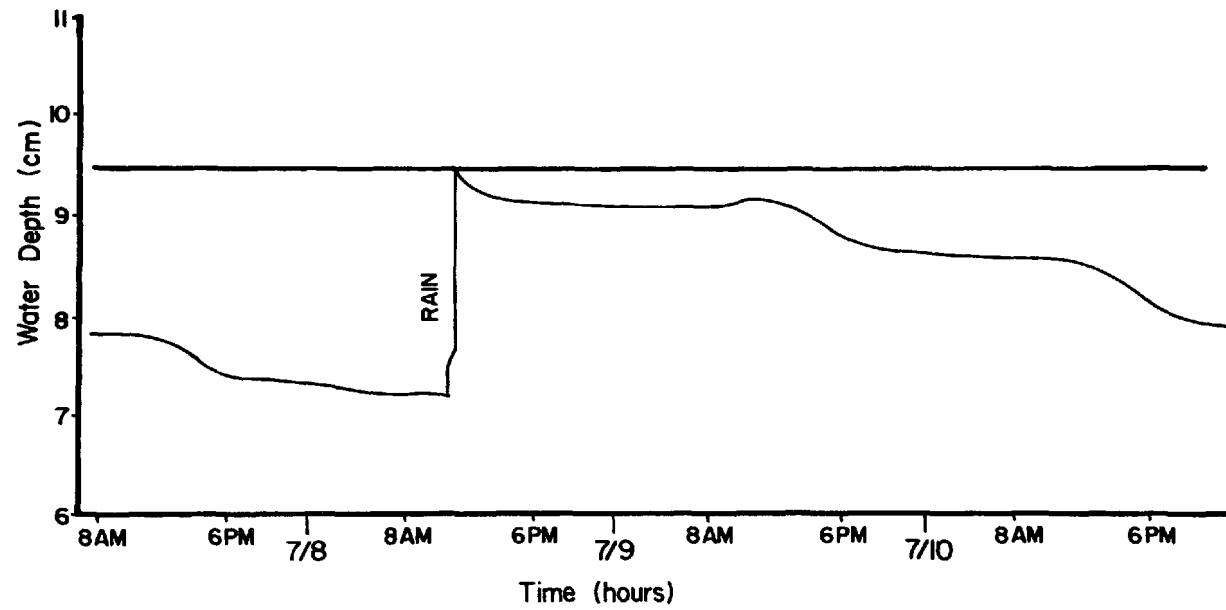


Figure 14. Details of the water depth in an intermittently irrigated plot. The line at 9.4 cm represents the depth of the bottom of the 10° outflow weir.

piration were very small. The major decrease in water depth occurred during the midday, and the slope again flattened during sunset. The 2.2 cm rain which occurred as a brief shower, followed by a downpour, can be clearly seen. The rapid drop just after the rain represents the water running out through the 10⁰ weir.

A continuous record of two plots, one each intermittently irrigated and one each continuously irrigated for 1974 and 1975, are shown in Figures 15, 16, 17, and 18. The detail shown in Figure 14 cannot be seen on these figures. The general seasonal patterns, however, are evident. During 1974, some out-flow occurred early in the season for the intermittently irrigated plot as a result of excessive rains or over-irrigating. By July 21, the level of water was very low, and a large irrigation overflowing the weir was applied July 22. During the rest of the season, the rain was great enough to keep water flowing out at all times until the paddy was drained August 22.

The water level of the continuous flowing plot from 1974 was above the bottom of the weir and flowing out throughout the flooded period except between June 16 and 21. Irrigation water was siphoned into the plot June 21 to bring the level above the bottom of the weir.

The difference on the diurnal pattern can be seen by comparing these plots. For the intermittently irrigated plot when no water is flowing out the weir, the level drops during the day due to evapotranspiration and remained nearly constant or dropped slightly during the night. For the continuously irrigated plot, the water level drops slightly during the day, but increases again during the night since the water continues to run into the plots. A prolonged period of these oscillations uninterrupted by rainfall can be seen in Figure 17 starting July 19.

The water depths were read at three hour intervals and utilized to calculate the water balance.

Infiltration

Water loss was calculated from the water depth data in the impounded plots and the lysimeter box data during 1974 and 1975. Periods typically three to four days long during times when no water was flowing out of the plots, between rainfalls, and irrigations were selected. The difference in water loss between the plots and the lysimeter boxes during this time period may be attributed to either infiltration or possibly, but less likely, to evaporative losses from the earthen levees. Efforts were made to keep the exposed levee surface surrounding the plots small, but it is estimated that the soil surface was equivalent to about 1/6 of the water covered surface of the plot. This could contribute significantly to water loss if the soil surface was wetted from the flood water for extended periods of time.

The average water loss in excess of evaporation is shown in Figure 19 for 1974 and 1975. To further isolate the nature of the loss, the levees of one plot were covered with plastic during the 1975 season only. Water loss from this plot is shown separately in the figure. Only small differences are noted between the water loss from the plastic-covered plot and the average of

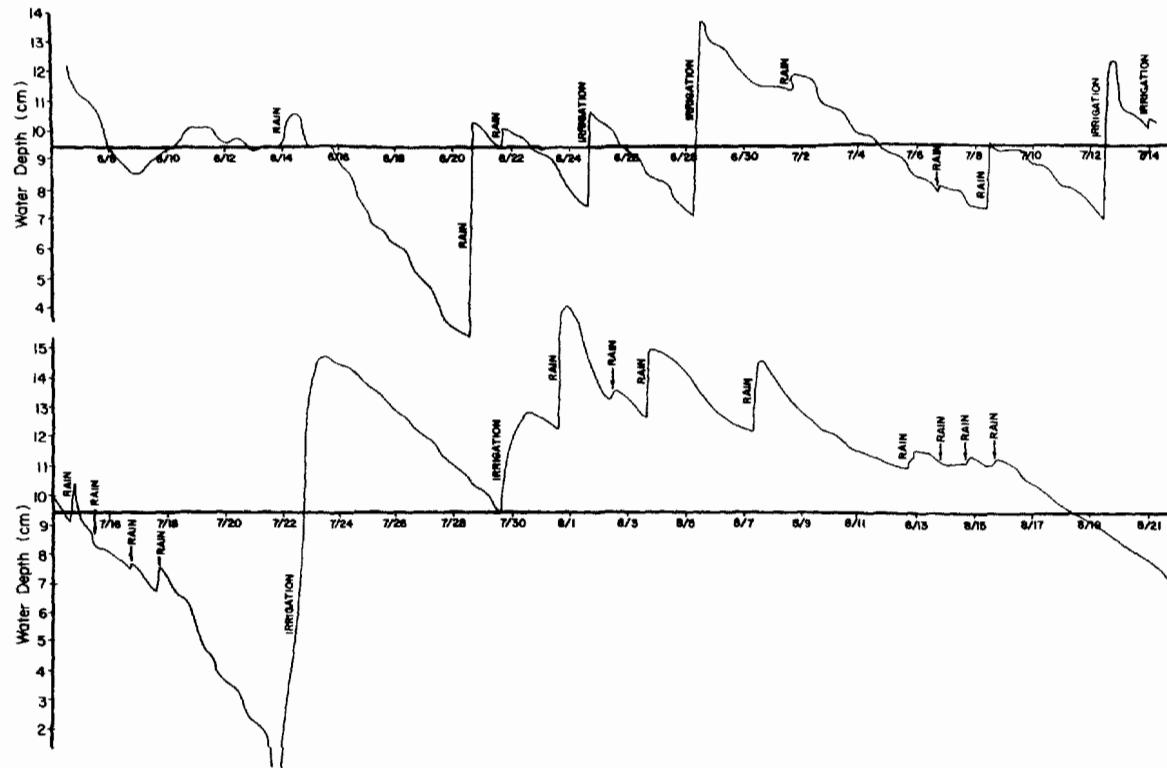


Figure 15. Seasonal patterns of water depth in intermittently irrigated plots during 1974.
The date line represents the bottom of the 10° outflow weir.

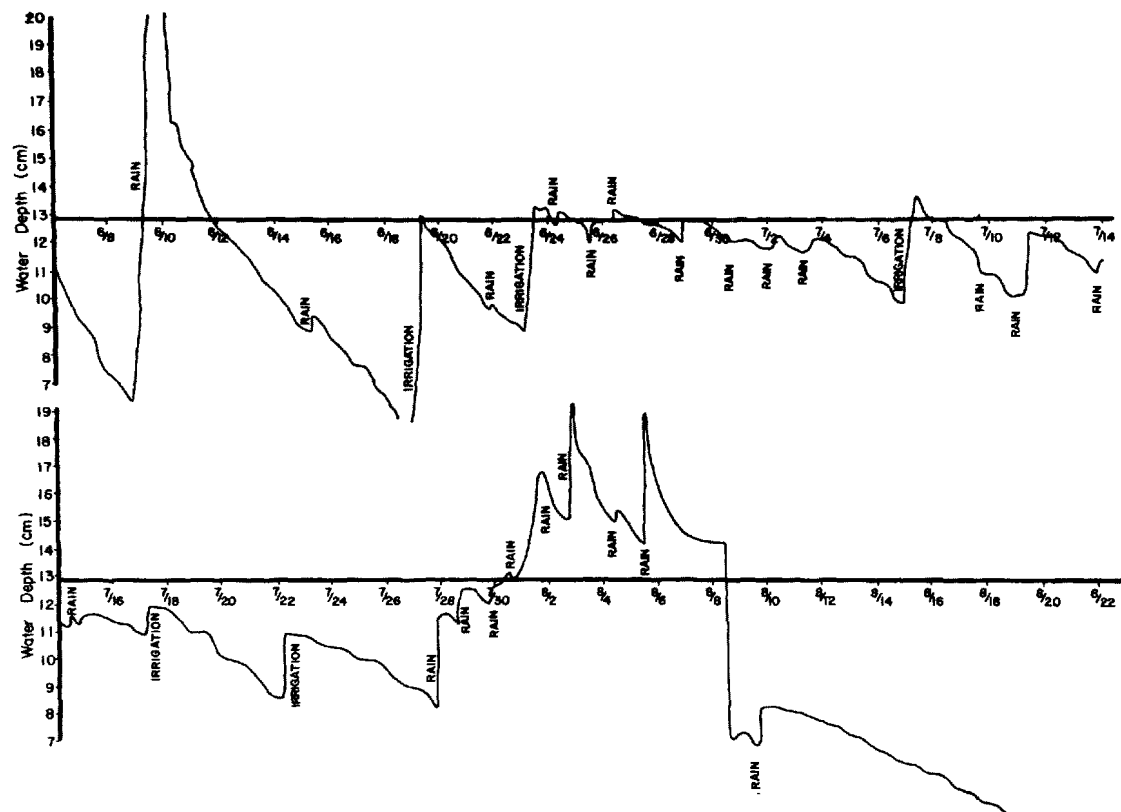


Figure 16. Seasonal patterns of water depth in intermittently irrigated plots during 1975. The date line represents the bottom of the 10° outflow weir.

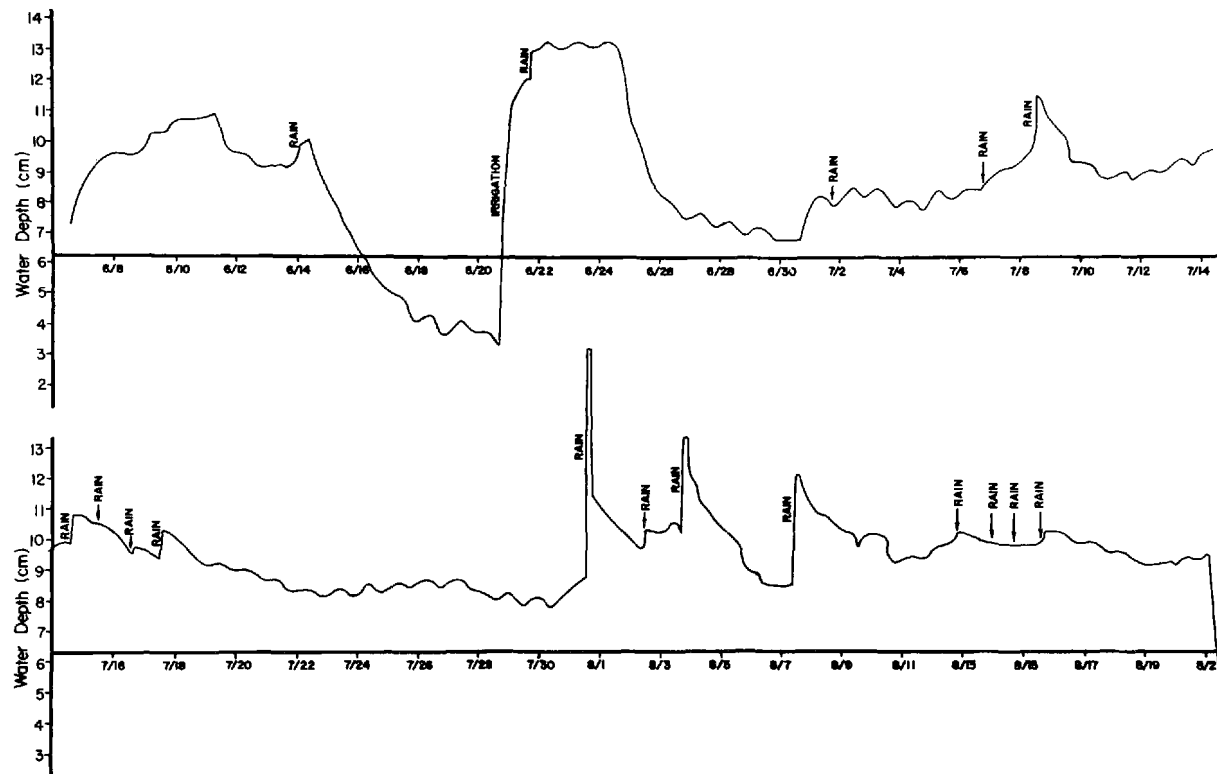


Figure 17. Seasonal patterns of water depth in continuously irrigated plots during 1974. The date line represents the bottom of the 10° outflow weir.

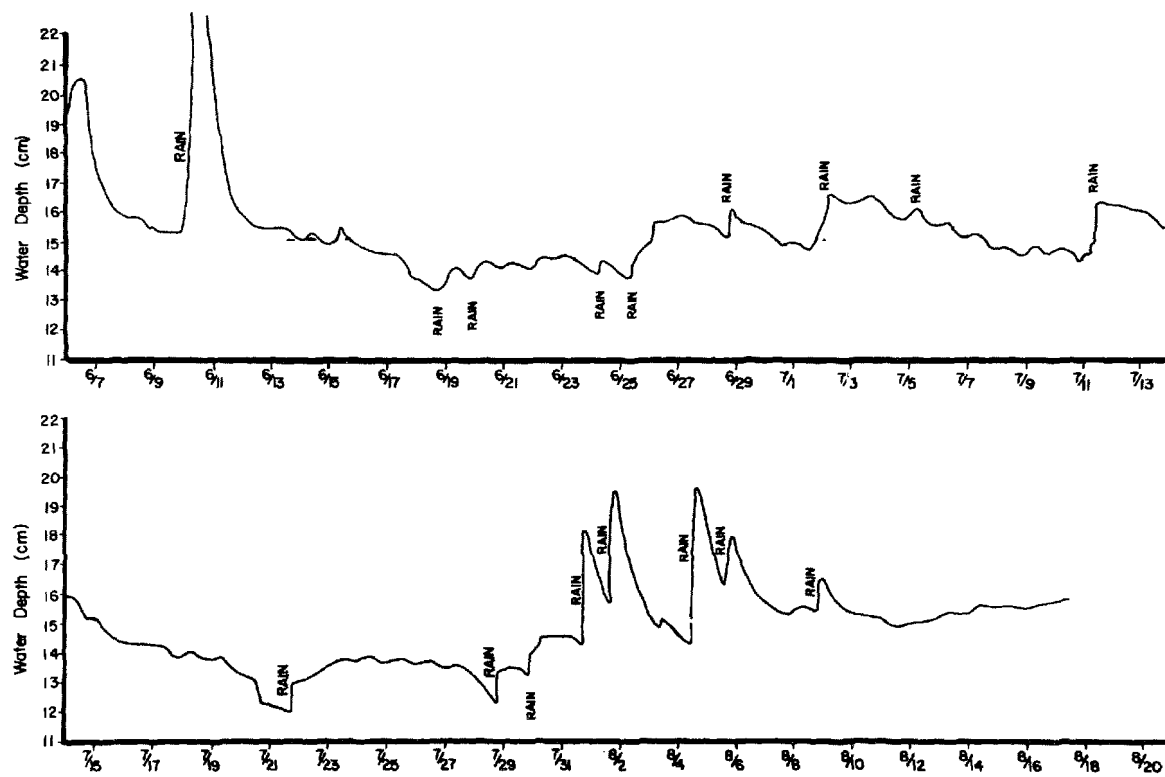


Figure 18. Seasonal patterns of water depth in continuously irrigated plots during 1975. The date line represents the bottom of the 10° outflow weir.

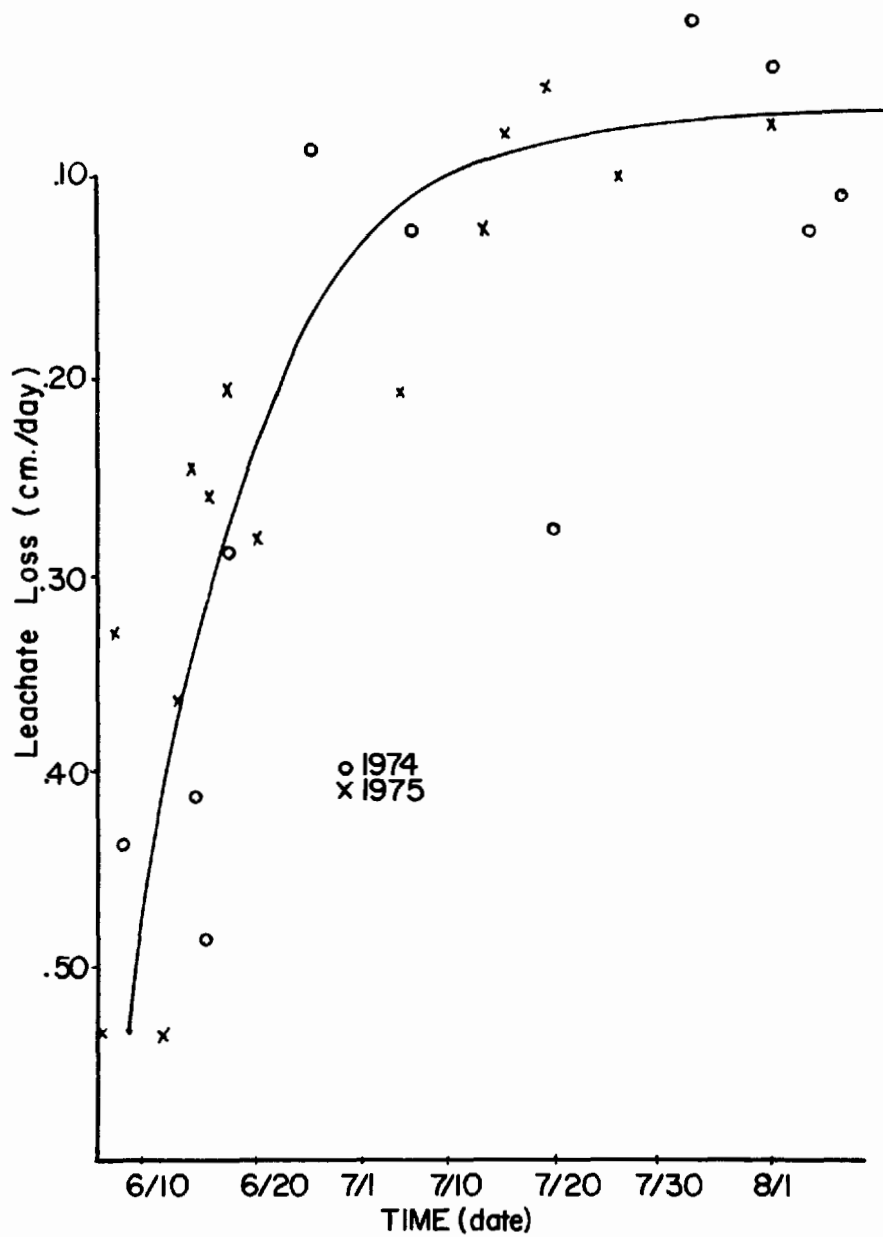


Figure 19. The loss of water due to leaching for all plots during the 1974 and 1975 growing seasons.

those not covered. Field observations indicated that the soil surface did dry out between rains. The dry surface layer thus apparently prevented significant evaporative losses. The losses thus determined must then be attributed to infiltration. During 1974, the infiltration rate decreased from 0.29 cm per day at the beginning of the season to 0.1 or less by the end of the season. While the infiltration during 1975 was as great as 0.20 cm per day soon after permanent flood, only on two occasions during the middle of the season did it drop below 0.10 cm per day.

Piezometer Data--

The depth of the water measured by the piezometers in 1975 is shown in Figure 20. The flood water wet the top 10 cm within a few hours and reached 20 cm within one day. Three more days were required to reach the 30 cm depth, and each increment past that required considerably more time. By the end of the season, the saturated zone reached only 70 cm. Piezometers to a depth of 150 cm showed no water table through the entire period. These data indicate that water movement into the profile was very slow and that throughout the period of flooding the wetting front did not join with the water table below. Since the most rapid transpiration is expected to be under saturated conditions, it is suggested that the leaching of soluble salts or other contaminants in the water from the flooded zone of the soil was negligible during the period of the study.

Bulk Density--

Since the clay soil studied is well structured, it was of interest to measure the bulk density as a function of depth. The data are also useful for converting measurements including water content and root density from the unit weight to the unit volume basis.

The profiles of the bulk density of natural wet peds taken at different depths are shown in Figure 21. The greatest bulk density is found in the surface sample. This is probably a result of the puddling and compacting which results from the heavy equipment used during soil preparation, planting and fertilizing. The bulk density decreases to a minimum value at 25 cm and increases again slightly with depth below that level. The values below the surface are typical of what would be expected for a vegetated shrinking-swelling clay soil.

The greater bulk density at the surface did not appear to restrict infiltration immediately since the piezometer data and the calculated infiltration rate indicated that water moved most rapidly through the surface and slowed down as it reached lower layers. It may have restricted the infiltration later by blocking pores as it swelled.

Moisture Content--

On several occasions, large soil cores were taken from the field. These were portioned in depth increments and moisture content determined on a dry weight basis. This data was converted to the percent moisture on a volume basis shown in Figure 22. The wetting front had moved deeper than the 20 cm depth well before the sample was taken on July 10. Thus, both the July 10 and August 21 samples were from saturated soil. The range of values may be a result of soil variability in the vertical direction in the field. In both

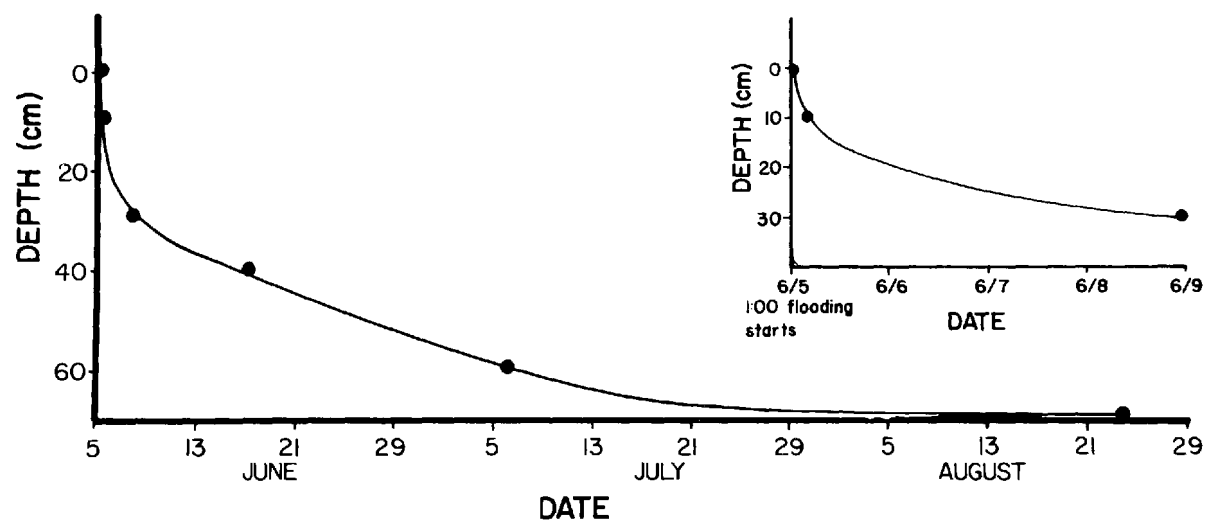


Figure 20. Depth of irrigation water in rice paddies during 1975 measured with piezometers.

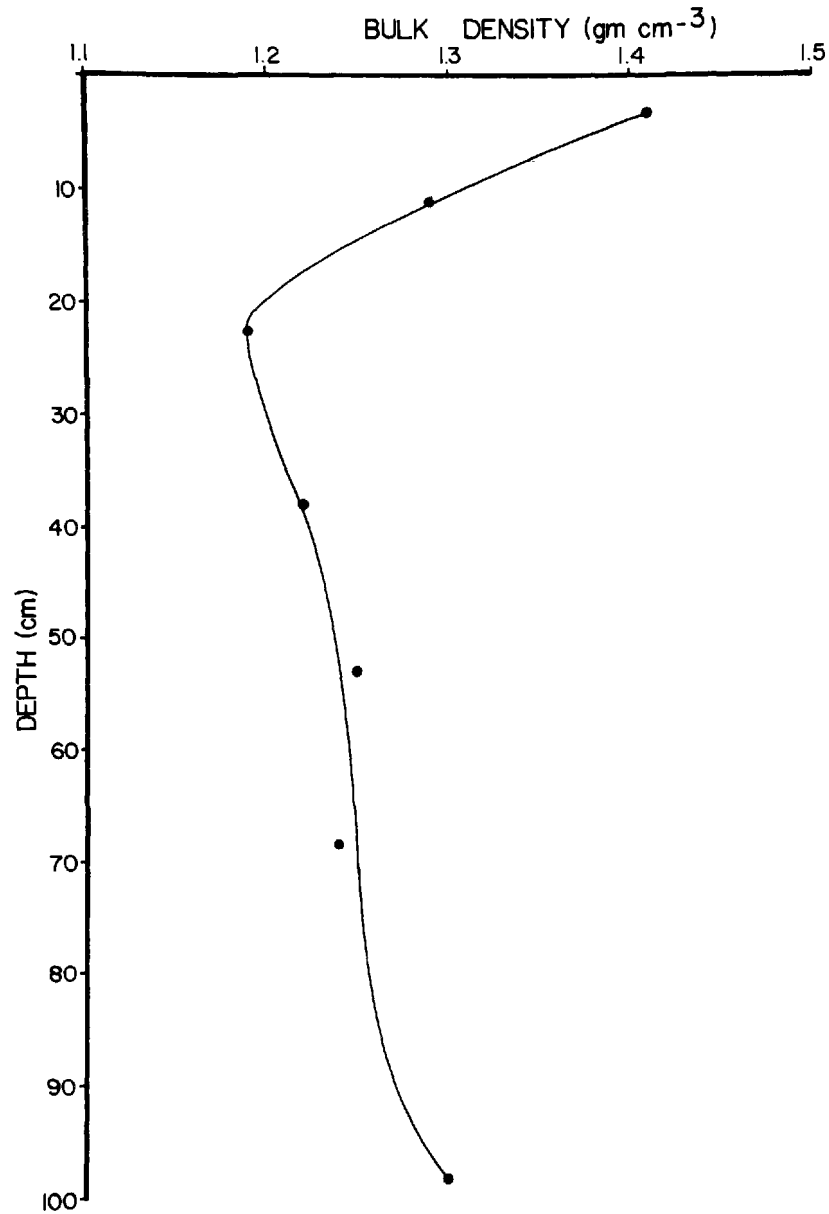


Figure 21. Bulk density profile in the flooded rice paddies.

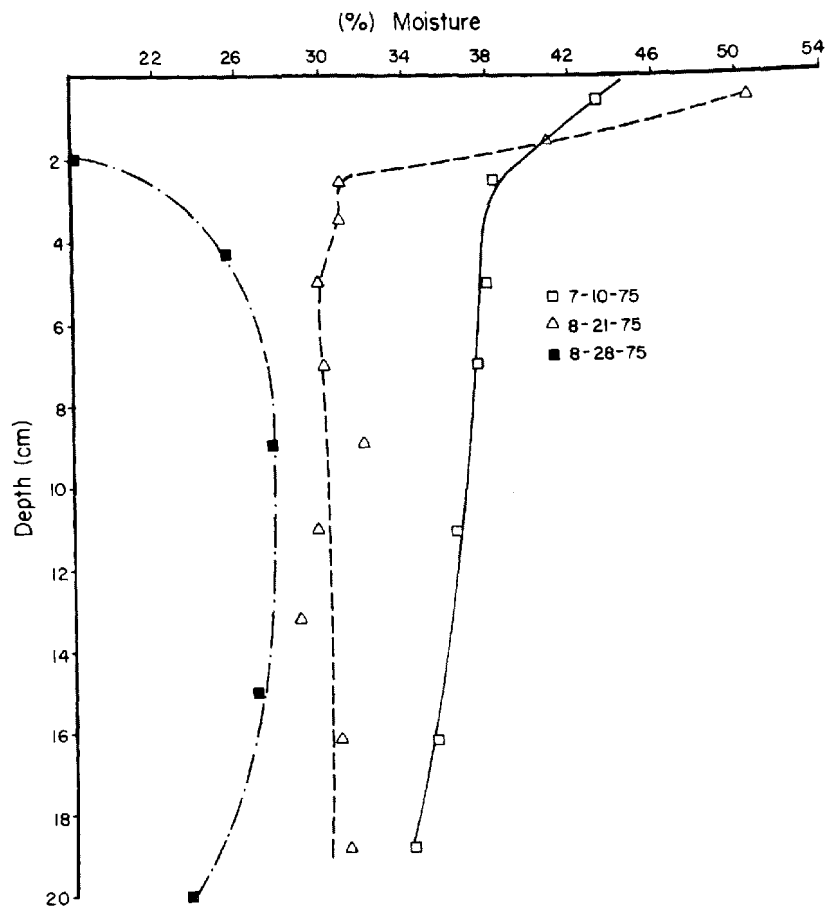


Figure 22. Moisture content by volume on several dates at various depths in the rice paddies.

cases, the moisture content at the surface was the greatest and decreased to a depth of 2 cm. They were essentially constant below this level. The moisture contents at the surface and the bulk density of 1.4 g cm^{-3} indicates that nearly all the pores were filled with water. While the soil below was at potentials of zero and above, indicating saturation, the moisture content indicated that a considerable fraction of the pores was filled with air.

The sample on August 28 was taken several days after the flood had been drained. The surface had dried, but changes in moisture content below 4 cm were small.

Root Distribution--

Water, nutrients and ions are removed from the soil profile to roots. To achieve a better understanding of the distribution of uptake and movement of water and ions in the soil profile, we must have data on the distribution of roots and the change in distribution with time. Replicated cores were, therefore, taken periodically throughout the 1975 season and dissected for root distribution. The roots were separated and dried; the length to weight ratios were developed for different layers; and the different sampling dates were used to convert the weight to the length basis. The results expressed as length of root per volume of soil are shown in Figure 23. Just before flooding on June 4, the root distribution was very linearly decreasing from 4 cm/cm^3 at the surface. The density decreased linearly to a depth of 5 cm. Roots had proliferated below this level by this date and extended down to 19 cm. Subsequent distribution of root density did not differ greatly from the data of June 28, with the exception that the root density near the surface increased to as great as 20 cm/cm^3 .

These results indicate that despite the abundance of water in the system, the roots continue to proliferate after the field is flooded. Much of the additional growth appears to take place during the first month after flooding. Although the roots are denser in a thin layer near the surface, the majority of these are found below the 2 cm depth representing a considerable sink for nutrients and perhaps water within the profile.

Meteorological Data

The detailed meteorological data are given in Appendix B. This data will be used to calculate an estimate of the evapotranspiration. The water and soil temperature data are also given in Appendix E. A plot of the minimum and maximum water and soil temperature data are given in Figures 24 and 25 for the 1974 season. The maximum temperatures were greatest during June and the first half of July while the weather was clearer. The amplitude of the diurnal water temperature cycle was typically 5°C while that of the soil temperatures was typically 3° . Both decreased with time as the maximum decreased. The water temperature averaged 30° for the season. This temperature should be in the optimum range for biological decomposition of most organic pesticides and is above the temperature at which channel catfish can survive bacteriological infestations.

Estimated Evapotranspiration

The loss of water from the paddy by evaporation will have the result

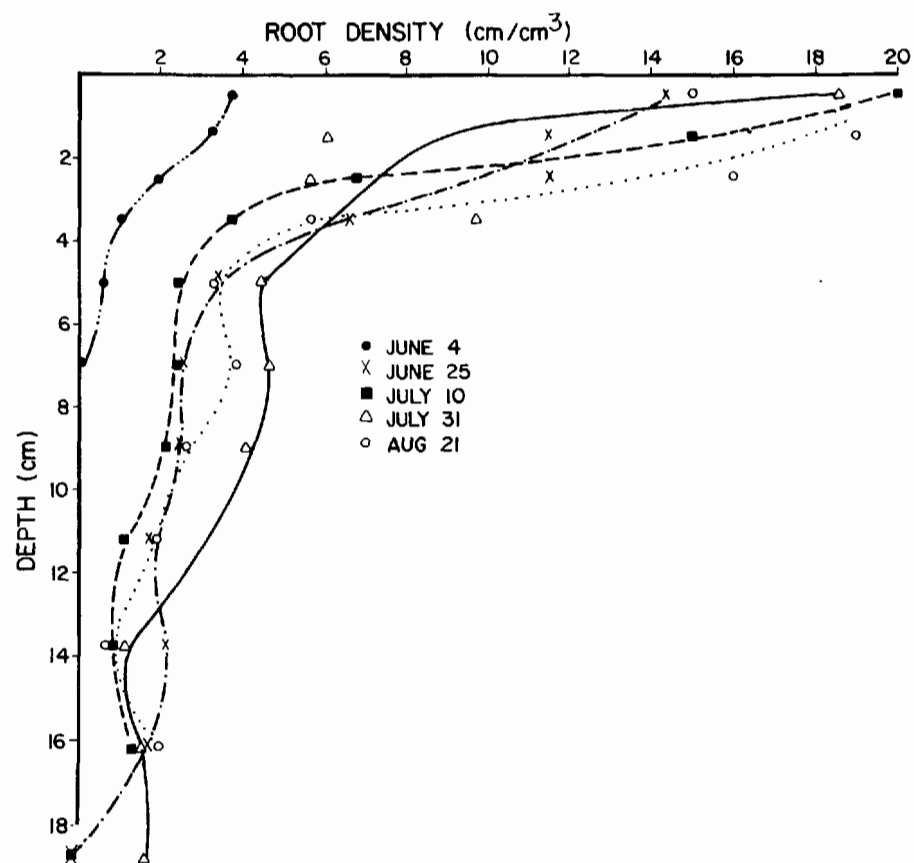


Figure 23. Root density, expressed as length of root per cm³ of soil, as a function of depth for five sampling dates during the growing season.

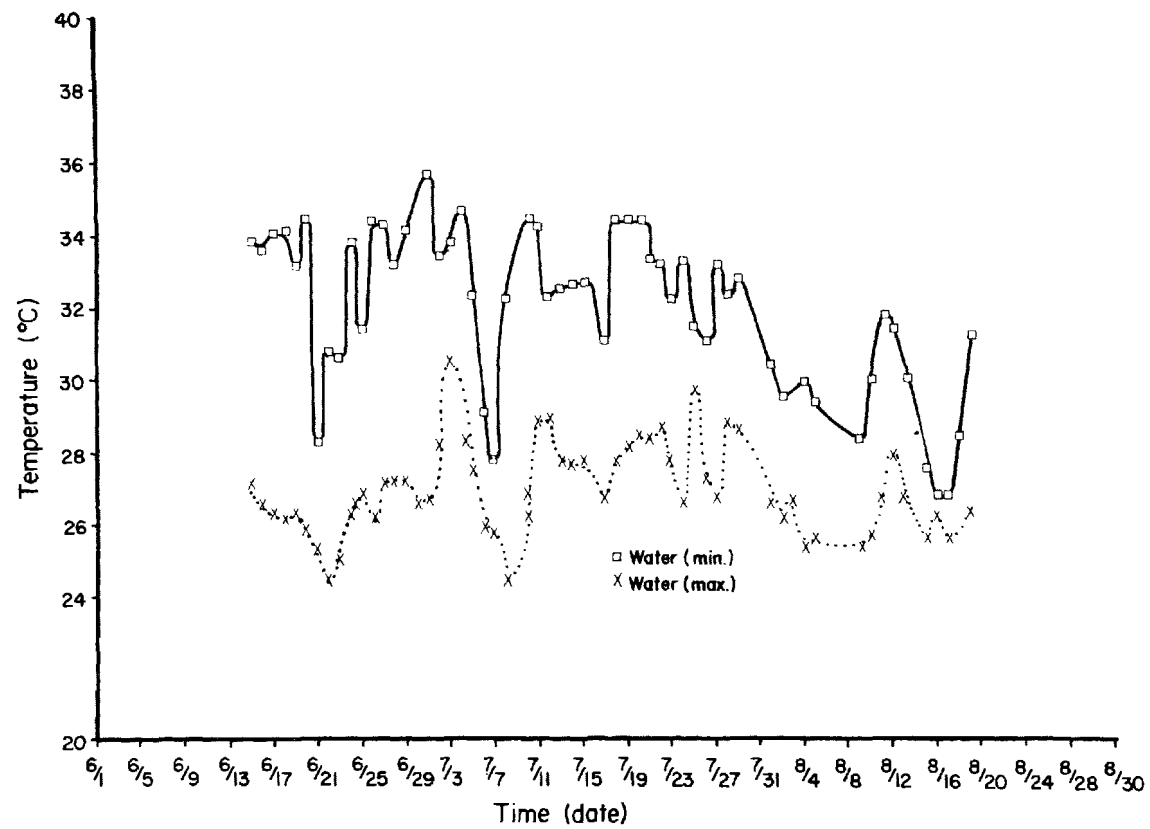


Figure 24. Minimum and maximum water temperatures during the 1974 season.

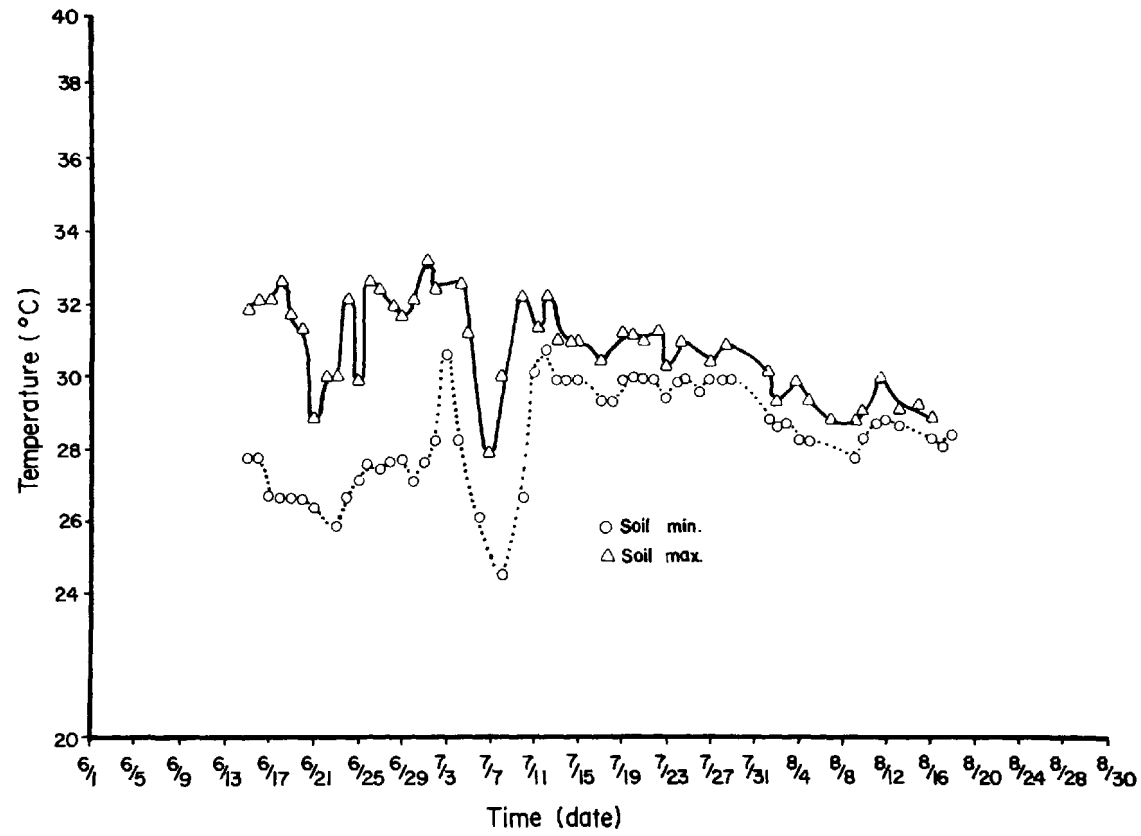


Figure 25. Minimum and maximum soil temperatures during the 1974 season.

of concentrating the salts in the water that remains. The amount of water lost by this means is thus important in determining the quality of the irrigation return. Since detailed information is not available on a regional basis, it is of interest to develop correlations between measured evapotranspiration, evapotranspiration calculated from meteorological data, and that characterized by pan evaporation.

Several approaches may be used to calculate the evapotranspiration from meteorological data. A combination equation, which takes into account wind speed, radiation temperature, vapor pressure and crop characteristics was developed by van Bavel (1966) as:

$$LE_o = \frac{-\Delta/\gamma H + 2 B_v d_a}{\Delta/\gamma + 1}$$

where L = the latent heat of vaporization in cal/g

E_o = the potential evaporation in cm day⁻¹

Δ = the slope of the saturation vapor pressure curve

γ = the psychrometric constant

H = the RN-S where RN is the net radiation and S is the heat stored in the water and the soils both in cal/cm²/min at standard pressure

d_a = the vapor pressure deficit in mbars

B_v is a wind dependent transfer coefficient given as:

$$B_v = \frac{pek^2}{\rho_a} (u_a / \{\ln(\frac{Z_a}{Z_o})\})^2$$

in g/cm²/min/mbar, where:

p = the ambient pressure in mbar

e = vapor pressure

k = Von Karman's constant (0.40)

ρ_a = air density in gm cm⁻³

u_a = the windspeed in cm/sec

Z_a = the elevation above the surface at which the measurements were taken in cm

Z_o = the roughness parameter in cm.

For the present study, RN was calculated from measured incident radiation

using modification of the equation of Uchijima (1969) to take into account the crop height. Net radiation is given as:

$$RN = (0.70 - .001753 DN) \cdot IR$$

where IR = incident radiation in $\text{cal cm}^{-2}\text{day}^{-1}$

DN = the number of days after flooding of the paddy

The DN factor takes into account the growth and development of the rice crop.

S was taken as the change in heat stored in the water layer as calculated from the difference between the minimum and maximum water temperatures. Changes in the heat stored in the soil were anticipated to be even smaller than those in the water and were, thus, not taken into account. The roughness length as a function of crop height developed by Monteith (1973) is given as:

$$Z_o = 0.13 h$$

where h is crop height in cm.

Measured evapotranspiration, evapotranspiration calculated as described above, and measured class A pan evaporation are given during the period of permanent flood in Tables 8 to 13 and for 1974 and 1975. The regression equations and values of r are given in Table 14 (Barr et al., 1976). All the regression equations had large positive intercepts and slopes which were much less than 1.0. The r values were not significant. It was suspected that the discrepancy between the times that the measured and meteorological and pan data were taken may have had some influence on the poor relationship. The measured data was the total water loss between midnight one day and midnight the next, while the weather data and the pan measurements were supposed to be made at 8:00 a.m. each day. While the minimum and maximum temperatures were arranged so that they were used to calculate the potential evapotranspiration on the appropriate days, it was not possible to adjust the wind record. On some occasions, the observer did not record the data until as late as 10:00 a.m., adding to the discrepancies. The four sets of data for each year were, therefore, summed over seven day periods to eliminate day-to-day fluctuations and the regressions were run again. The correlation improved some, but the regression equations still poorly predicted the measured evapotranspiration rates. These results are in contrast with what would be expected from a rice crop. One would suspect that the flooded rice would be closely approximated by calculated potential and pan evaporation. These results are also different from the report of Evans (1971) of an r value of 0.91 between pan evaporation and measured evapotranspiration for flooded rice.

The reason for the poor correlation between the measured and calculated values is not evident, and we may conclude that for our climate, daily losses cannot adequately be reflected by calculated evapotranspiration or measured pan evaporation.

When the water loss was summed over the entire period during which the rice was flooded, the results shown in Table 15 were in better agreement.

TABLE 8. MEASURED DAILY EVAPOTRANSPIRATION RATE, CALCULATED POTENTIAL EVAPORATION, CLASS A EVAPORATION, AND EVAPORATION FROM A 60 CM SUNKEN PAN

Date	Measured EVTS cm	June, 1974	Class A Pan	60 cm Pan
		Calculated E _o cm		
1	-	0.46	.22	.20
2	-	0.49	.27	.18
3	-	0.60	.27	.15
4	-	0.61	.29	.15
5	-	0.68	.32	.24
6	.18	0.36	.29	.18
7	.50	0.54	.23	.18
8	.66	0.44	.32	.19
9	.26	0.28	.27	.18
10	.47	0.67	.39	.26
11	.60	0.46	.27	.17
12	.52	0.59	.31	.17
13	.70	1.04	.35	.24
14	.57	0.68	.32	.09
15	.78	0.75	.34	.11
16	1.05	1.07	.30	.20
17	.95	0.77	.34	.21
18	.86	0.64	.31	.21
19	.86	0.70	.29	.20
20	.74	0.62	.32	.21
21	.45	0.55	.33	.21
22	.92	0.89	-	.23
23	.82	0.53	-	.31
24	1.01	0.49	.46	.41
25	1.00	0.30	.40	.33
26	.80	0.56	.36	.27
27	.86	0.62	.33	.24
28	.71	0.63	.54	.37
29	.66	0.63	.16	.12
30	.65	0.64	.24	.17
Total	17.52	18.29	8.77	6.38
Mean	.7008	0.61	0.29	0.21

TABLE 9. MEASURED DAILY EVAPOTRANSPIRATION RATE, CALCULATED POTENTIAL EVAPORATION, CLASS A EVAPORATION, AND EVAPORATION FROM A 60 CM SUNKEN PAN

Date	Measured EVTS cm	July, 1974	Class A Pan	60 cm Pan
		Calculated E_o cm		
1	.49	0.44	.18	.15
2	.74	0.69	.31	.19
3	.84	0.54	.35	.29
4	.78	0.59	.33	.19
5	.82	0.83	.40	.26
6	.61	0.71	.25	.19
7	.60	0.77	.22	.18
8	.25	0.77	.24	.15
9	.75	0.75	.29	.19
10	.69	0.84	.33	.21
11	.50	0.56	.21	.14
12	.70	0.61	.33	.27
13	.54	0.88	.34	.21
14	.57	0.32	.28	.22
15	.18	0.29	.11	.10
16	.33	0.49	.23	.14
17	.33	0.43	.21	.13
18	.70	0.61	.27	.19
19	.57	0.78	.28	.16
20	.67	0.53	.30	.28
21	.65	0.65	.31	.19
22	.81	0.54	.34	.22
23	.89	0.56	.32	.23
24	.68	0.48	.28	.21
25	.65	0.48	.29	.20
26	.76	0.23	.41	.33
27	.94	0.54	.25	.34
28	.62	0.38	.33	.26
29	.70	0.67	.31	.30
30	1.00	0.61	.40	.32
31	.20	0.49	overflow	overflow
Total	19.56	18.06	8.94	6.44
Mean	0.631	0.583	0.29	0.21

TABLE 10. MEASURED DAILY EVAPOTRANSPIRATION RATE, CALCULATED POTENTIAL EVAPORATION, CLASS A EVAPORATION, AND EVAPORATION FROM A 60 CM SUNKEN PAN

Date	Measured EVTS cm	August, 1974		
		Calculated E _o cm	Class A Pan	60 cm Pan
1	.53	0.61	.25	.25
2	.18	0.36	.12	.10
3	.30	0.42	overflow	.18
4	.62	0.41	.21	.14
5	.64	0.51	.29	.20
6	.27	0.31	.12	.09
7	.40	0.53	overflow	overflow
8	.67	0.52	.18	.18
9	.50	0.31	.31	.20
10	.83	0.34	.21	.16
11	.56	0.48	.28	.23
12	.48	0.41	.26	.17
13	.49	0.54	.29	.27
14	.47	0.56	.27	.21
15	.28	0.51	.20	.18
16	.52	0.58	.24	.18
17	.64	0.50	.26	.19
18	.63	0.52	.27	.18
19	.69	0.47	.29	.20
20	.59	0.47	.28	.18
21	.52	0.45	.23	.18
22	.41	0.69	.28	.20
23				
24				
25				
26				
27				
28				
29				
30				
31				
Total	11.22	10.5	4.56	3.67
Mean	.51	.477	.207	.167

TABLE 11. MEASURED DAILY EVAPOTRANSPIRATION RATE, CALCULATED POTENTIAL EVAPORATION, CLASS A EVAPORATION, AND EVAPORATION FROM A 60 CM SUNKEN PAN

Date	June, 1975			
	Measured EVTS cm	Calculated E_o cm	Class A Pan	60 cm Pan
1	-	0.43	.34	.16
2	-	0.57	.27	.17
3	-	0.60	.33	.18
4	-	0.69	.28	.17
5	.14	0.67	.34	.20
6	.60	0.82	.26	.14
7	.55	0.42	.16	.15
8	.48	0.51	overflow	overflow
9	-	0.13	overflow	overflow
10	4.45	0.31	.06	.08
11	.27	0.26	.24	.19
12	.56	0.55	.30	.20
13	.72	0.58	.38	.26
14	.87	0.93	.25	.18
15	.75	0.62	.34	.17
16	.85	0.80	.37	.20
17	.95	1.08	.31	.21
18	1.01	0.81	.23	.17
19	.93	0.72	.13	.19
20	.80	0.78	.26	.19
21	.77	0.52	.27	.14
22	.54	0.58	.28	.20
23	.48	0.85	.20	.12
24	.50	0.50	.11	.12
25	.11	0.21	.10	.08
26	.23	0.31	.21	.11
27	.36	.38	.20	.22
28	.58	0.49	.15	.12
29	.26	0.33	.21	.12
30	.36	0.42	.22	.15
Total	18.12	16.86	6.93	4.65
Mean	.724	.562	.231	.155

TABLE 12. MEASURED DAILY EVAPOTRANSPIRATION RATE, CALCULATED POTENTIAL EVAPORATION, CLASS A EVAPORATION, AND EVAPORATION FROM A 60 CM SUNKEN PAN

Date	Measured EVTS cm	July, 1975		
		Calculated E _o cm	Class A Pan	60 cm Pan
1	.47	0.59	.23	.02
2	.52	0.58	.07	.19
3	.14	0.29	.24	.14
4	.56	0.42	.30	.17
5	.81	0.74	.32	.25
6	.79	0.80	.34	.21
7	.75	0.99	.26	.19
8	.77	0.84	.26	.19
9	.88	0.73	.34	.21
10	.81	0.81	.19	.15
11	.32	0.43	.25	.13
12	.50	0.59	.30	.17
13	.59	0.82	.16	.14
14	.21	0.40	.13	.08
15	.13	0.35	.18	.12
16	.40	0.49	.18	.10
17	.36	0.47	.28	.20
18	.60	0.58	.36	.18
19	.73	0.80	.27	.17
20	.56	0.62	.28	.17
21	.71	0.73	.13	.09
22	.30	0.30	.14	.10
23	.15	0.40	.11	.11
24	.33	0.45	.24	.11
25	.47	0.52	.22	.14
26	.50	0.55	.33	.16
27	.68	0.76	.29	.18
28	.98	0.70	.28	.21
29	.46	0.69	.16	.15
30	.39	0.50	overflow	overflow
31	.84	0.37	overflow	overflow
Total	16.81	18.31	7.06	4.58
Mean	.542	.591	.235	.153

TABLE 13. MEASURED DAILY EVAPOTRANSPIRATION RATE, CALCULATED POTENTIAL
EVAPORATION, CLASS A EVAPORATION, AND EVAPORATION FROM A 60
CM SUNKEN PAN

Date	Measured EVTS cm	August, 1975		
		Calculated E _o cm	Class A Pan	60 cm Pan
1	-	0.63	.09	.14
2	1.04	0.50	.37	.13
3	.34	0.47	overflow	overflow
4	-	0.25	-	.12
5	1.27	0.41	.06	.12
6	.67	0.38	.27	.21
7	.85	0.57	.42	.21
8	.62	0.53	.36	.18
9	.34	0.44	.15	.10
10	.37	0.32	.24	.14
11	.52	0.48	.21	.13
12	.37	0.37	.25	.13
13	.48	0.49	.25	.16
14	.64	0.55	.28	.20
15	.66	0.58	.18	.09
16	.30	0.38	.21	.17
17	.51	0.44	-	.17
18	-	0.51	-	.15
19	-	0.33	-	.14
20	-	0.28	-	.11
21	-	0.38	-	.18
22	-	0.20	-	.21
23	-	0.30	-	overflow
24	-	0.51	-	.10
25	-	0.42	-	.12
26	-	0.30	-	.15
27	-	0.13	-	.16
28	-	0.20	-	.14
29	-	0.36	-	.08
30	-	0.36	-	-
31	-	0.36	-	-
Total	8.98	7.79	3.34	2.23
Mean	.528	.458	.196	.131

TABLE 14. REGRESSION EQUATIONS AND CORRELATION COEFFICIENTS
BETWEEN MEASURED EVAPOTRANSPIRATION (E_M), CALCULATED
POTENTIAL EVAPORATION (P_0), EVAPORATION FROM A 61CM
DIAMETER PAN (P_{61}) AND EVAPORATION FROM A 122 CM
PAN, CLASS A (P_{122})

1974		
$E_M = 0.341 + 0.495 \cdot P_0$		$r = 0.38^*$
$E_M = 0.626 + 0.171 \cdot P_{61}$		$r = 0.58^*$
$E_M = 0.739 + 0.240 \cdot P_{122}$		$r = 0.58^*$
1975		
$E_M = 0.119 + 0.784 \cdot P_0$		$r = 0.55^*$
$E_M = 0.340 + 0.371 \cdot P_{61}$		$r = 0.30^*$
$E_M = 0.201 + 0.911 \cdot P_{122}$		$r = 0.41^*$

*Significant at the 0.05 level.

During both years, the total calculated potential evapotranspiration closely approximated the measured evapotranspiration. The 61 cm second pan gave the second best approximation, being slightly high both years. The class A pan deviated from the first for the measured total. During the 1974 season, the class A total was 15% low, while during the 1975 season the class A pan total was 51% low.

TABLE 15. TOTAL CALCULATED, PAN, AND MEASURED EVAPOTRANSPIRATION
DURING THE PERIOD OF PERMANENT FLOOD GIVEN IN CM

	1974	1975
Calculated Potential Evapotranspiration	43.2	39.8
61 cm pan	55.5	42.0
122 cm pan	40.5	28.9
Measured Evapotranspiration	47.9	40.2

Water Balance

Details of the daily water balance averaged over all replications of the irrigation treatments during 1974 and 1975 are given in Appendix F, Tables F1, F2, F3, and F4. The cumulative inputs and outputs for the time between planting and harvesting are shown in Figures 26, 27, 28, and 29. The amounts of runoff early in the season were calculated from data on the amount of water required to wet the soil during the flooding or during and immediately after the rainfall which were large enough to cause runoff. Since no measurements of evapotranspiration were available before permanent flood, calculated potential evapotranspiration was utilized to approximate the total loss between planting and permanent flood.

During both years, the cumulative evapotranspiration increased nearly linearly throughout the season. During 1974, the rate was 0.55 cm per day, and during 1975 the rate was 0.6 cm per day. The rainfall during 1974 was lower than during 1975. During 1974 the rainfall alone, had it been properly spread over the season, would not have supplied the evapotranspirational needs of the crop. The 1975 rainfall should have more than satisfied the evapotranspirational losses provided it could have been retained on the field. Most of the water from the two intense storms early in the season were lost to runoff. The rain on May 28, 29, and 30 was nearly all lost since the permanent flood had not yet been initiated, and the levees were opened. Nearly all of the 20 cm rain of July 9 was also lost since the water levels in the paddies were high before the rain and most of it washed over the levees.

For the impounded flow irrigation systems during both years, the water applied approximated the evapotranspirational losses. Thus, an amount nearly equivalent to the rainfall was lost to runoff from the plots.

After the initial large runoff at the beginning of the 1975 season, little water was lost as runoff from the plots until late in the season. Even had the levees been large enough to retain the rainfall of July 9, most of the water would have had to be released since the depth would have the height of the young plants. As a result of several excess irrigations throughout 1974 on the impounded plots, runoff losses accumulated slowly throughout the season.

The continuous flow plots' water balances during both years are characterized by water applications which far exceeded the evapotranspirational losses throughout the season. During 1974 the cumulative irrigation plus rainfall exceeded the evapotranspiration rate by a factor of 2.5 or more throughout the season. This resulted in large runoff losses throughout both seasons.

These plots were managed as best as possible to approximate the two water management systems presently in use. It can readily be seen that both systems result in excessive irrigation return flow. Continuous irrigation is obviously a wasteful practice and increases the probability that chemicals in the water will be lost in irrigation return flow. The impounded plot management could have been improved by using smaller irrigations so that rainfall could have been trapped and utilized rather than being lost. Data, to be dis-

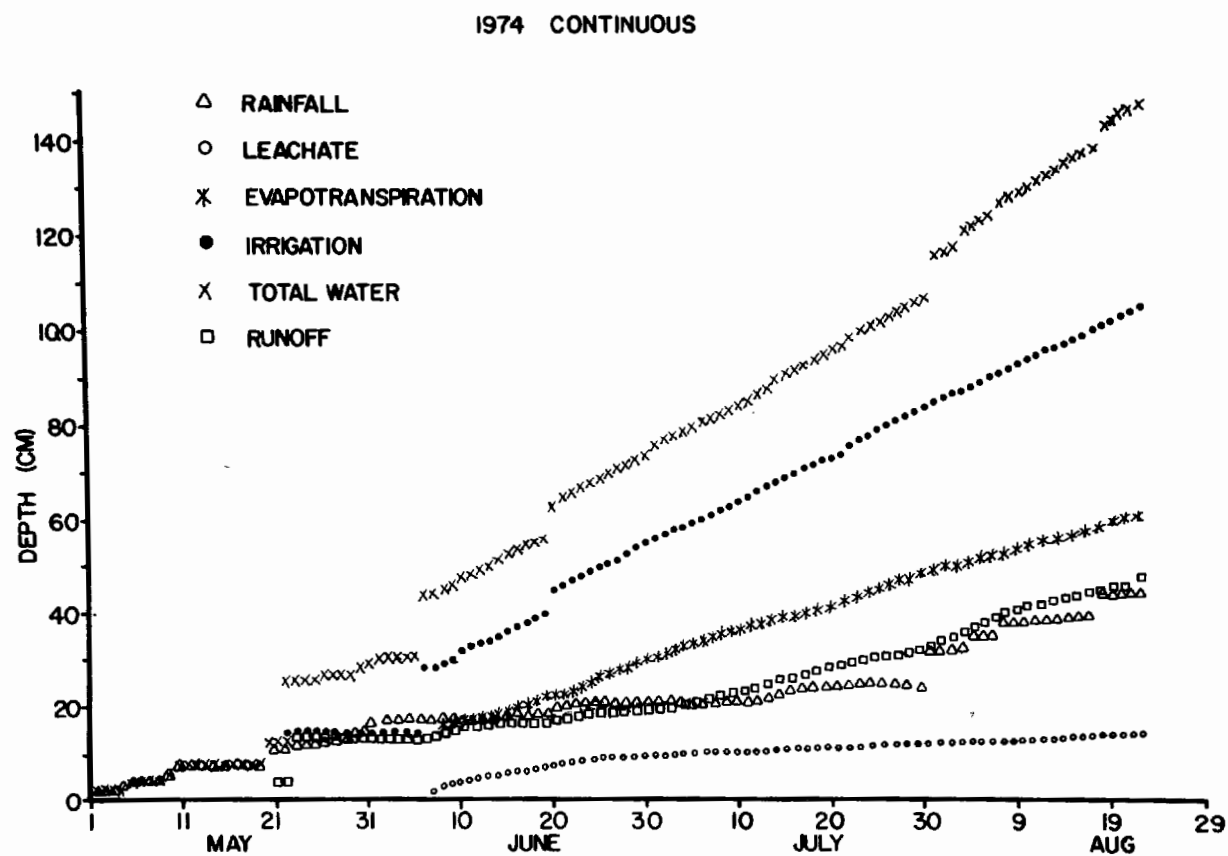


Figure 26. The water balance for the continuous irrigated plots during 1974.

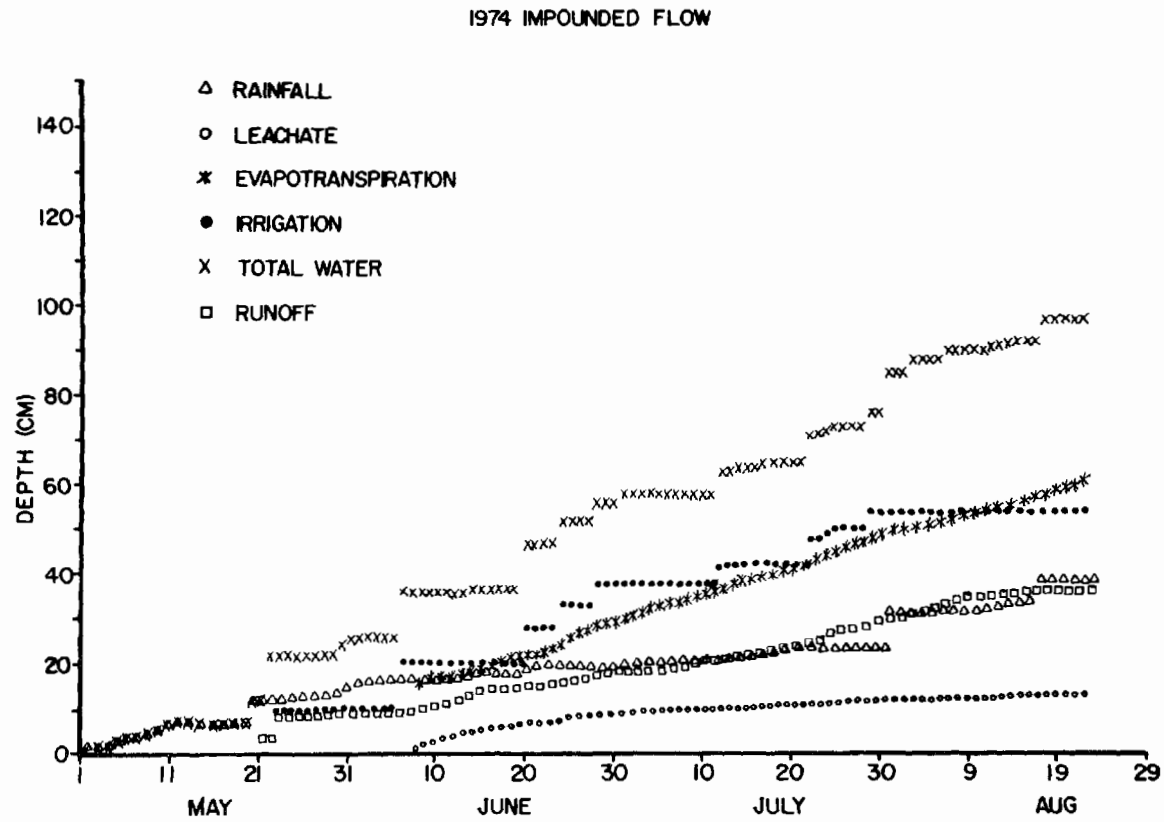


Figure 27. The water balance for the impounded irrigated plots during 1974.

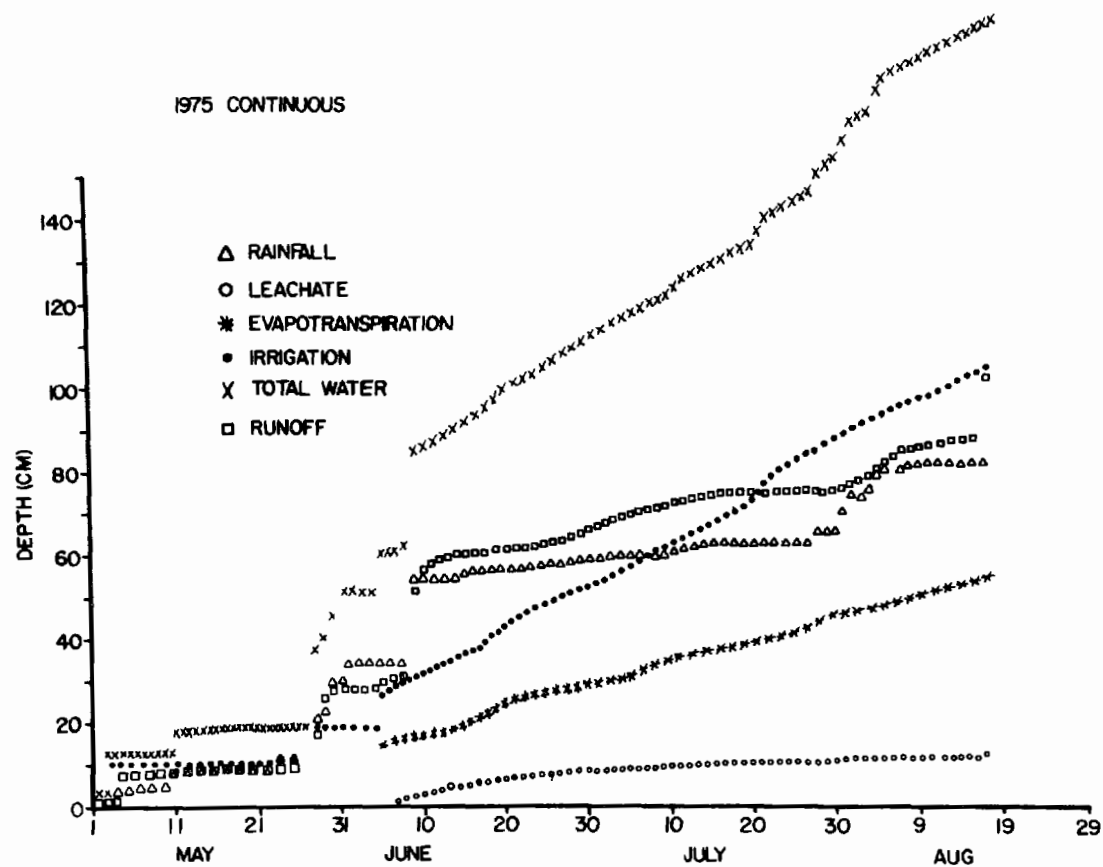


Figure 28. The water balance for the continuous irrigated plots during 1975.

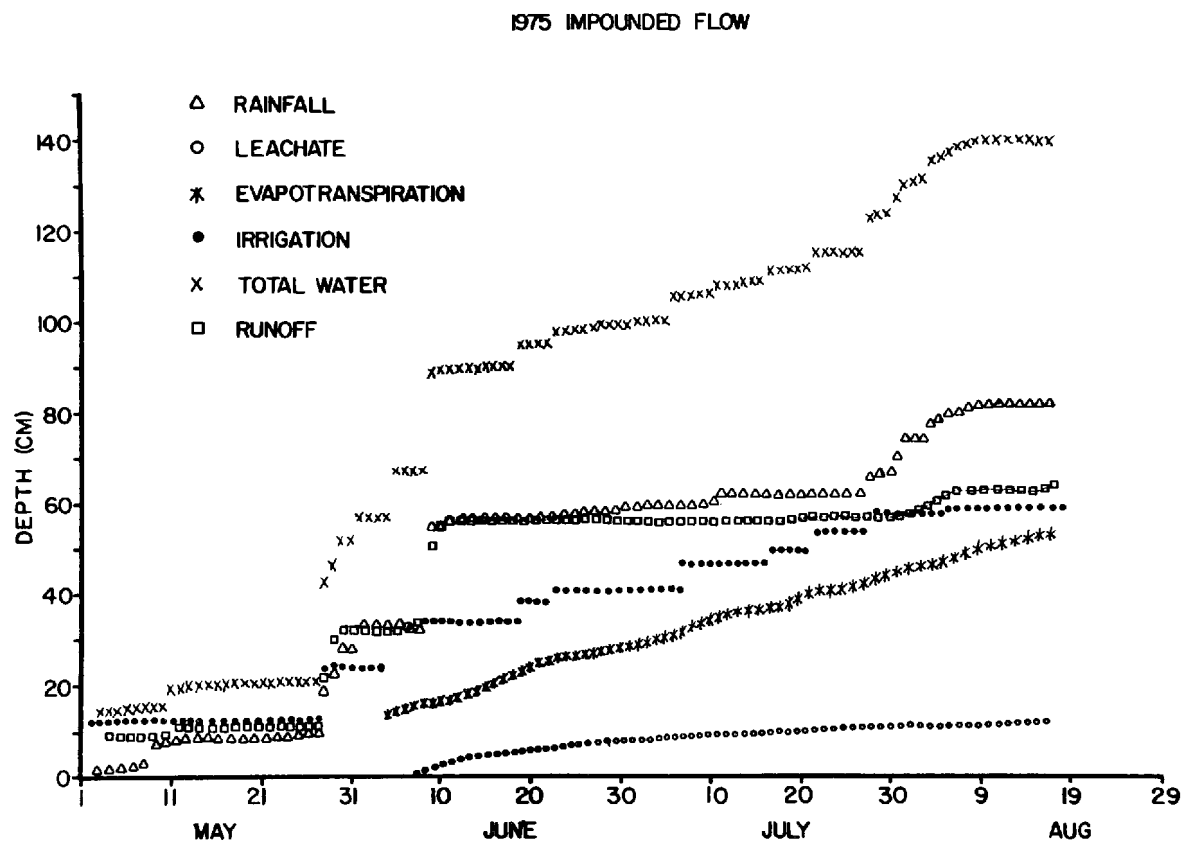


Figure 29. The water balance for the impounded irrigated plots during 1975.

cussed later, show that withholding water at the end of the season could have reduced the irrigation needs and the irrigation return flow without lowering the yield. While deep floods may be necessary to some fields during the early part of the season to kill weeds, they may not be necessary in the fields that do not have excessive weeds. In these cases, only enough water need be applied to completely wet the surface of the field. While it is impossible to schedule pre-permanent flood herbicide applications the day before a heavy rainfall, some of the pre-permanent flood rain could be used for irrigation if the levees had been kept closed during this period.

The seasonal water balance for the entire growing season is given in Table 16, while the balance during the flooded period is given in Table 17. As mentioned above, a few of the values used to calculate the balance before the permanent flood had to be estimated, thus more confidence can be placed in the budget during the permanent flood. The inclusion of the pre-permanent flood period does not change the distribution of the energy balance greatly and thus, the balance from the entire season will be considered in detail. Total irrigation exceeded rainfall in all plots during both years. The gross excesses in application to the continuous plots are evident with over a meter of irrigation water being used to supply crop needs of .59 and .53 meters. Leachate varied from 6.5 to 12.8 % of the total water applied. The measured losses accounted for 80.9 to 111% of the applied water throughout the entire season. Storage changes in the profile were neglected and may have contributed to some of the discrepancies, but considering the factors involved, the agreement between gains and losses is reasonable. The water balance data was used to calculate the salt balance which will be presented in a later section.

SALTS AND NUTRIENTS

Introduction

It has long been recognized that an occasional purge of salts from the plant root zone is required in some soils to control salinity (U.S. Salinity Laboratory, 1954). Naturally, water of relatively high quality is needed which may result in the degradation of the irrigation return flow, either by increasing the concentration or by altering the composition of dissolved and suspended constituents.

Although the load of naturally occurring salts in irrigation return flow may contribute to degradation of ground and surface water quality, more serious problems can occur from fertilizer residues in drain waters. Nitrogen and phosphorus stimulate aquatic plant growth in the conveyance and water storage systems resulting in eutrophication. The full impact of irrigation return flow on quality of water resources is not easily assessed because of the difficulty of obtaining meaningful data relating quality of return flows with past and present water resource quality in irrigated areas. Federal legislation to establish a national policy for the prevention, control, and abatement of water and pollution through enactment of the Federal Water Pollution Control Act (Law, 1971) illustrates the concern for conserving and preserving our water resources.

TABLE 16. WATER BALANCE FROM PLANTING TO HARVESTING DURING 1974
AND 1975 FOR BOTH IRRIGATION TREATMENTS GIVEN IN CM

	<u>Intermittent Irrigation</u>		<u>Continuous Irrigation</u>	
	1974	1975	1974	1975
Gains				
Rainfall	43.4	81.7	43.4	81.7
Irrigation	52.9	58.9	103.0	104.1
Total	96.3	140.2	146.4	185.8
Losses				
Runoff	35.0	63.7	46.4	101.5
% of total app.	36.3	45.5	31.7	54.6
Leachate	12.3	12.0	12.3	12.0
% of total app.	12.8	8.6	8.4	6.5
EVTS	59.6	53.8	59.8	53.8
% of total app.	61.9	38.2	40.8	28.9
Total	106.8	129.5	118.5	167.3
% of total app.	111.0	92.2	80.9	90.0

TABLE 17. WATER BALANCE DURING THE PERIOD OF PERMANENT FLOOD FOR
1974 AND 1975 FOR BOTH IRRIGATION TREATMENTS GIVEN IN CM

	<u>Intermittent Irrigation</u>		<u>Continuous Irrigation</u>	
	1974	1975	1974	1975
Gains				
Rainfall	27.6	48.4	27.6	48.4
Irrigation	43.6	24.7	90.0	77.9
Total	71.2	73.1	117.6	126.3
Losses				
Runoff	26.2	31.2	34.3	73.7
% of total app.	36.8	42.6	29.2	58.3
Leachate	12.4	12.0	12.4	12.0
% of total app.	17.3	16.4	10.5	9.5
EVTS	45.6	39.6	45.8	39.6
% of total app.	64.0	54.0	38.9	31.4
Total	84.0	82.9	92.5	125.3
% of total app.	118.1	113.1	78.6	99.2

The leaching and removal of excess salts from the soil in irrigated areas by drainage and surface water frequently cause an undesirable increase in salinity of the irrigation return flow (Flaigg, 1953; Wilcox, 1962; Eldridge, 1963; Sylvester and Seabloom, 1963; Law et al., 1970; Nightingale and Bianchi, 1974).

As McGauhey (1968) has summarized from several sources of data, most of the studies dealing with the effect of irrigation return flow on salinity of the receiving stream come from the areas of low rainfall in the western United States and indicate that salinity of the receiving stream increases from 5 to 10.8 times due to irrigation. Even higher increases (20-fold) in salinity as a result of irrigation return flow into the Sevier River in central Utah were reported by Thorne and Peterson (1967).

Williams (1972) has measured changes in salinity of soil solution of two flooded rice soils in Australia to characterize the physicochemical properties of soil solution in flooded rice fields. However, this data was not conclusive enough to allow an evaluation of the effect of rice culture on the salinity of the irrigation return flow.

Ponnamperuma's (1965) study of specific conductance revealed that the ionic strength of soil solution increased following submergence until maximum reduction is obtained after which conductance subsides. He noted that Ca^{++} and Mg^{++} in alkaline soils and Fe^{++} in acid soils make appreciable contributions to the specific conductance of reduced soils. He suggested that these ions are present as bicarbonates or soluble hydroxides because of a high correlation between specific conductances and alkalinity.

Electrical Conductivity

Electrical conductivity (E.C.) values of the irrigation supply and plot flood water, averaged over the respective treatments, are given in Figures 30 and 31 for data collected in 1973, 1974, and 1975, respectively. Analyses of variance indicated that time of sample collection, fertilizer application rate, and irrigation management had highly significant effects on mean E.C. values in 1974 and 1975 (Appendix G, Tables G1 and G2). The data from 1973 are too sparse to indicate significant trends due to treatments, although the means did vary significantly with time (Appendix G, Table G3).

The excessive fertilizer application rate resulted in higher E.C. values in 1974 and 1975 (Figures 30 and 31). The detailed data are given in Appendix H. Electrical conductivity values were greater under the impoundment irrigation management. The continuous flow system either flushes significant amounts of salt from rice paddies, or the salts are decreased by some other mechanism at an accelerated rate in the continuous flow plots.

The highly significant first order interaction between time and irrigation treatment in 1974 (Appendix G) is indicative of the former when one considers this interaction was not significant in 1975. As previously mentioned, a smaller percentage of the total water volume was exchanged under the continuous flow management scheme in 1975.

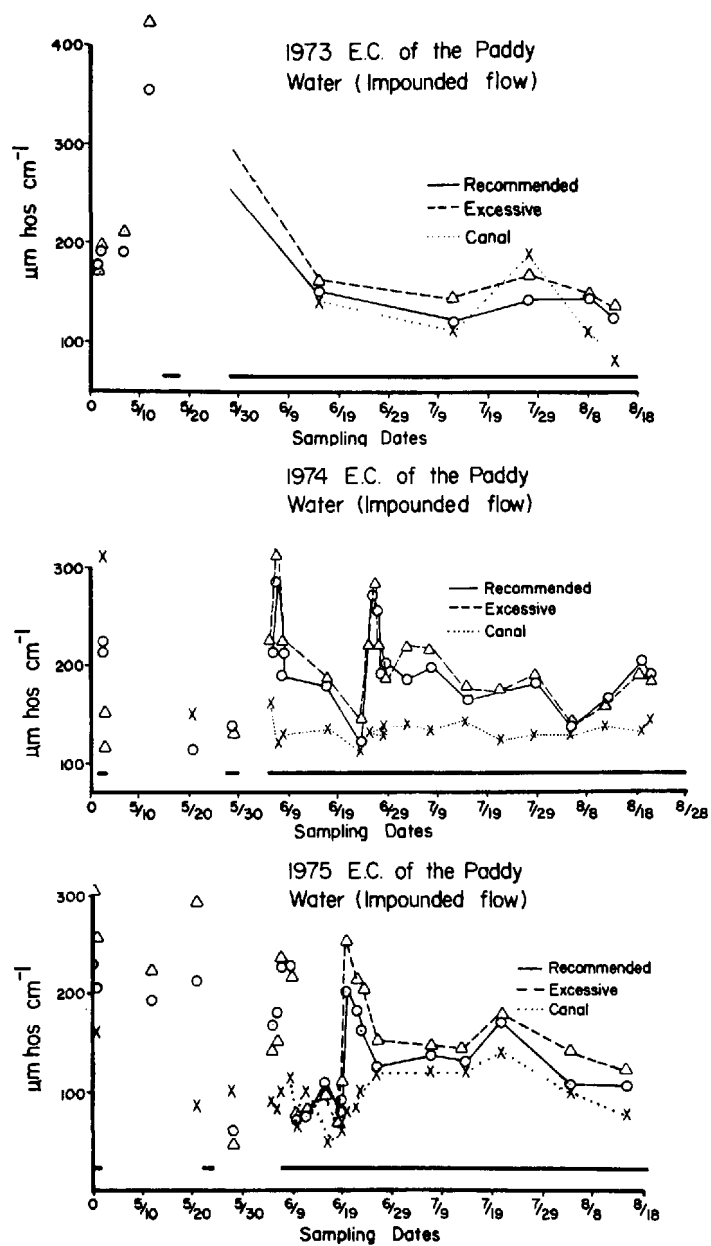


Figure 30. Electrical conductivity in $\mu\text{mhos/cm}$ for water in impounded plots and in the canal.

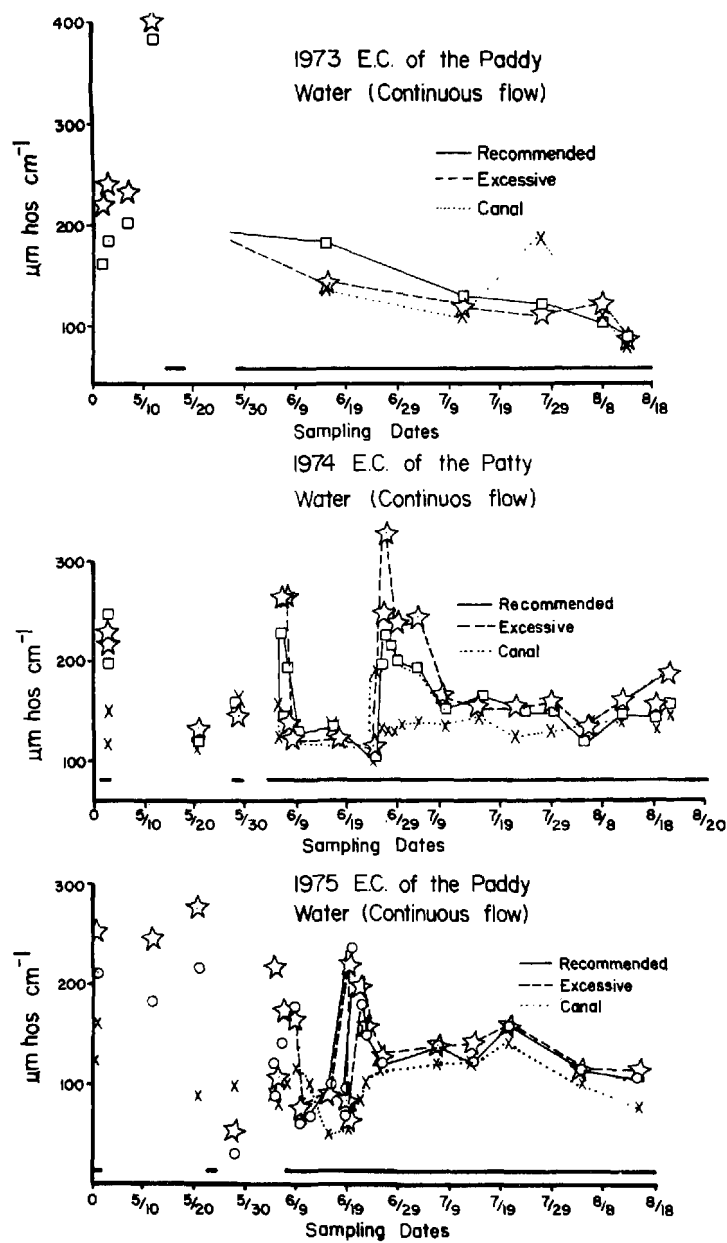


Figure 31. Electrical conductivity in $\mu\text{mhos/cm}$ for water in continuous flow plots and in the canal.

A Duncans' multiple range test was conducted on E.C. values, averaged over treatment blocks, to determine which means were significantly different with respect to time in 1974 and 1975 (Figures 32 and 33). The relatively high initial E.C. values are due to the pre-plant fertilizer applications. The drastic decrease in E.C. noted for the sample average on May 21, 1974 (Figure 32) corresponds to the 5 cm rain logged on May 20, 1974 (Appendix A). The extremely low E.C. value noted May 28, 1975 (Figure 33) corresponds to a 10 cm rain (Appendix A). Peak E.C. values noted after June 6 and June 19, 1975 are analogous to the significant decreases in pH resulting from the $(\text{NH}_4)_2\text{SO}_4$ applications. These data are completely consistent since pH represents the negative log of the hydrogen ion concentration, and the hydrogen ion is approximately five times more mobile in aqueous solutions than any other ions belonging to the alkali metal or halogen families. Conductance is a measure of the current carried by electrolytes. Faster ions carry the larger load. Thus, small decreases in pH can induce relatively large increases in electrical conductance; conversely, dilution of the hydrogen ion by rain, which is essentially neutral in pH, would effect a decrease in E.C. as noted above.

It is evident from these data that the increase in E.C. following fertilizer application was primarily a temporary effect. The E.C. returned to approximately that of the irrigation canal water within 15 days (Figures 30 and 31). Fertilizer incorporation into the soil and/or applied to dry soil prior to flood, resulted in lower salt levels in the floodwater, as evidenced by the fact that peak concentrations were about equal, although the pre-plant and tillering application rates were twice the panicle differentiation application rate.

The E.C. values of the irrigation source indicate a low salinity hazard (as categorized by the U. S. Salinity Laboratory, 1954) and paralleled the E.C. values for the Neches River, which has good quality water compared to the other rivers within the Texas Rice Belt (Westfall et al., 1971). The E.C. of the good irrigation water increased only slightly by the end of the growing season as a result of irrigation of rice plots in this study. It is likely that irrigation return flow from the experimental rice plots would have little effect on increasing the salinity of the receiving stream. This observation concerning the salt load of irrigation return flow from rice fields is in contrast to the 5- to 20-fold greater salt load of irrigation return flow in Western States (McGauhey, 1968; Thorne and Peterson, 1967).

pH of the Water

The pH of acid soils tends to increase to near neutrality after flooding; whereas, alkaline soils decrease in pH to near pH 7.0. This phenomenon, which helps explain chemical changes in flooded soils, was clearly defined in a report by Ponnampetuma et al. (1966). They established that the pH of reduced acid and alkaline soils high in iron were buffered near pH 7.0 by the $\text{Fe}_3(\text{OH})_8-\text{H}_2\text{O}-\text{CO}_2$ system. The dominating effect of CO_2 on the pH of alkaline soils was established by Bradfield (1941) and Whitney and Gardner (1943). Ponnampetuma et al. (1966) related this CO_2 effect to the decrease in pH of reduced alkaline soil and showed that the pH values of reduced alkaline and calcareous soils are controlled by the partial pressure of CO_2 through the $\text{Na}_2\text{CO}_3-\text{H}_2\text{O}-\text{CO}_2$ and

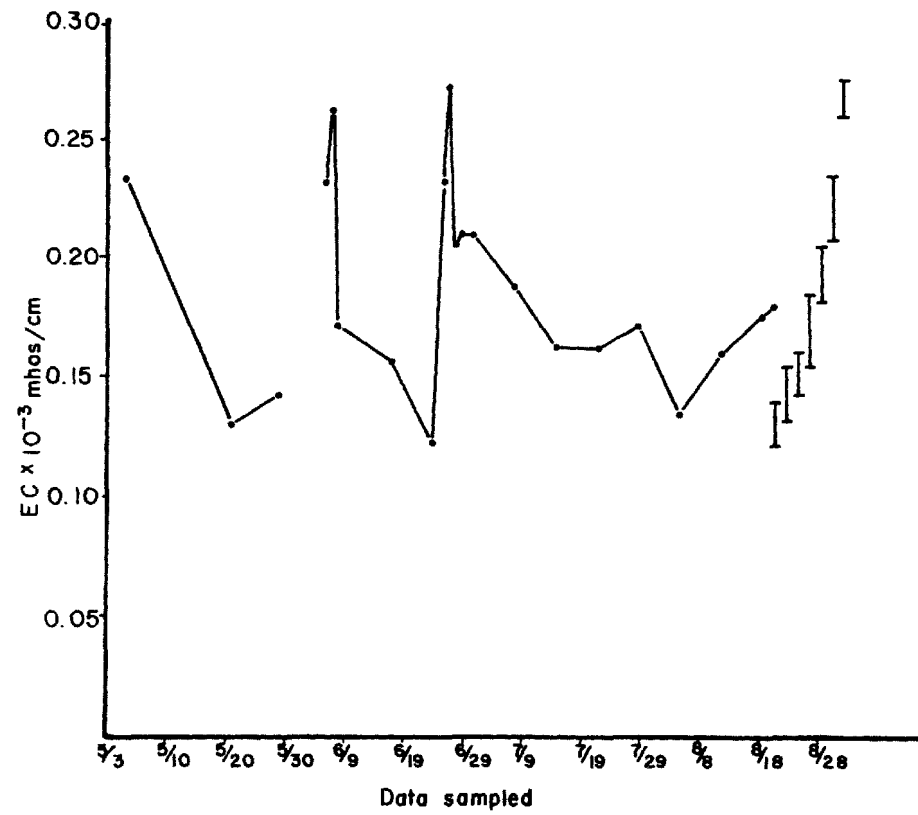


Figure 32. Electrical conductivity averaged over treatment blocks for plot water sampled in 1974, and results of Duncan's multiple range test at a 5% level of significance.

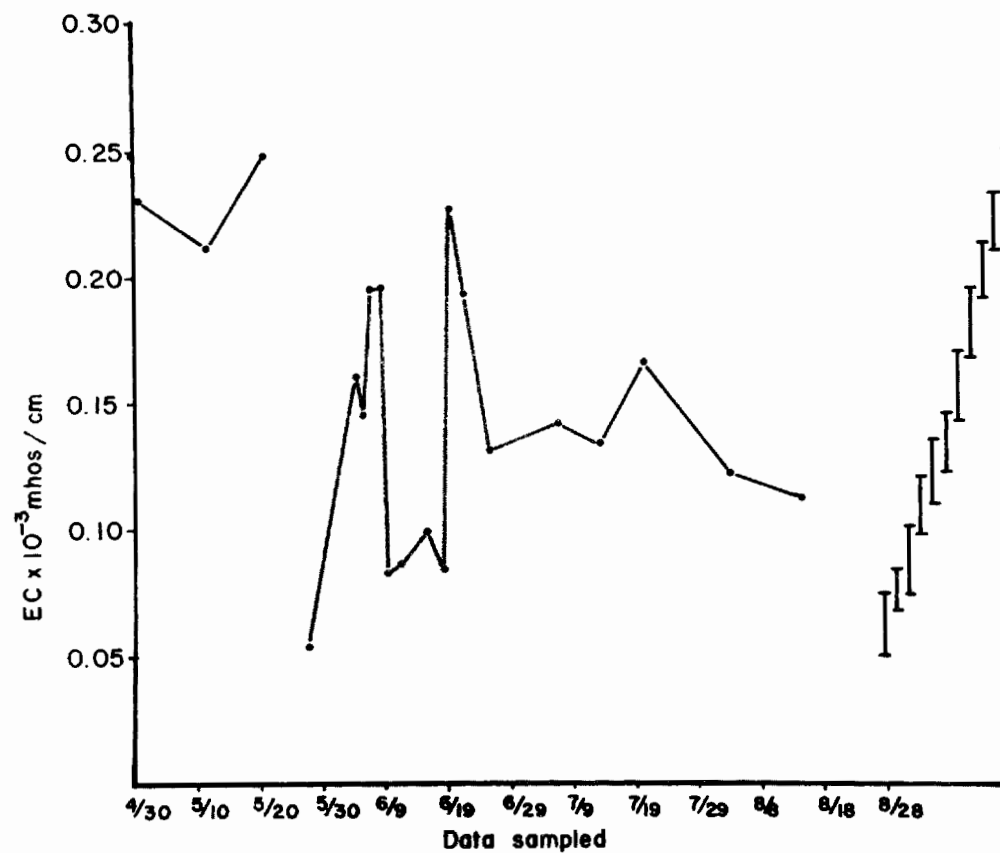


Figure 33. Electrical conductivity averaged over treatment blocks, for soil solutions collected prior to permanent flood, and for plot water sampled following permanent flood in 1975, and results of Duncan's multiple range test at a 5% level of significance.

the $\text{CaCO}_3\text{-H}_2$) buffer systems, respectively.

Irrigation and paddy water pH values for the continuous flow and impoundment irrigation management schemes are given in Figures 34 and 35, respectively. The general trend was for the pH of the paddy water to increase towards that of the irrigation water with time. It has long been established that soils tend toward neutrality under saturated moisture regimes. Analyses of variance indicated the change in pH with time was highly significant in each of the three growing seasons (Appendix G, Tables G4, G5, and G6).

Resultant pH values averaged over treatment blocks for soil solution collected prior to permanent flood and for plot water sampled following permanent flood, are given in Figures 36, 37, and 38.

Definite trends were noted in the 1974 and 1975 averages (Figures 37 and 38), due mainly to the more exhaustive sampling schedule employed in these years. The arrows in Figures 37 and 38 represent the dates that $(\text{NH}_4)_2\text{SO}_4$ is an acidic salt. While the high rate fertilizer treatment resulted in generally lower pH values, analyses of variance indicated that rate of application was not significant at a 5% level in either 1974 or 1975 (Appendix G, Tables G5 and G6). Rate of application had a highly significant effect on resultant pH values in 1973 but so were deviations with replication (Appendix G, Table G4). The fact that the low and high rate had about the same effect on pH suggests that the flood is tenuously buffered, a point further substantiated by the way plot water deviations corresponded with irrigation canal water deviations (Figures 35 and 36).

The impoundment irrigation scheme resulted in a significantly lower pH in 1974 but imparted little variation on the treatment means in 1975. The difference between the two years may be due to the fact that a smaller percentage of the total water volume was exchanged under the continuous flow management scheme in 1975. Continuous flow plots had been made deeper in 1975 to investigate the influence of plot depth on propanil. Thus, the deeper plots resulted in a larger total water volume, resulting in less impact from the 1 cm/day flow rate.

The peak in pH noted on June 10, 1975, between the two N applications, is attributed to dilution of the H^+ ion in the flood. Rain in excess of 20 cm was recorded within a 24-hour interval between June 9 and June 10, 1975.

The pH values of the irrigation return flow are certainly within acceptable levels or criteria enacted for release into surface waters or imposed on public drinking water supplies.

Salts and Nutrients in the Water

Introduction--

The general topic of irrigation return flow has been reviewed by the Utah State University Foundation (1969). Skogerboe and Law (1971) have outlined problems, possible solutions, and research needs associated with irrigation return flows. The potential for controlling quality of irrigation return flows has been studied by Law and Skogerboe (1972). Although Garman (1973)

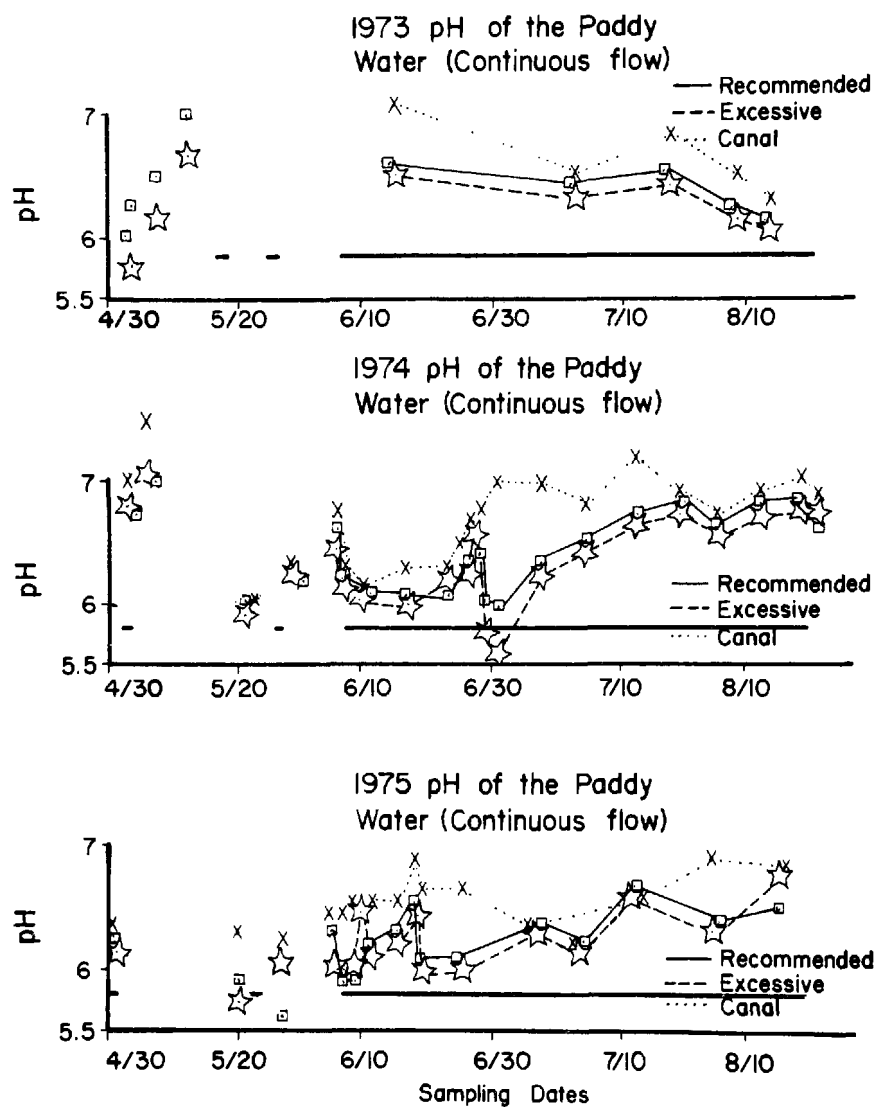


Figure 34. pH of water in continuous flow plots and in the canal.

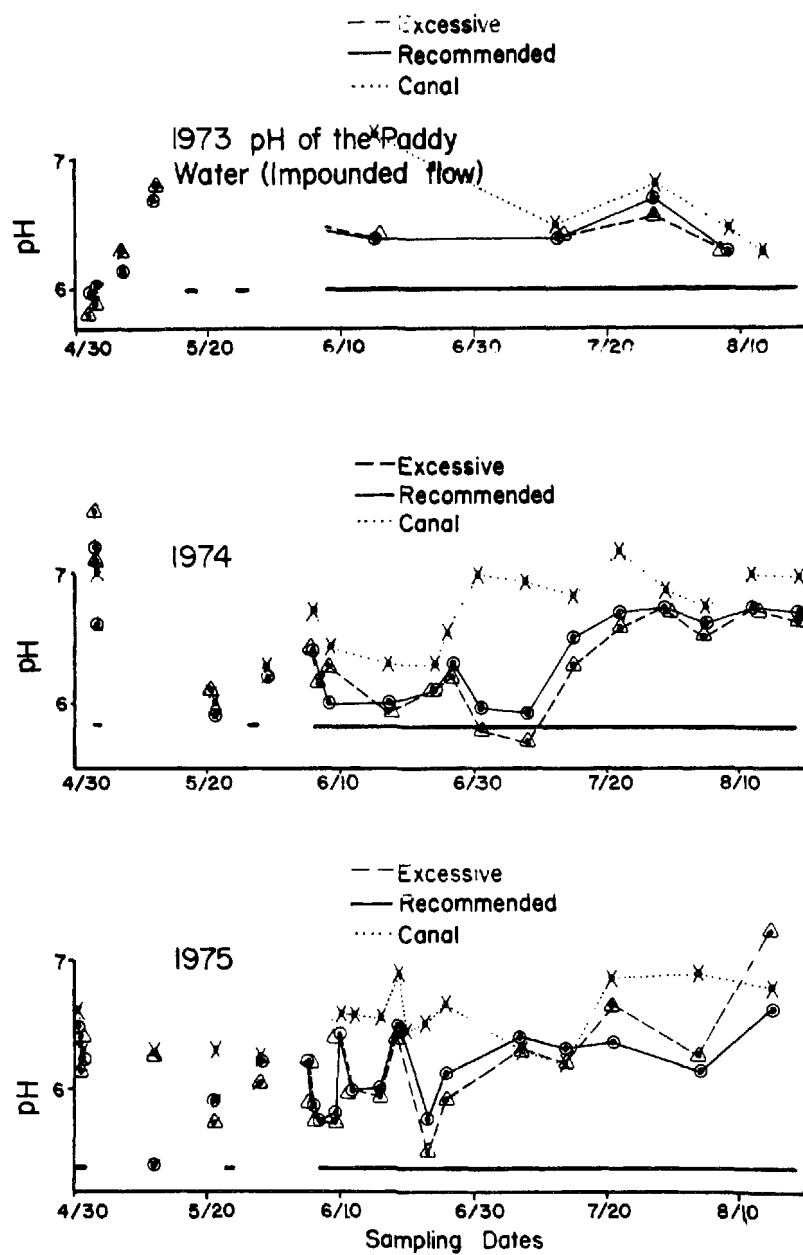


Figure 35. pH of water in impounded plots and in the canal.

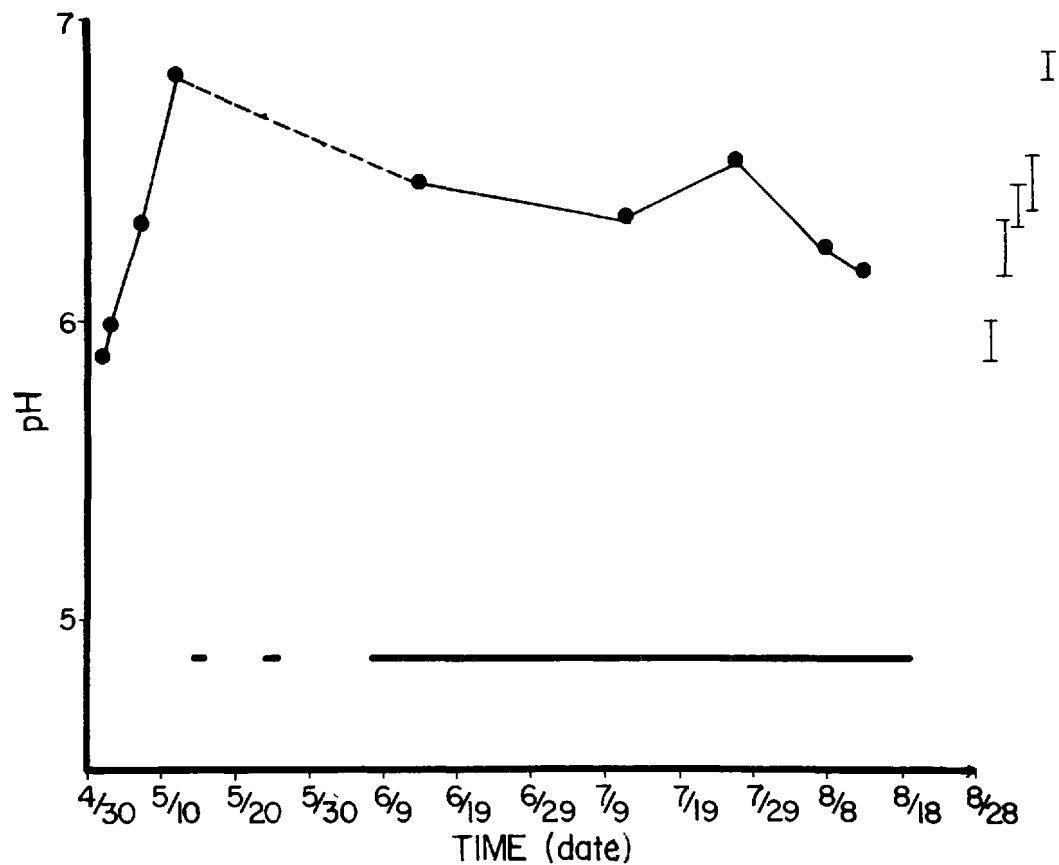


Figure 36. Resultant pH averaged over treatment blocks, for soil solution collected prior to permanent flood (4/30 - 6/5) and for plot water samples following permanent flood (6/6 - 8/20) in 1973. The heavy horizontal line indicates when the plots were flooded. The results of DMR test at a 5% level of significance are shown in the upper right section of the figure.

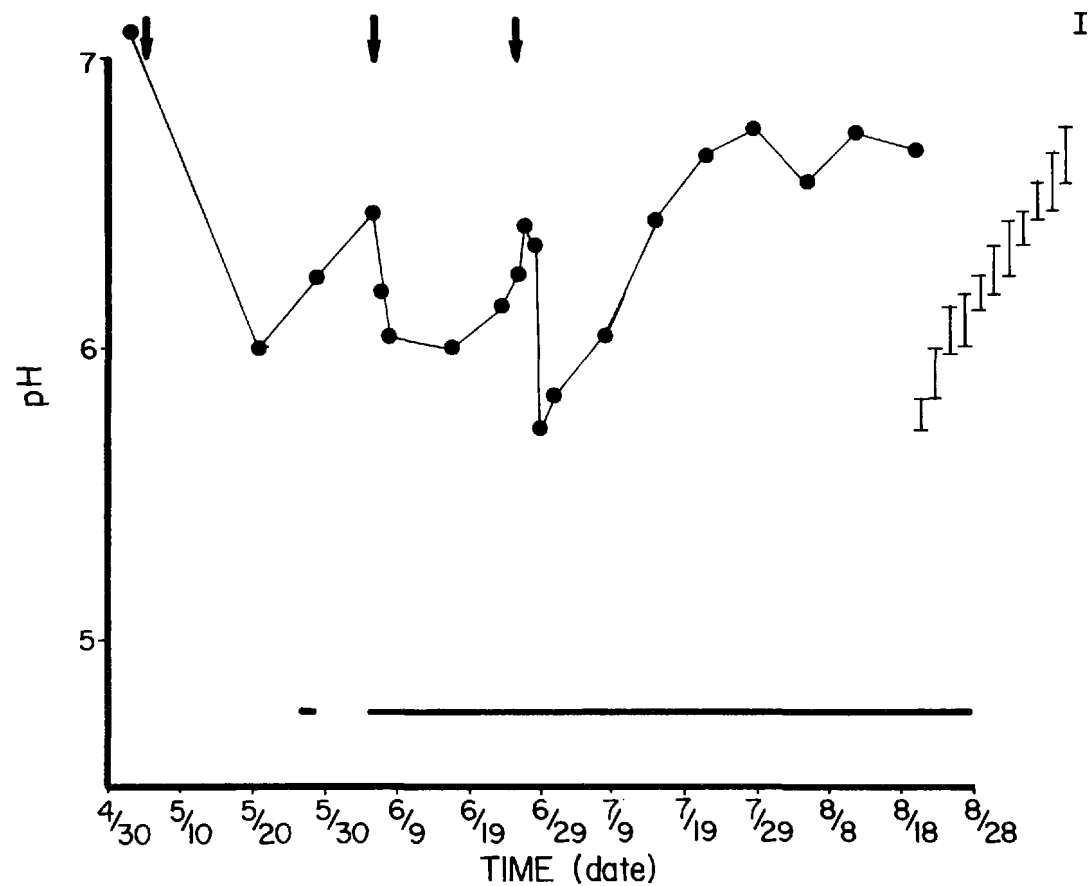


Figure 37. Resultant pH averaged over treatment blocks, for soil solution collected prior to permanent flood (4/30 - 6/5) and for plot water samples following permanent flood (6/6 - 8/20) in 1974. The heavy horizontal line indicates when the plots were flooded. The results of DMR test at a 5% level of significance are shown in the upper right section of the figure.

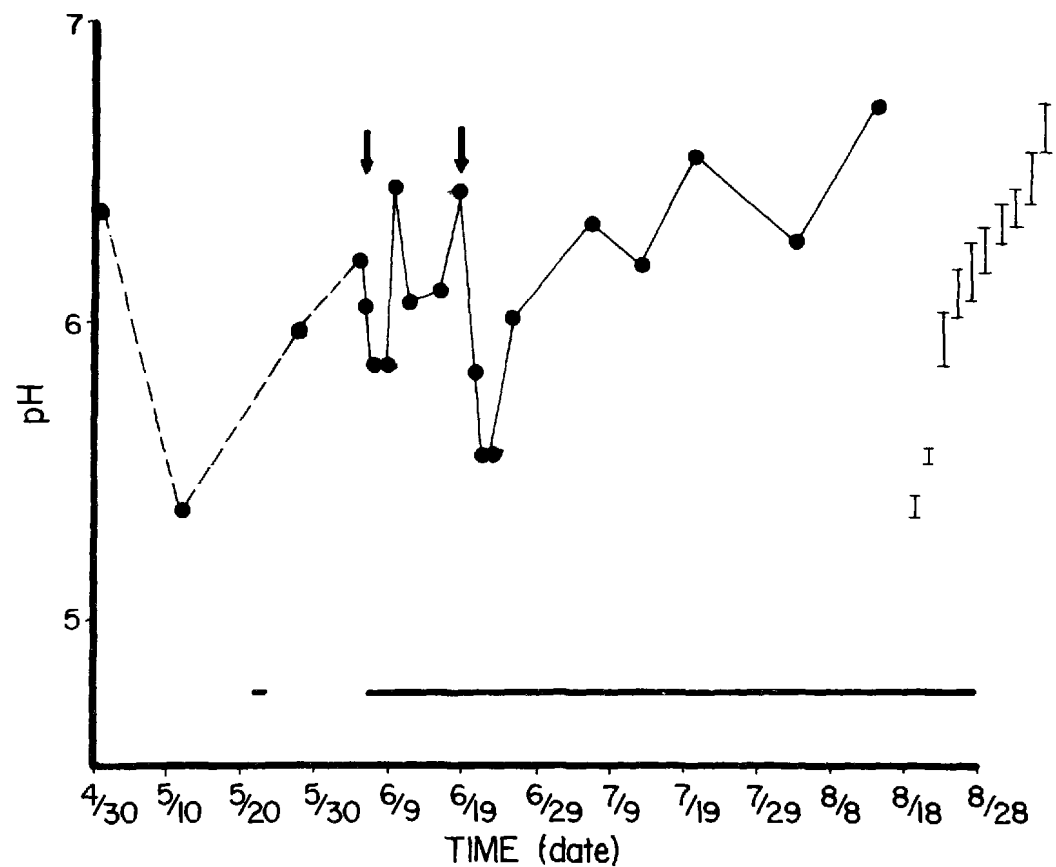


Figure 38. Resultant pH averaged over treatment blocks, for soil solution collected prior to permanent flood (4/30 - 6/5) and for plot water samples following permanent flood (6/6 - 8/17) in 1975. The heavy horizontal line indicates when the plots were flooded. The results of DMR test at a 5% level of significance are shown in the upper right section of the figure.

has argued that water quality degradation through irrigation usage has been overestimated, it is evident from the above reviews that irrigation usage can reduce water quality by increasing sediment mass, salinity, or inorganic nutrient content of waters. These three water quality problems as related to irrigation return flows will be considered separately.

Reviews of nutrient losses from soils indicated that nutrient loss to drainage water is dependent on a number of factors (Barrows and Kilmer, 1963; Soileau, 1969; Garman, 1970; Veits, 1971; Veits and Hageman, 1971; Kilmer and Barber, 1974; Kilmer and Joyce, 1971; Kilmer, 1972). Factors that increase surface water runoff, water percolation through soil, and fertilization in excess of crop uptake tend to enhance the possibility of eutrophication and high nitrate in drinking water. In a considerable number of studies, (Erickson and Ellis, 1971; Hanway and Laflen, 1974; Kilmer et al., 1974; Gilliam et al., 1974) the nutrient content of the drainage water from fertilized land was low considering the level of naturally occurring nutrients in soil and rainwater. In fact, Garman (1973) suggested that carbon in the runoff from agricultural lands induced eutrophication, not the nutrients, since most fresh water bodies already contain a sufficient nutrient level for eutrophication. Thus, few situations likely occur where decreasing agricultural nitrogen and phosphorus contribution would stop eutrophication.

Others, equally adamant to their position, suggest that runoff and irrigation return flow percolated through soils fertilized in excess of crop needs can contribute appreciably to pollution of water resources. As a result, Law and Skogerboe (1972) have suggested potential methods for control of irrigation return flow quality by altering water delivery systems, farm management systems and changing water removal systems. Meek et al. (1970) and Gilliam et al. (1974) have shown how controlling water tables under fertilized fields can be used as a means of removing unused nitrogen through denitrification and, thus, reduce the contribution of irrigation return flow to water pollution.

Ammonia, nitrate, and nitrite concentrations in soil and soil solutions are the result of the following processes and/or factors: (1) amount, time, and method of nitrogen fertilizer application, (2) nitrification rate, (3) denitrification rate, (4) rate of diffusion between soil and soil solutions, (5) nitrogen immobilization by rice plants and microbes, and (6) nitrogen content of irrigation water. Nitrification, denitrification, and uptake of N by rice plants are the primary processes governing N transformation in flooded rice soils. A diagram illustrating N transformation in rice fields is given in Figure 39. Generally nitrification and denitrification processes occurring simultaneously in the oxidized and reduced layers, respectively, are believed to be responsible for low N use-efficiency of 23 to 56% recovery of added N (Patrick et al., 1971 and Westfall, 1972).

Although the mechanisms of N transformation are adequately understood, it is difficult to quantitatively account for the N added to rice fields. Generally N is applied as $(\text{NH}_4)_2\text{SO}_4$ to reduce losses by denitrification and leaching. Ammonium dissolution and adsorption to soils are shown in the equations given below:

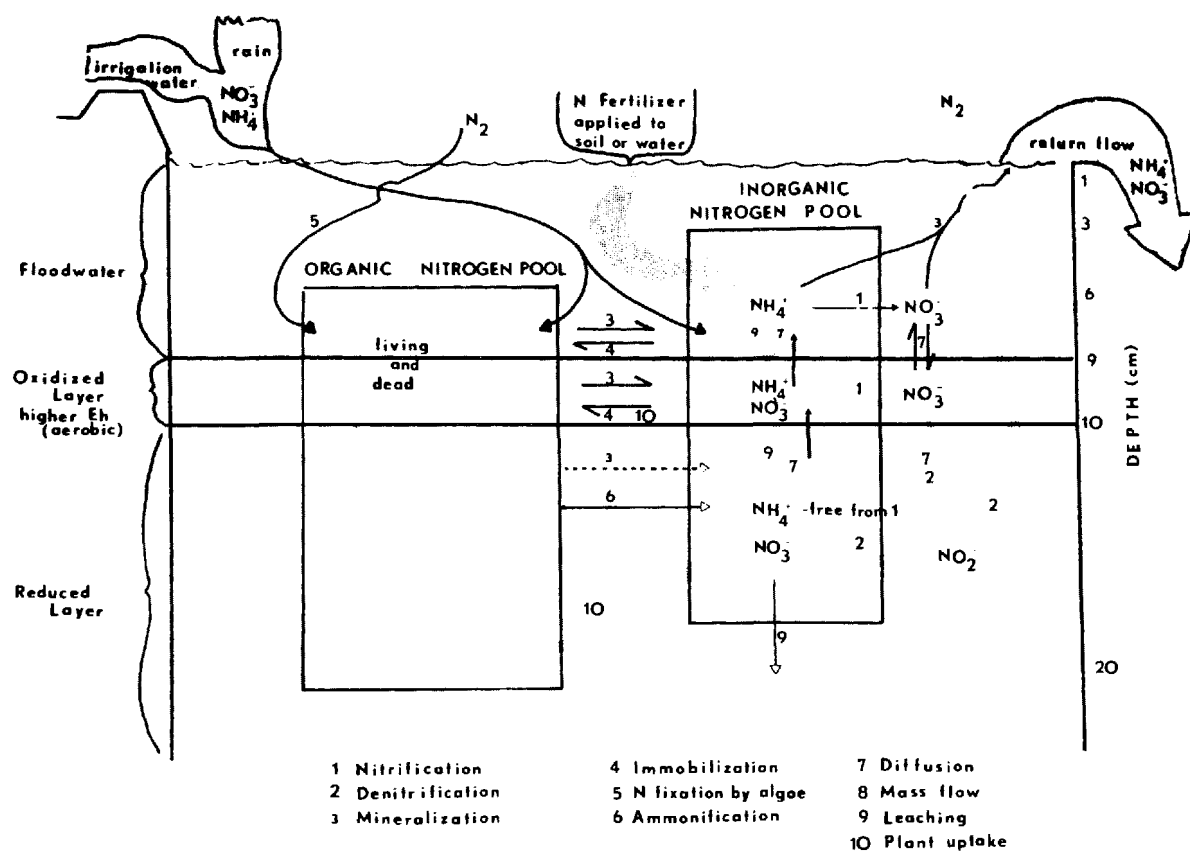
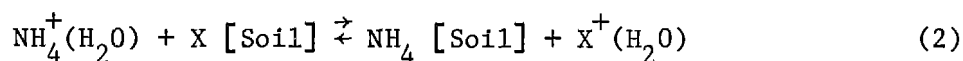
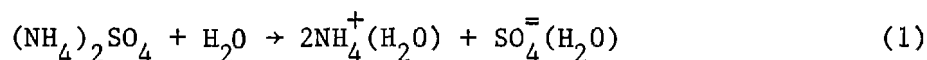


Figure 39. Diagram of nitrogen pathways and transformations in flooded rice soils.



The equilibrium in equation (1) depicts the complete dissociation of $(\text{NH}_4)_2\text{SO}_4$ in H_2O , and equation (2), the sorption-desorption of NH_4^+ where soil is the exchange complex, and X is another cation.

Cation Concentrations--

Ammonia was measured in the soil solutions collected prior to permanent flood and in the plot water sampled following the flood application in 1973, 1974, and 1975. Data, reported as $\text{NH}_4\text{-N}$, for the continuous and impounded flow irrigation systems are given in Figures 40 and 41, respectively. Peak concentrations correspond to the N topdressing applied at tillering and panicle differentiation stages of rice growth. The interval between these stages was somewhat shorter in 1975 due to better climatic conditions. Ammonium was rapidly diminished in the plot water following the peak, primarily due to NH_4^+ adsorption by the soil.

Evidence of the soils capacity to remove $\text{NH}_4\text{-N}$ from the floodwater is presented in the laboratory experiment summarized in Figure 42. Ammonium nitrogen applied at 84 kg/ha to the 10 cm flood diffused from the floodwater into the soil, as indicated by the decrease in $\text{NH}_4\text{-N}$ in the simulated floodwater, and increase in the NH_4^+ level of the soil. Although water movement was restricted, NH_4^+ concentrations were notably greater than that of the control to a depth of 4 cm. It should be noted that $(\text{NH}_4)_2\text{SO}_4$ had been applied to the floodwater in an aqueous phase so that movement to the soil and within the soil was essentially by diffusion in the laboratory. Mixing of plot water by thermal convection, irrigation activity, wind induced plant disturbances, and the fact that granular $(\text{NH}_4)_2\text{SO}_4$ was deposited at the soil surface may account for the more rapid NH_4 dissipation in the field.

Perhaps the most conclusive evidence from NH_4^+ adsorption by the soil was the increase of Ca^{++} , Mg^{++} , K^+ , and Na^+ concentrations in the plot water following the fertilizer applications. Calcium concentrations in 1973, 1974 and 1975 for continuous and impounded flow plots are given in Figures 43 and 44. Corresponding data for Mg^{++} are given in Figures 45 and 46. K^+ data are plotted in Figures 47 and 48; and Na^+ concentrations are given in Figures 49 and 50. These data exemplify the exchange equilibria given in Equation 2. The background levels of the various cations were much greater in the irrigation water in 1973 than in either 1974 or 1975. This was due to the fact that irrigation water was sampled in the feeder canal adjacent to the plots and indicated a contamination during fertilizer application. The 1974 and 1975 irrigation water samples were collected from the main irrigation canal. Thus, rather than base conclusions on obviously erroneous data, the remainder of this discussion will entail the 1974 and 1975 results.

Increases in the K^+ were of short duration and concentrations generally

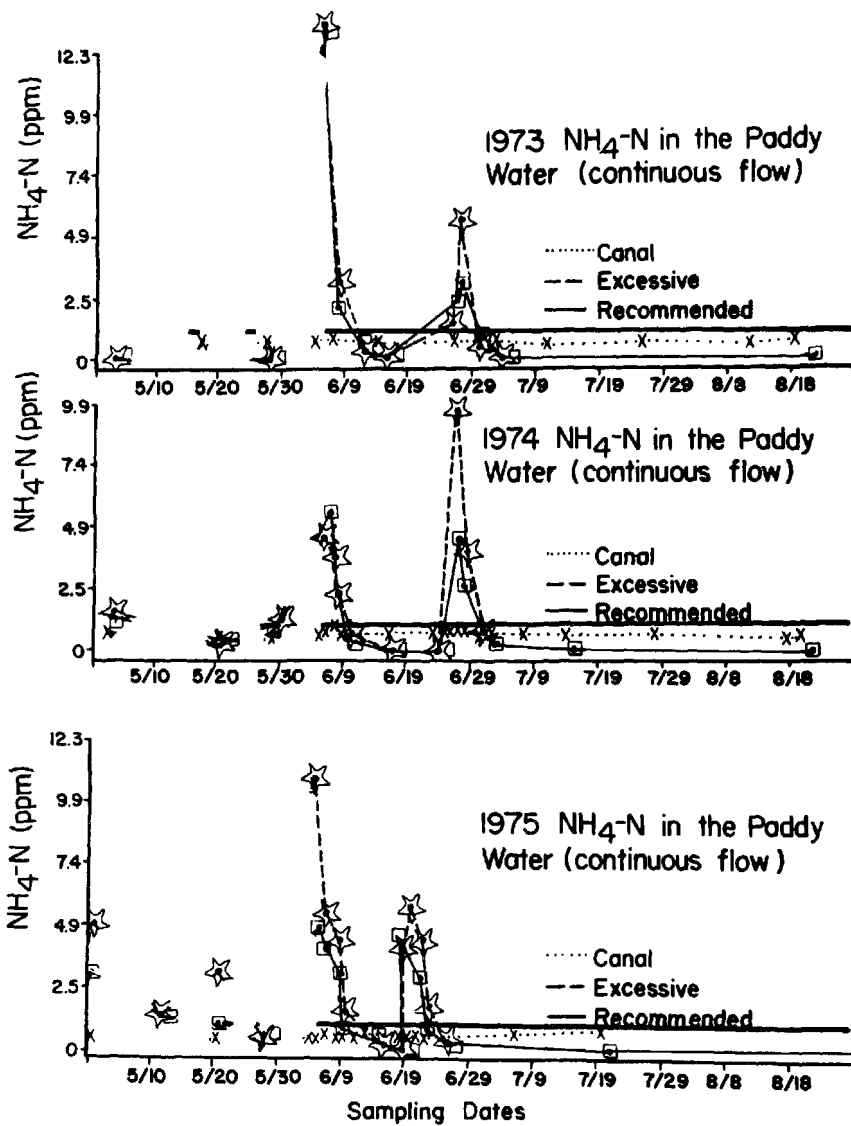


Figure 40. Concentration of NH_4^+ in ppm in continuous flow plots and in the canal water.

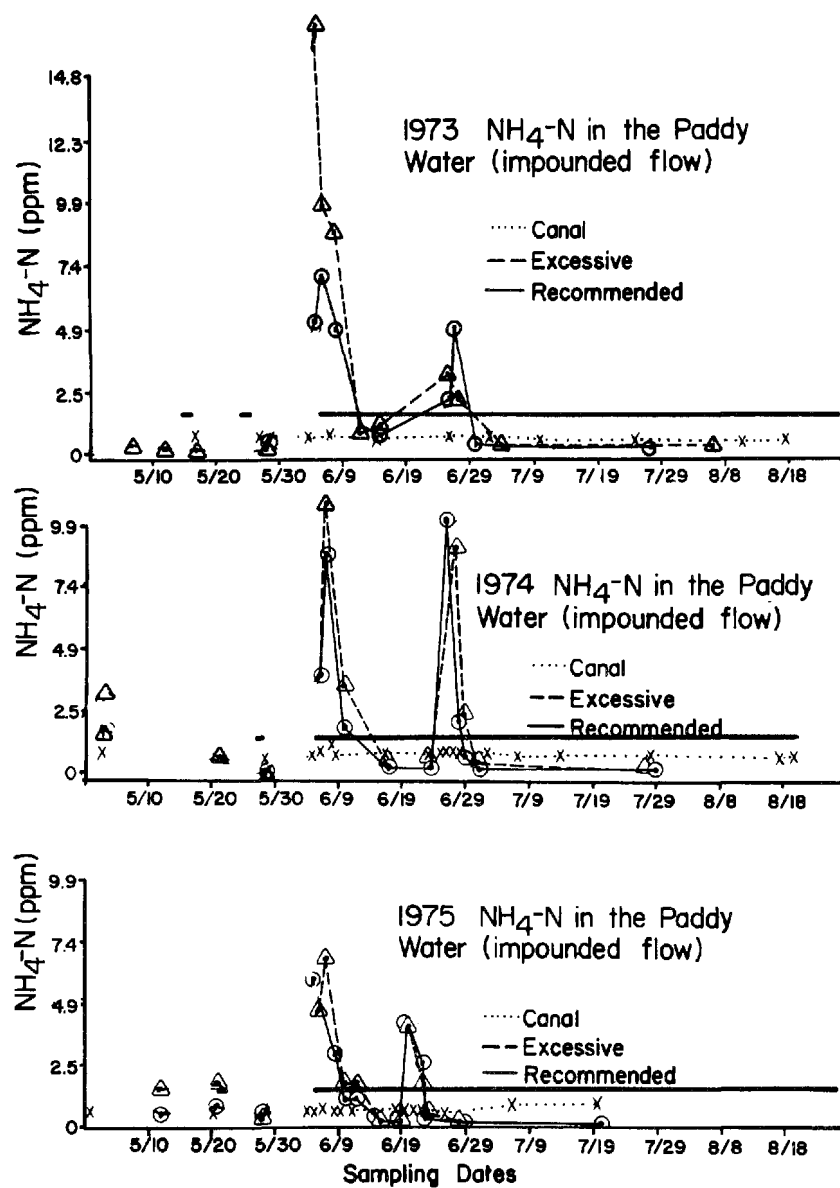


Figure 41. Concentration of NH_4^+ in ppm in imponded plots and in the canal water.

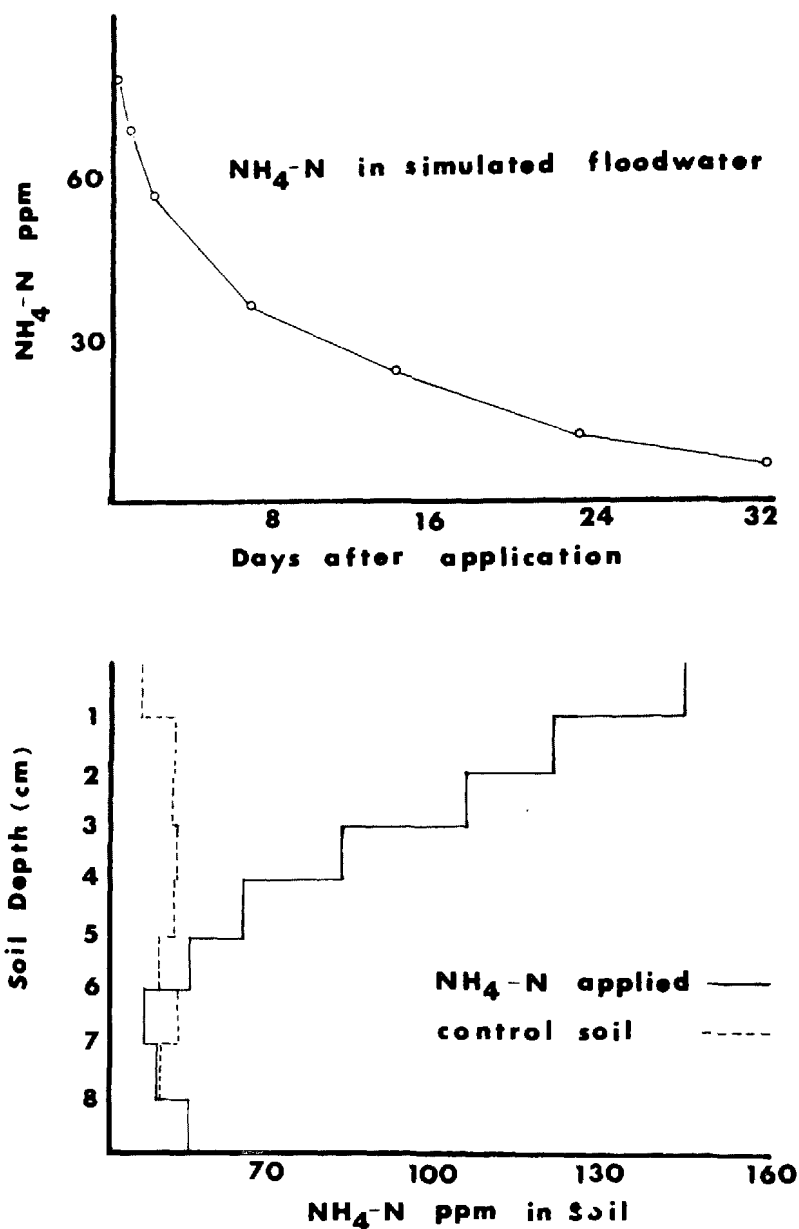


Figure 42. The top graph represents the $\text{NH}_4\text{-N}$ concentration in a 10 cm layer of water over a 10 cm layer of soil after pipetting $(\text{NH}_4)_2\text{SO}_4$ (at the rate of 84 kg N ha^{-1}) into the water layer. The lower graph represents the distribution of the $\text{NH}_4\text{-N}$ within the same 10 cm layer of soil 32 days after 0 and 84 kgs N ha^{-1} were applied to the simulated floodwater. This experiment was conducted under laboratory room condition in the absence of rice plants.

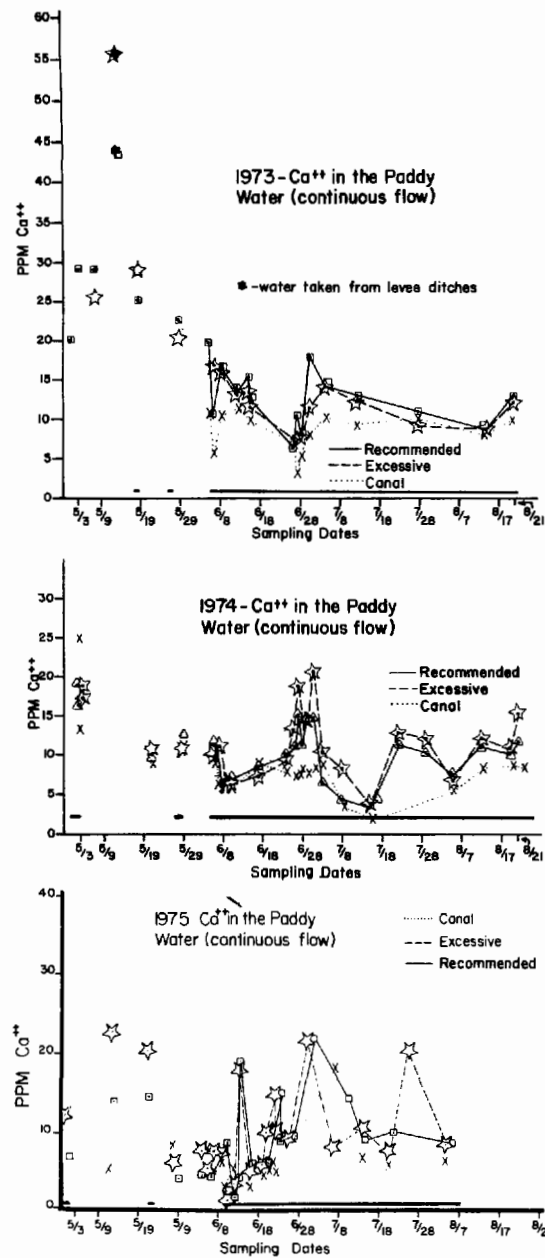


Figure 43. Concentration of Ca⁺⁺ in ppm in continuous flow plots and in the canal water.

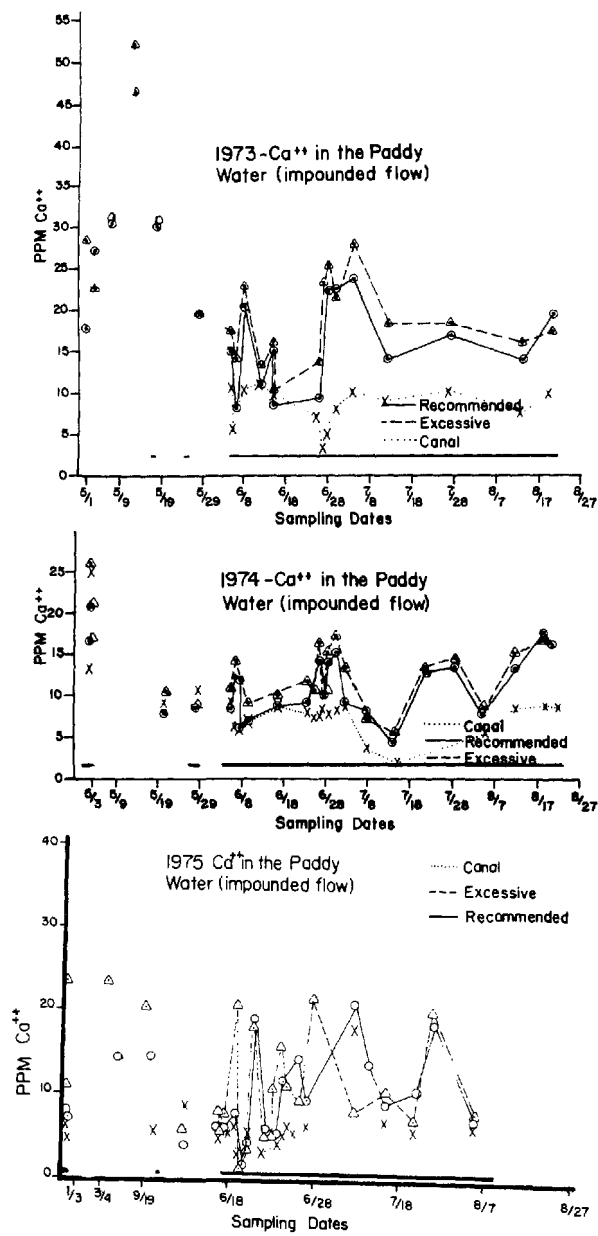


Figure 44. Concentration of Ca⁺⁺ in ppm in impounded plots and in the canal water.

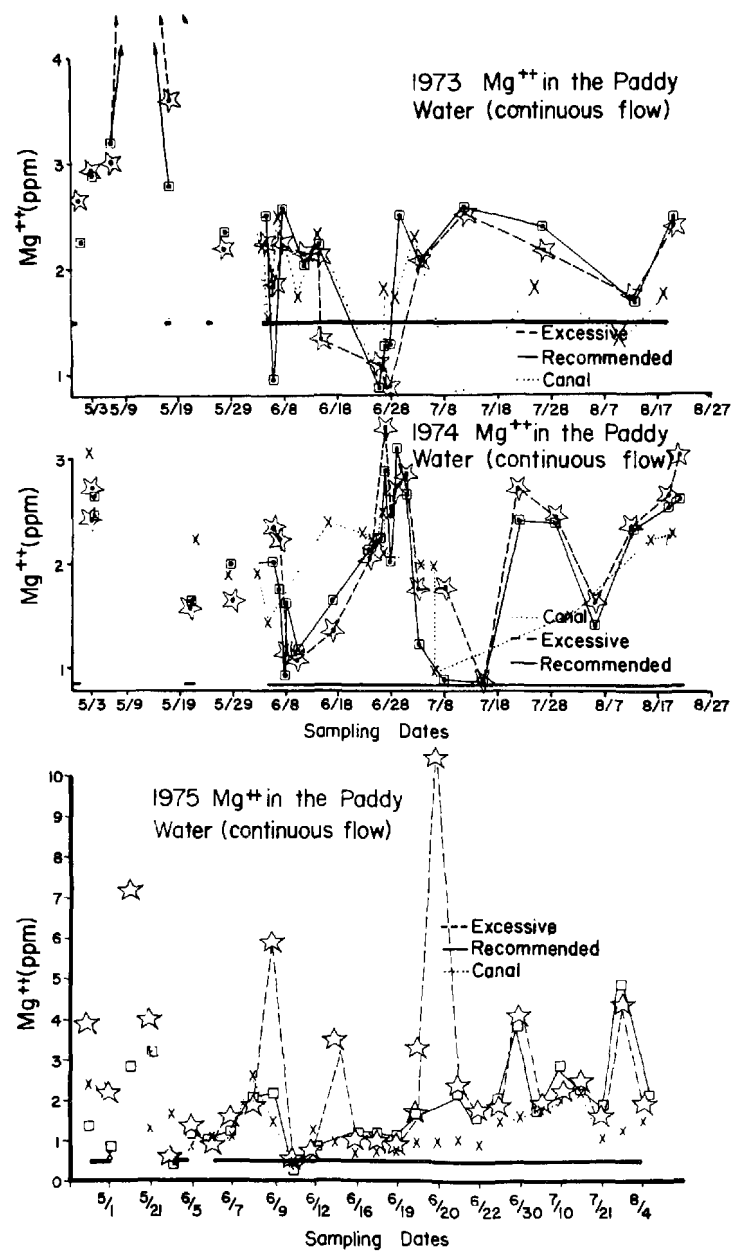


Figure 45. Concentration of Mg^{++} in ppm in continuous flow plots and in the canal water.

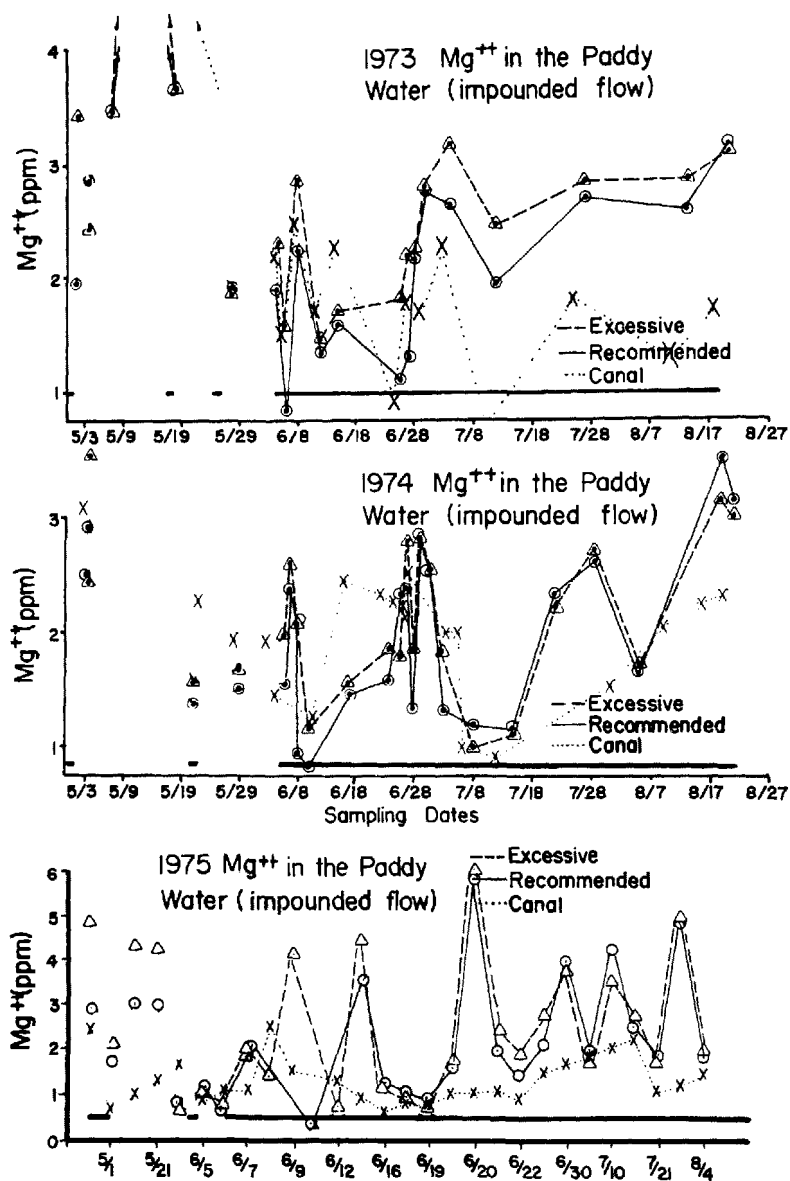


Figure 46. Concentration of Mg^{++} in ppm in impounded plots and in the canal water.

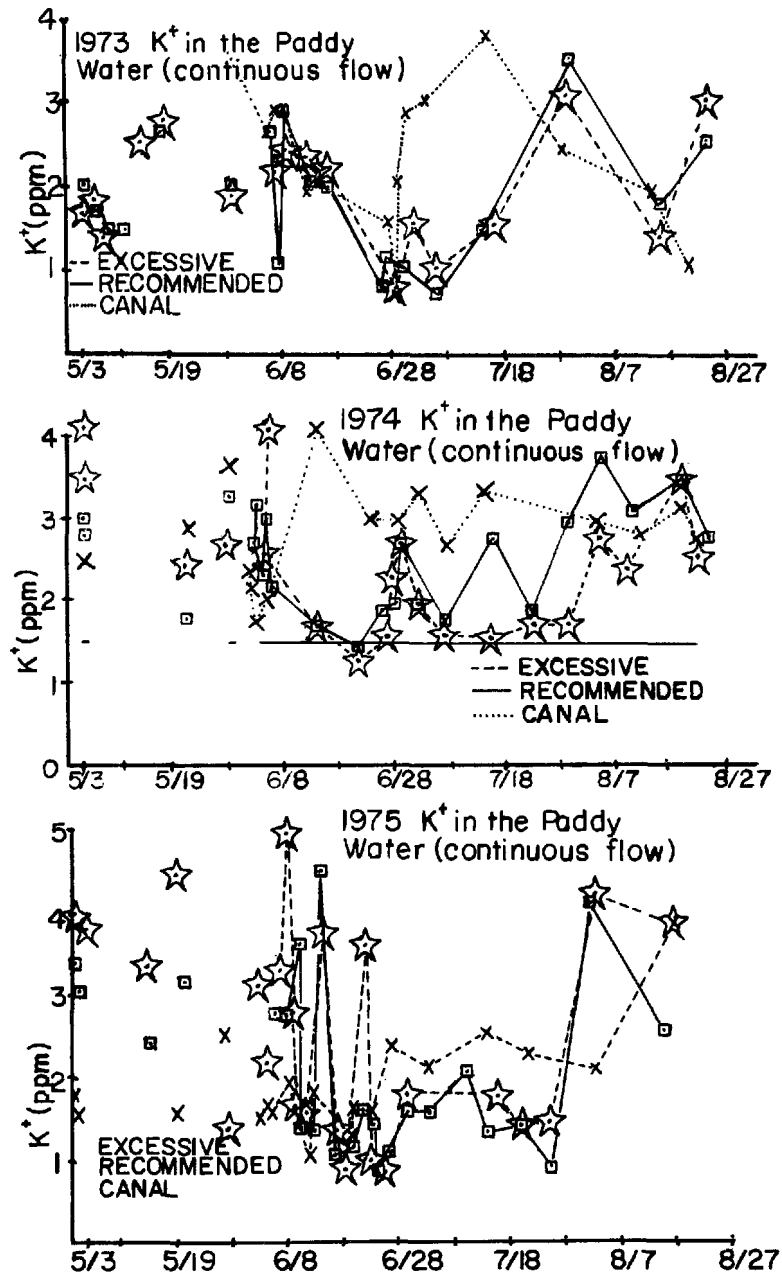


Figure 47. Concentration of K^+ in ppm in continuous flow plots and in the canal water.

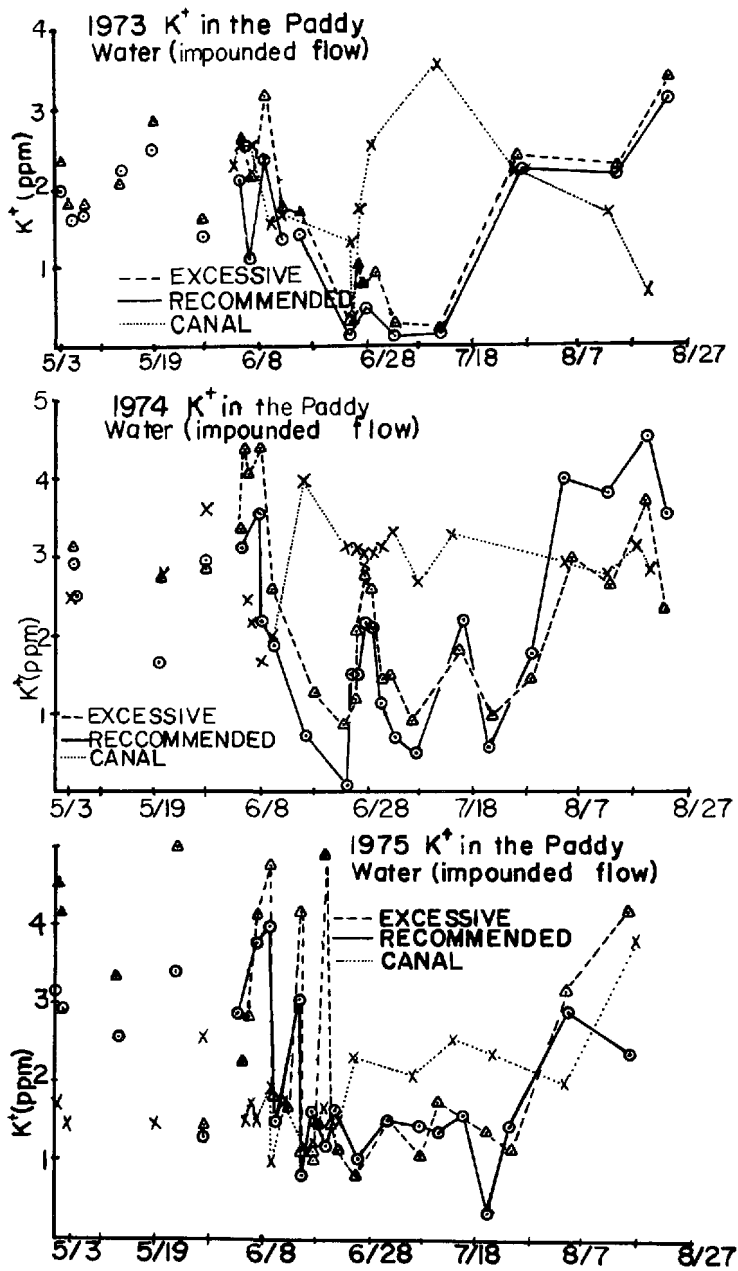


Figure 48. Concentration of K^+ in ppm in impounded plots and in the canal water.

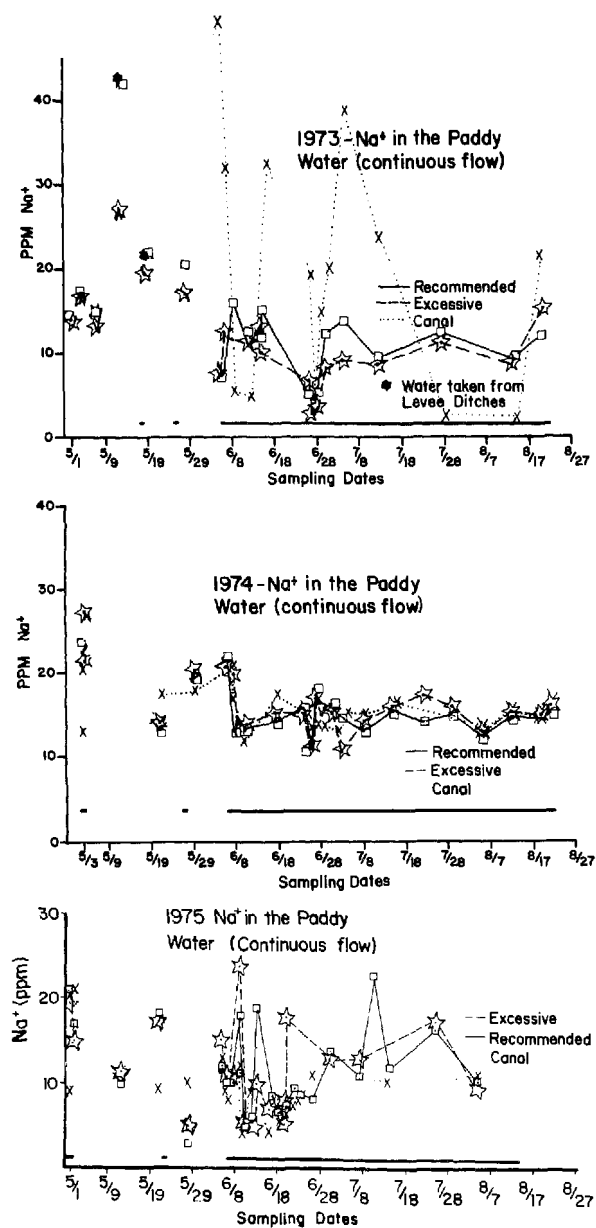


Figure 49. Concentration of Na^+ in ppm in continuous flow plots and in the canal water.

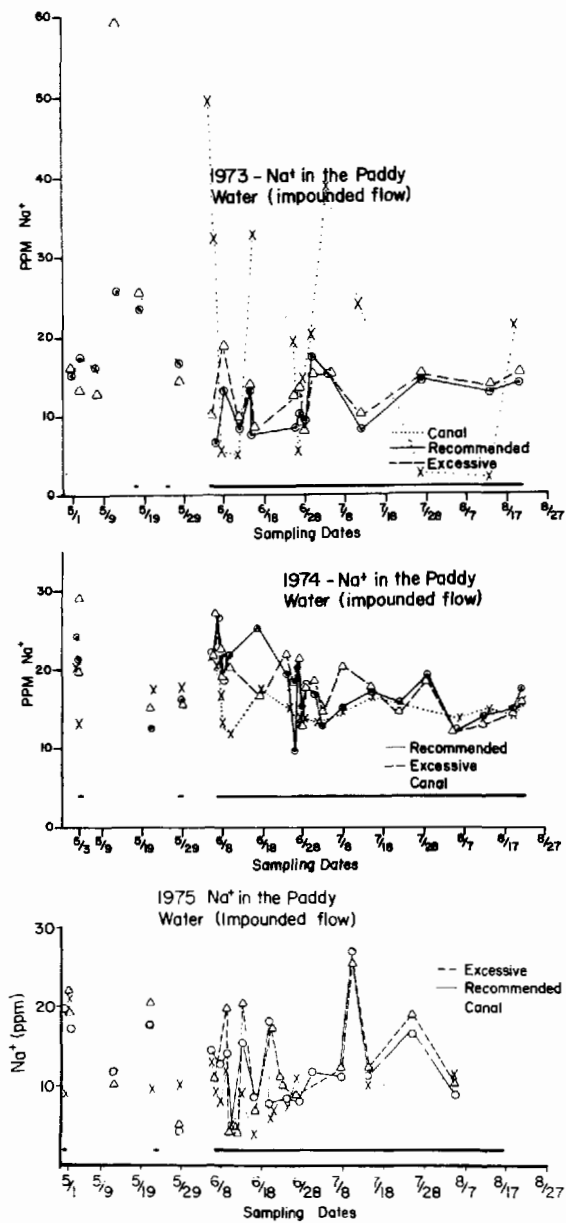


Figure 50. Concentration of Na⁺ in ppm in impounded plots and in the canal water.

were lower in the plot water than in the irrigation canal water, suggesting a strong affinity by the soil for K^+ (Figures 47 and 48). Increases in Mg^{++} (Figures 45 and 46) were small compared to the increases in Ca^{++} (Figures 43 and 44) and Na^+ (Figures 49 and 50). Thus, NH_4^+ adsorbed appears to be at the expense of Ca^{++} and Na^+ . This is reasonable since Ca^{++} predominates the exchange sites of Beaumont clay soil and Na^+ is easily exchanged. Calcium and sodium were diminished in the plot water following peak concentrations due in part to dilution by irrigation and rain and the establishment of a new equilibrium. However, the new equilibrium did not reflect readsorption of Ca^{++} and Na^+ at the expense of NH_4^+ since concentrations of the latter were nil following the peaks (Figures 40 and 41). Amounts of Ca^{++} and Na^+ readsorbed were finite since the concentrations remained higher than that of the canal H_2O over the remainder of the growing season, all of which is consistent with an NH_4^+ fixation mechanism in a Beaumont clay soil similar to that previously reported for K^+ (Carson and Dixon, 1972).

The tenacity with which NH_4^+ is adsorbed may account for the low N recoveries and efficiency previously reported in rice soils (Patrick et al., 1971 and Westfall, 1972), more so than the nitrification-denitrification transformation mechanism. Many of the fluctuations in the concentrations of cations in the plot water were induced by heavy rains.

Anion Concentrations--

Anionic concentrations were measured on soil solution samples collected prior to permanent flood and in the plot water sampled following the permanent flood in 1973, 1974, and 1975. Anions measured included SO_4^{--} , Cl^- , NO_3^- , NO_2^- and PO_4^{--} .

Sulfate was the associated anion with ammonium, and peak concentrations in both continuous and impounded flow plots correspond to the application dates (Figures 51 and 52, respectively). Plot water concentrations prior to the second application indicate that much of the SO_4^{--} applied preplant had been dissipated from the surface water. It is reasonable to assume that the SO_4^{--} was leached into the soil by rain and the two temporary flood applications. Water percolating through the Beaumont clay soil was very slow following saturation by the permanent flood. Sulfate applied at tillering and panicle differentiation was more probably dissipated by sulfur reducing micro-organisms associated with the reduced soil environment created by the flood. This is substantiated by the faster dissipation rate later in the season (Figures 51 and 52). Fluctuation in the concentrations, as previously noted, corresponds to heavy rains. Chloride data for the continuous and impounded flow plots are given in Figures 53 and 54, respectively. Concentrations of Cl^- in the floodwater tended to parallel that of irrigation canal water, except following the pre-plant fertilizer application, and the N topdressings. The higher initial Cl^- levels are the result of the Cl^- added as the associated anion with the K pre-plant fertilizer. However, much of the Cl^- added preplant was leached into the profile and was not reflected in the plot concentrations following the permanent flood. Peaks associated with N topdressing are attributed to SO_4^{--} release from soil solution into the overburden flood by mass action. Plot water concentrations returned to that of the irrigation water once equilibrium was established and rain diluted that released from the soil solution. Nitrate concentrations in rice floodwater for the three cropping seasons were greatest

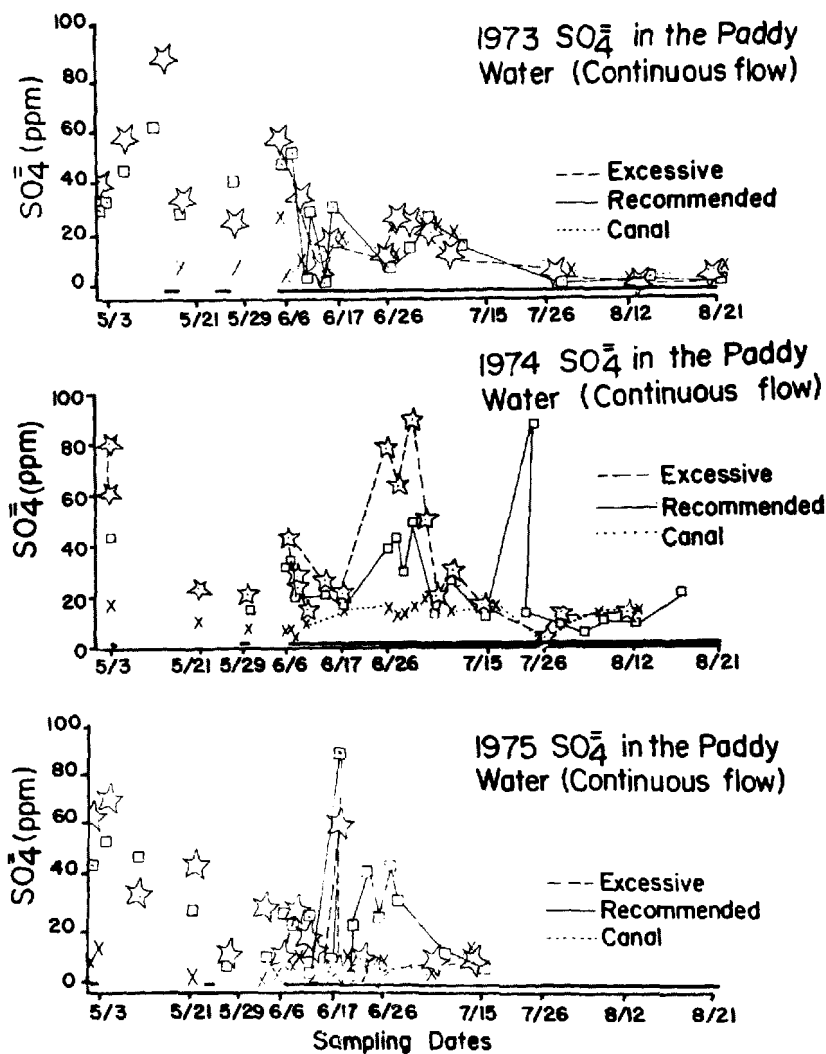


Figure 51. Concentration of SO_4^{2-} in ppm in continuous flow plots and in the canal water.

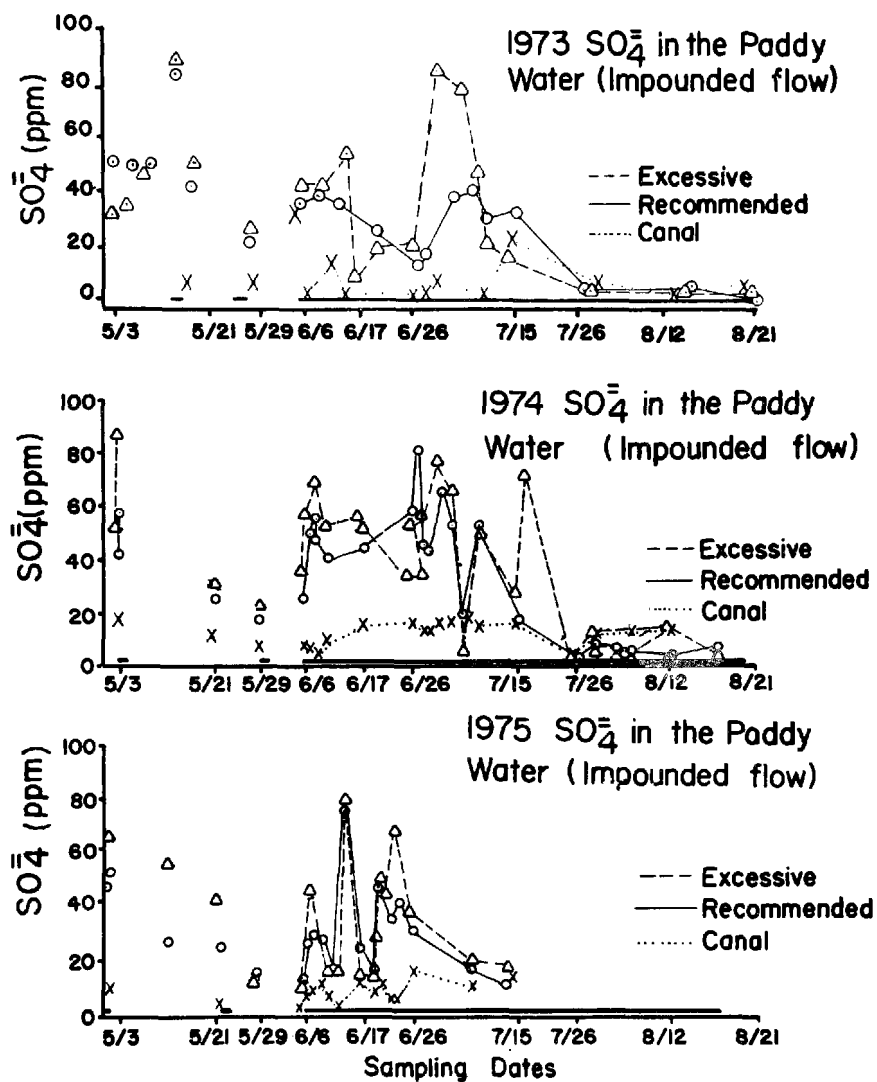


Figure 52. Concentration of SO_4^{2-} in ppm in impounded plots and in the canal water.

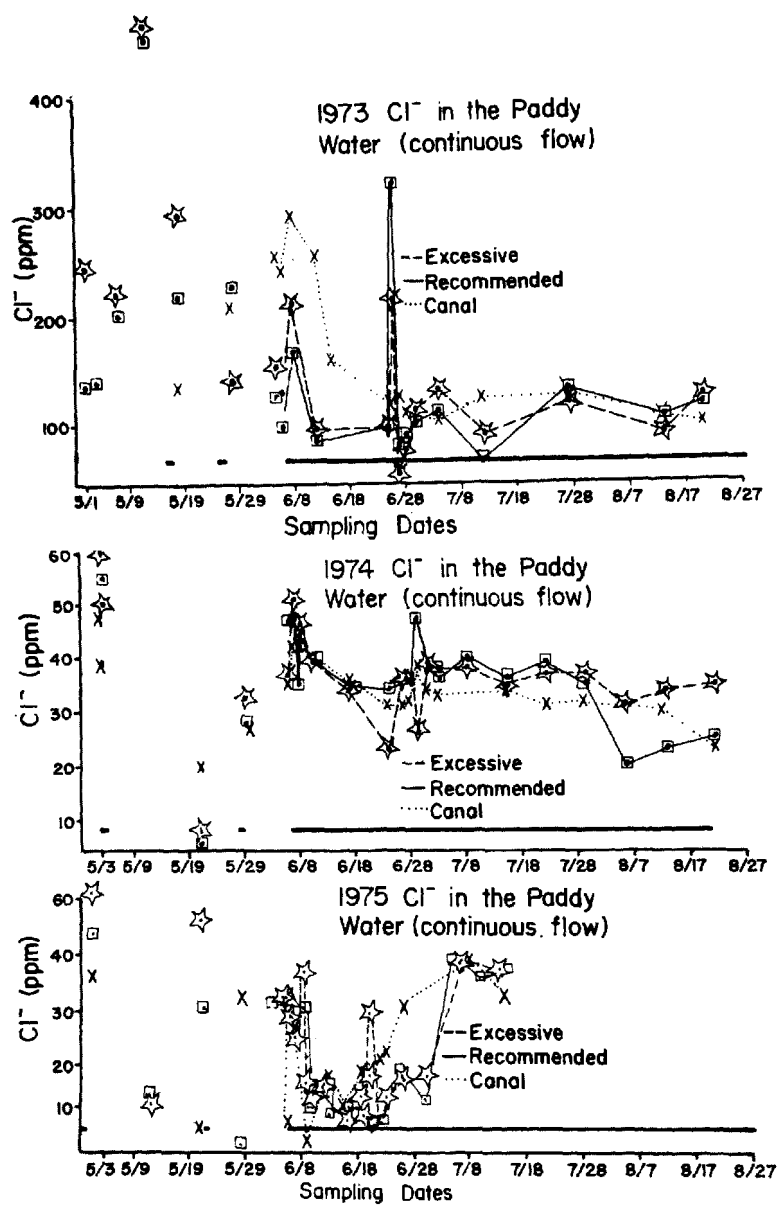


Figure 53. Concentration of Cl^- in ppm in continuous flow plots and in the canal water.

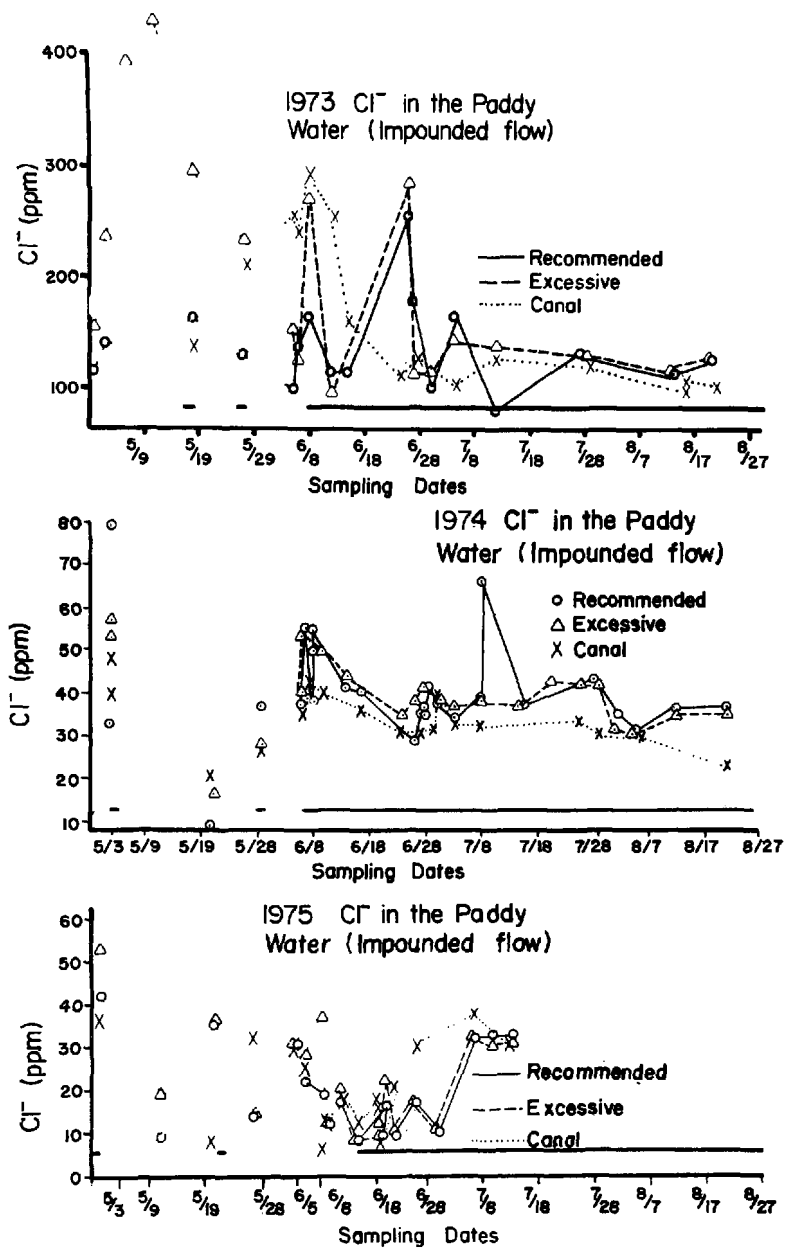


Figure 54. Concentration of Cl^- in ppm in impounded plots and in the canal water.

in the continuous and impounded flow plots in May resulting from nitrification of the preplant $(\text{NH}_4)_2\text{SO}_4$ fertilizer (Figures 55 and 56, respectively). The decrease in the NO_3^- concentrations correspond to the temporary floods applied for irrigation and weed control, which may have leached the nitrate into the soil or diluted the already comparatively low levels. Peaks in $\text{NO}_3\text{-N}$ occurred each year immediately following the permanent flood and at panicle differentiation. These smaller peaks are attributed to nitrification in the aerobic surface layer of the flooded soils. The rapid dissipation of NO_3^- was attributed to crop removal and denitrification stimulated by the reducing conditions. Although the presence of NO_2^- following the preplant fertilizer application confirmed the nitrification process, concentrations in the plot water after the permanent flood reflected that of the irrigation water and were generally less than the latter, suggesting that NO_3^- produced on nitrification of NH_4^+ and that introduced via the irrigation supply were rapidly denitrified (Figures 57 and 58).

Ortho-phosphate concentrations in the plot water reflected that of the irrigation supply except in those samples collected immediately after P fertilization (Figures 59 and 60). It is apparent that the initial increase following P fertilization was only temporary. The very low concentrations are indicative of a strong fixation such as precipitation reactions and specific absorption. This is further evidenced by the fact that the high SO_4^{2-} levels did not release PO_4^{3-} from the soil solution.

Treatment Effects

Analyses of variance were determined for the cation and anion concentrations of the floodwater samples collected in 1974 and 1975, to ascertain the statistical significance of time with respect to sample collection dates, irrigation management scheme, and fertilizer application rate. The data were normalized to kg/ha prior to analyses of variance to circumvent the variation imparted by plot water depth on concentration expressed in mg/liter. Data obtained from samples collected in the 1973 growing season were excluded from statistical interpretation since the irrigation supply water values were erroneous, negating meaningful cause and effect relationships based on the irrigation management schemes employed.

Cations--

Analyses of variance for NH_4^+ , Ca^{++} , Mg^{++} , and Na^+ indicated that the variability between the amounts per hectare in the plot water with respect to sampling date was highly significant in 1974 and 1975, with the exception of Mg^{++} in 1974 (Appendix G, Tables G7, G8, G9, G10, G11, G12, G13, and G14). A Duncan Multiple Range Test (DMR) was employed to determine significance between sampling dates at the 5% level. It should be noted that this test was determined on the amount per hectare averaged over treatment blocks at the respective sampling dates. The detailed ion concentration data are presented in Appendix H.

Ammonium applied preplant and incorporated into the surface was significantly lower than that applied to the soil surface just prior to permanent flood, although an average of 80 kg/ha was applied both times (Figures 61 and 62). Half as much NH_4^+ was applied at panicle differentiation but resulted in

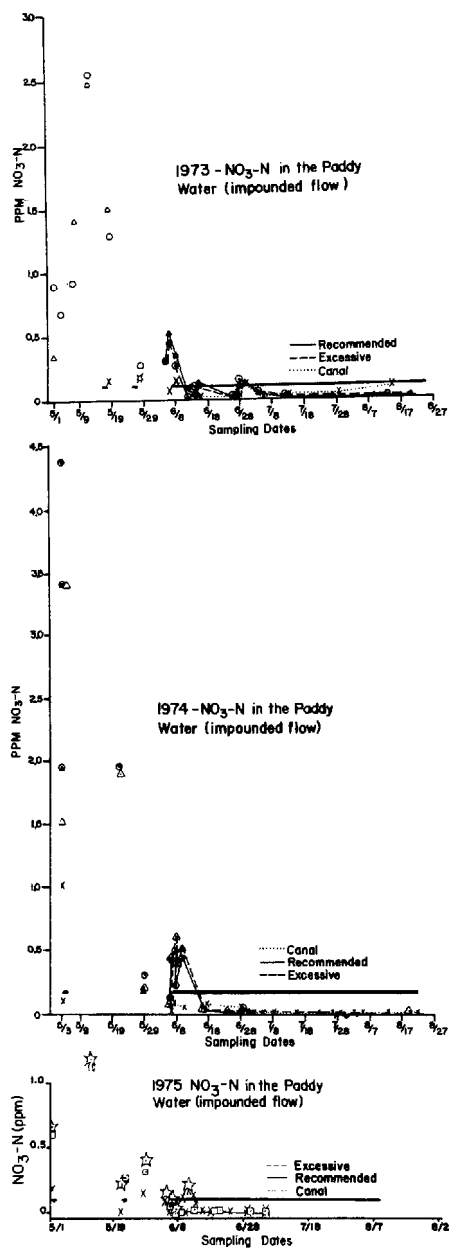


Figure 56. Concentration of NO₃-N in ppm in impounded plots and in the canal water.

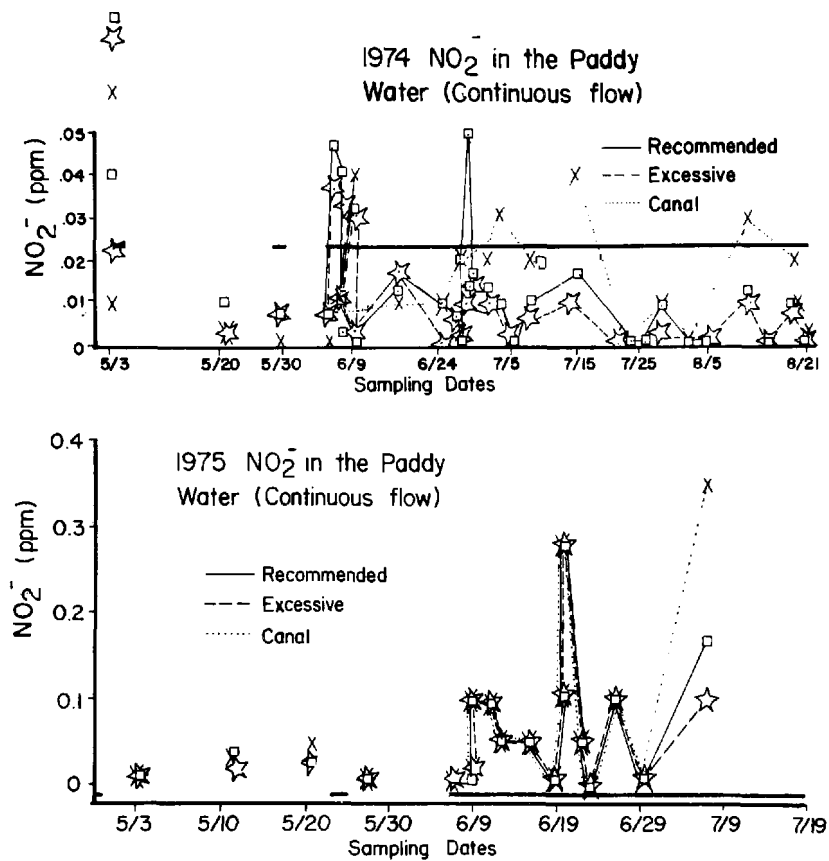


Figure 57. Concentration of NO_2^- in ppm in continuous flow plots and in the canal water.

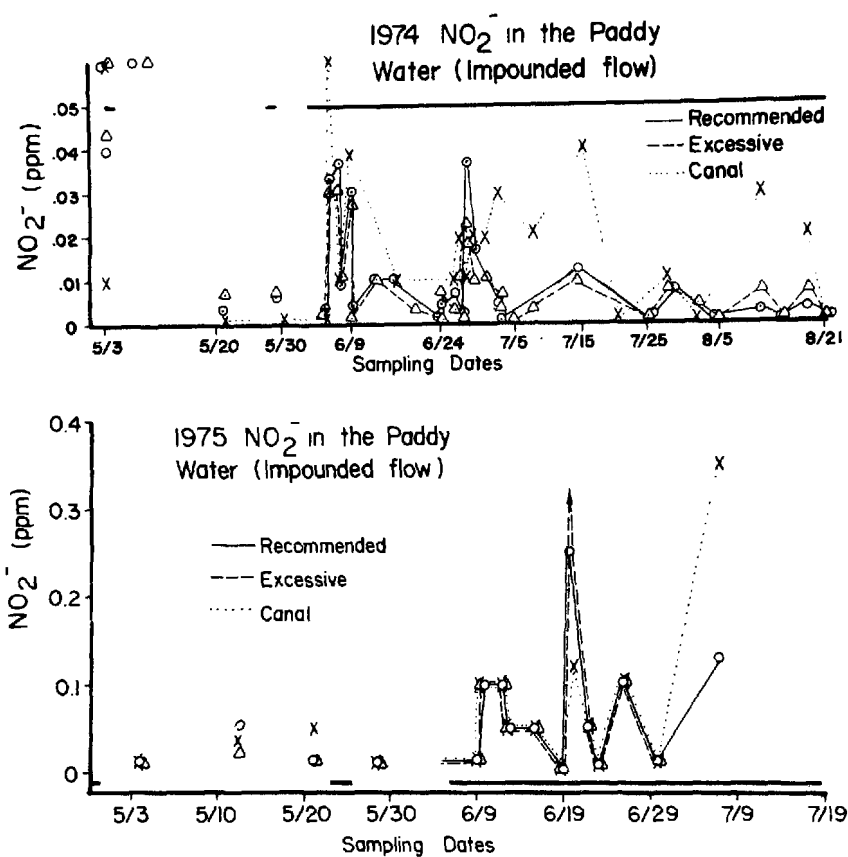


Figure 58. Concentration of NO_2^- in ppm in impounded plots and in the canal water.

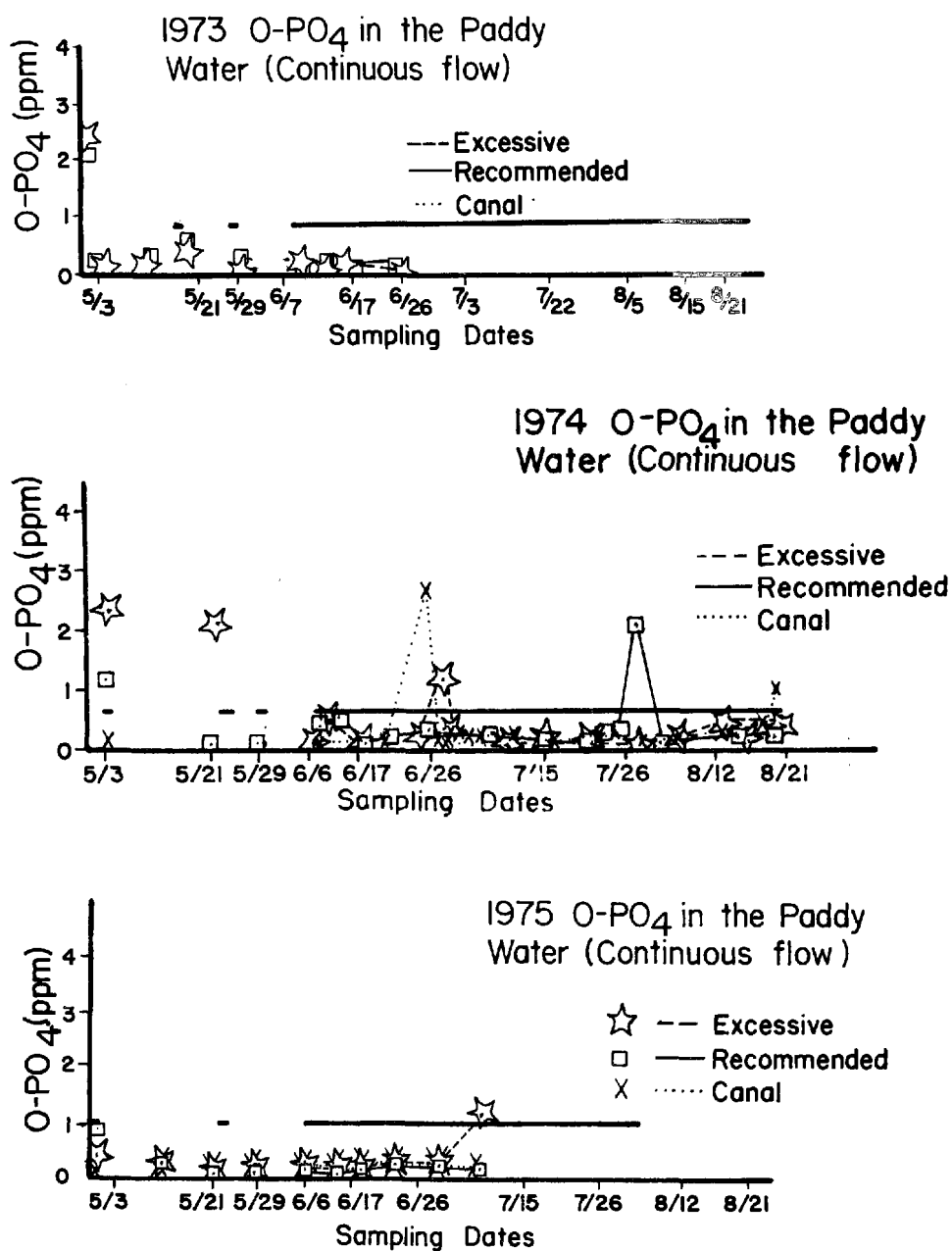


Figure 59. Concentration of O-PO₄ in ppm in continuous flow plots and in the canal water.

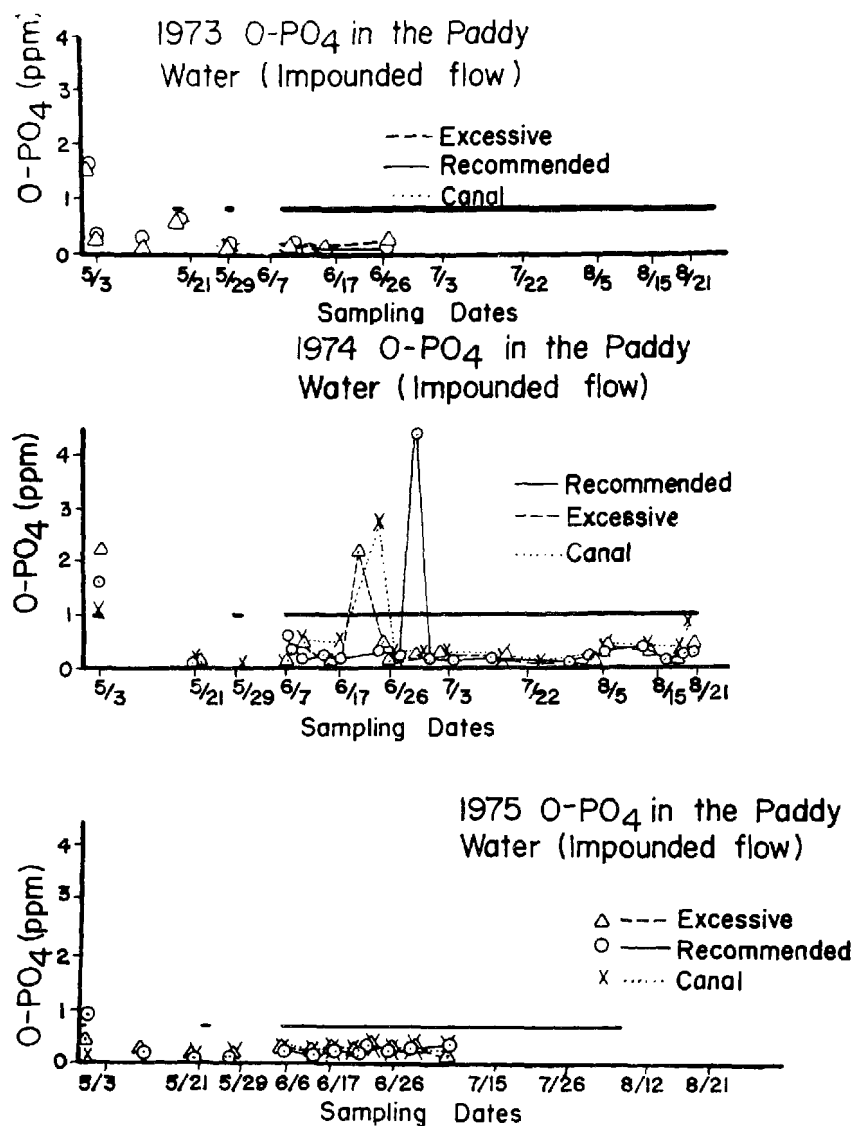


Figure 60. Concentration of O-PO₄ in ppm in impounded plots and in the canal water.

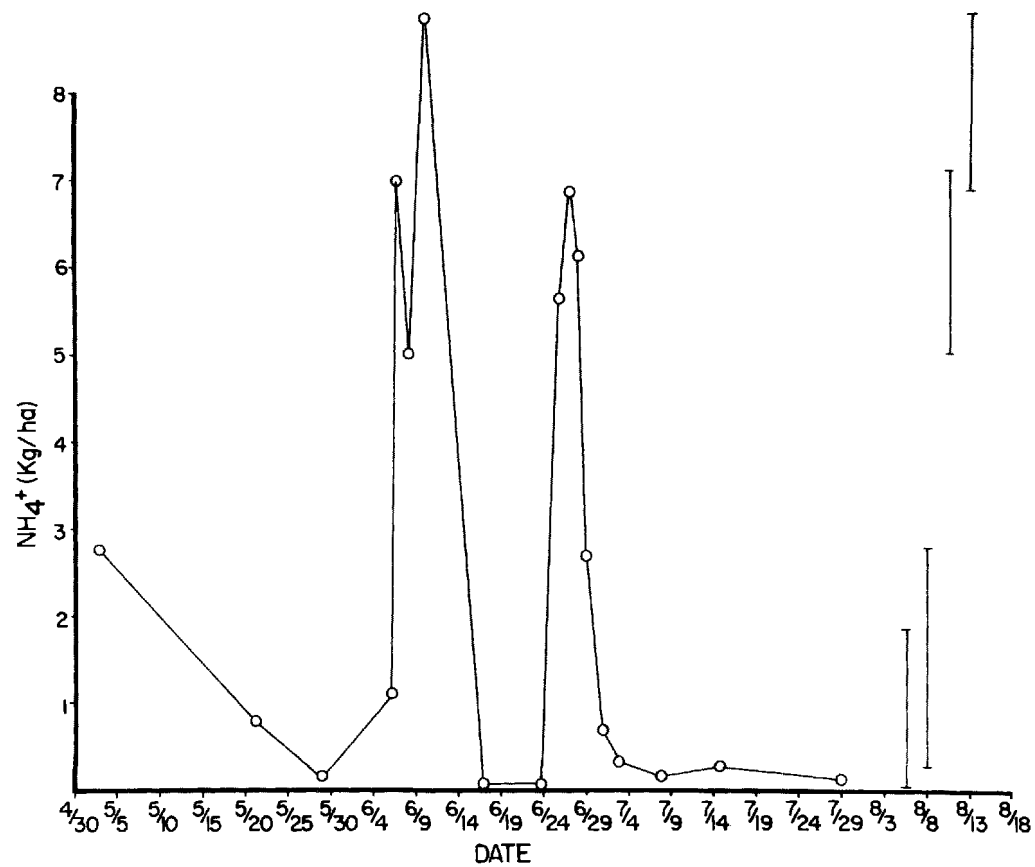


Figure 61. The amount of NH_4^+ per hectare in the floodwater during 1974. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

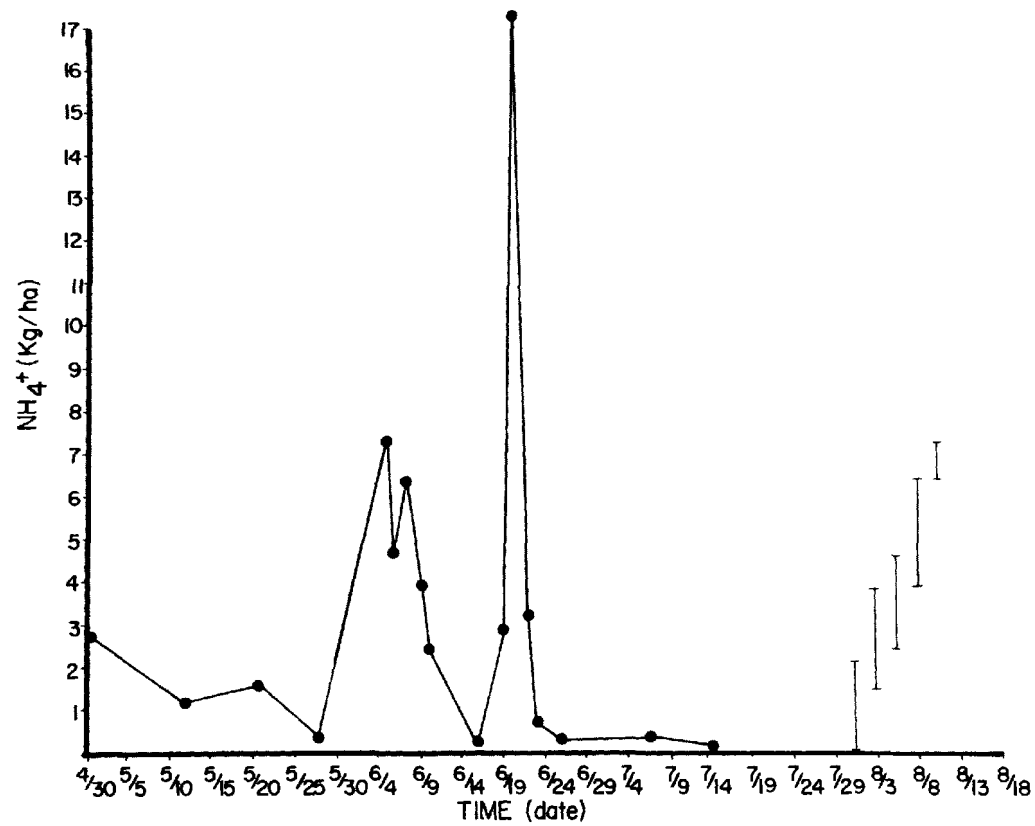


Figure 62. The amount of NH_4^+ per hectare in the flood water during 1975. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

statistically equivalent preflood and post flood peak plot water levels in 1974. The peak amounts per hectare at panicle differentiation were significantly greater than the peak following the applications made just prior to permanent flood in 1975. Thus, the more intimate contact of the NH_4 with the soil resulted in less NH_4^+ in the plot water.

Amounts of Ca^{++} and Na^+ in the plot water, although significant, did not reflect the quantities of NH_4 conserved in the soil following the preflood application in either 1974 or 1975 (Figures 63, 64, 65, and 66). This indicates that a considerable portion of the $(\text{NH}_4)_2\text{SO}_4$ solubilized on initiation of the permanent flood may have been washed by the wetting front in too deeply to affect amounts in the plot water. However, Ca^{++} and Na^+ in plot water following the panicle differentiation application generally reflect the difference between NH_4^+ applied and NH_4^+ in the plot water. For example, the amounts of $\text{Ca}^{++} + \text{Na}^{++}$ in the plot water were approximately 35 and 25 kg/ha in 1974 and 1975, respectively. Correspondingly, the difference between NH_4^+ applied and NH_4^+ in the plot water was 33 kg/ha in 1974 and 23 kg/ha in 1975. The comparison in kg/ha does not conserve charge but is reasonably accurate since the milliequivalent weights are similar.

The DMR indicated that Mg^{++} amounts per hectare corresponding to the peak levels for Ca^{++} and Na^+ were significant in 1975 (Figure 67), and may indicate some release by NH_4^+ . However, the insignificance of the 1974 data (Appendix G, Table G11) and the occurrence of a 22 cm rain on June 9, 1975, suggest that variations in the plot water concentration may have been induced by the higher background levels of the irrigation water (Figures 45 and 46). Similarly, Ca^{++} (Figures 43 and 44) and Na^+ (Figures 49 and 50) background levels in the irrigation water were higher in 1975 than in 1974. The influence of the irrigation supply is further evidenced by the fact that the irrigation treatment was highly significant in 1975 (Appendix G, Table G12). Continuous flow resulted in greater Mg^{++} levels than the impoundment irrigation scheme. The impact of NH_4^+ on the Mg^{++} levels is lessened even more when one considers that the application rate was not significant at a 5% level.

Generally, the irrigation management scheme employed significantly influenced the amount of cations in the plot water in 1974 and 1975 (Appendix G, Tables G7, G8, G9, G10, G11, G12, G13, and G14). The amounts of cations were higher under impoundment management in 1974. Conversely, the amounts were significantly lower in those plots under impoundment irrigation in 1975. The apparent anomaly in the results is actually consistent with cause and effect relationships previously discussed. Impoundment represents the more static system which entails less recharge of canal H_2O influx. Correspondingly, the impoundment irrigation scheme results in lower colloidal load, thereby lessening the absorptive capacity of the water. The heavy rains of 1975, however, tended to increase cationic concentrations of the background irrigation supply but dilute those released from the soil into the plots. The net result was an increase in cations for those plots under continuous flow irrigation management in 1975 following the return to normal irrigation schedules.

Ammonium levels were significantly affected by irrigation management in 1974 but not in 1975 (Appendix G, Tables G7 and G8). Impoundment resulted in higher levels with respect to time following application due to the low influx

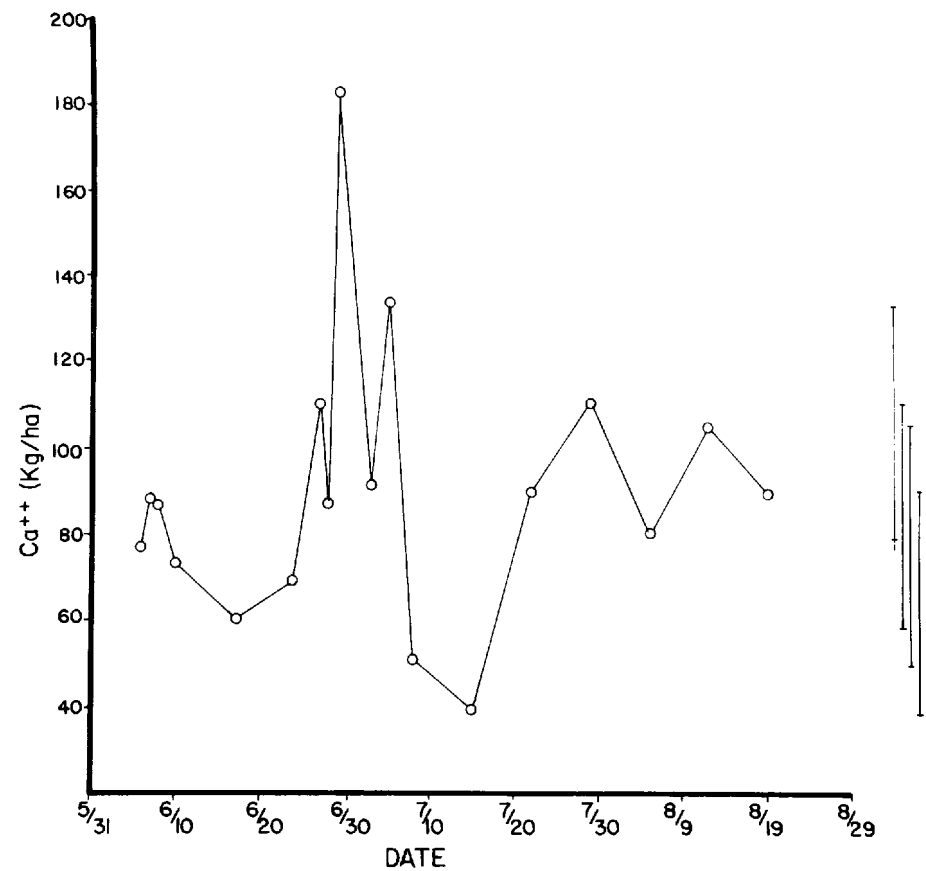


Figure 63. The amount of Ca^{++} per hectare in the floodwater during 1974. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

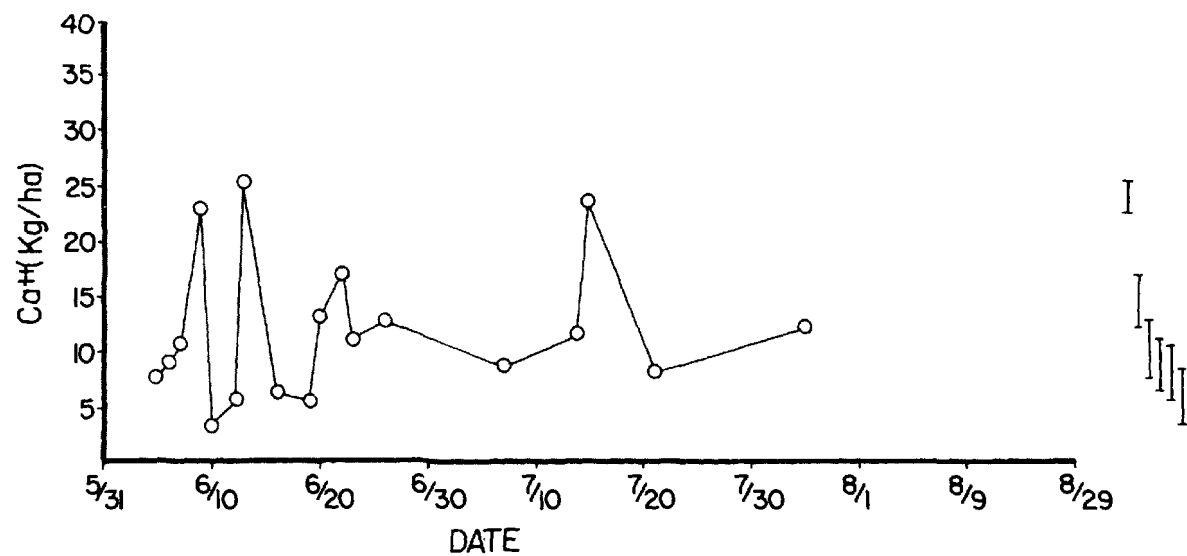


Figure 64. The amount of Ca^{++} per hectare in the floodwater during 1975. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

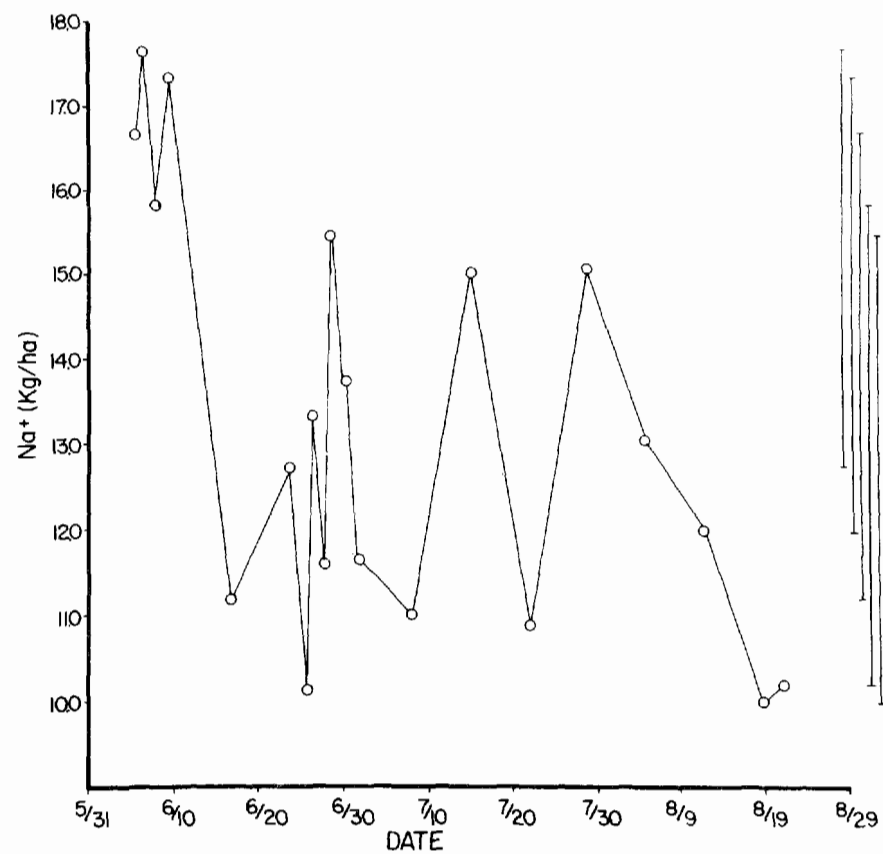


Figure 65. The amount of Na^+ per hectare in the floodwater during 1974. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

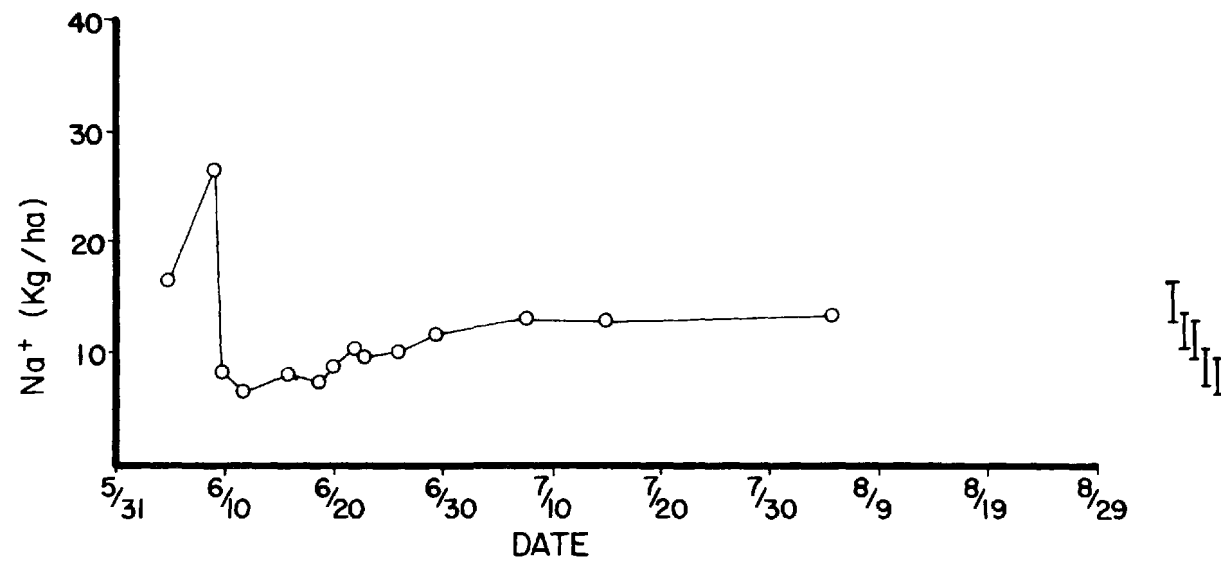


Figure 66. The amount of Na⁺ per hectare in the floodwater during 1975. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

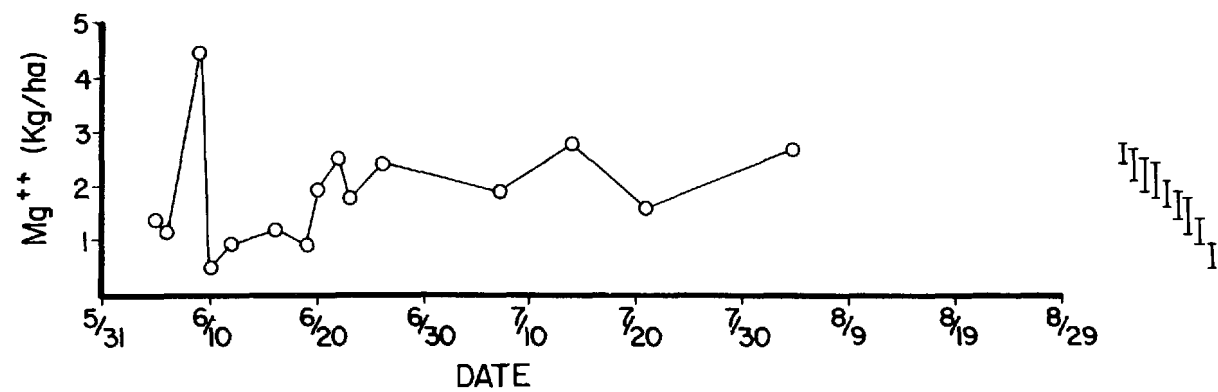


Figure 67. The amount of Mg^{++} per hectare in the floodwater during 1975. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

of colloids with the irrigation water compared to the continuous flow scheme. However, irrigation was not the factor in 1975 due to the dilution of NH_4^+ and colloids. The irrigation water was essentially free of NH_4^+ thus negating the infusion of NH_4^+ in the plots under continuous flow management, as noted for the other cations.

Fertilizer application rate generally had a highly significant effect on plot water cationic concentration variability. As one would expect, the excessive application rate resulted in greater amounts in the plot water.

Anions--

Analysis of variance, determined for $\text{SO}_4^{=}$, Cl^- and NO_3^- concentrations in the floodwater in 1974 and 1975, indicated significant variability between sampling dates both years (Appendix G, Tables G15, G16, G17, G18, G19, and G20). The excessive application rate resulted in significantly greater $\text{SO}_4^{=}$ and Cl^- levels than was found at the recommended rate in 1974 and 1975, but had no apparent affect on the amounts of NO_3^- either year. Generally, amounts of anions were significantly greater with time under the impoundment irrigation scheme in 1974. Weather and the narrower time interval between applications appeared to have negated the irrigation management affects in 1975, with the exception of Cl^- . Chloride levels were higher in the continuous flow plots in 1974, but then so was the irrigation supply levels.

A DMR test was employed to determine statistical significance of the anionic concentrations with respect to time. Significant peak amounts per hectare of $\text{SO}_4^{=}$ averaged over treatment blocks corresponded to the application of $(\text{NH}_4)_2\text{SO}_4$ (Figures 68 and 69). The amounts in the paddy water at panicle differentiation were either equivalent to or significantly greater than that applied preflood although twice as much was applied preflood (Table 18). Since Cl^- was only associated with the fertilizer applied preplant, peak levels corresponding to preflood and panicle differentiation fertilizer applications suggest a mechanism of displacement from soil solution to the floodwater by $\text{SO}_4^{=}$ (Figures 70 and 71). A significant peak was noted for NO_3^- following the preflood N topdressing (Figures 72 and 73). However, the NO_3^- peak may have been due to nitrification of NH_4^+ rather than displacement by $\text{SO}_4^{=}$ from soil solution. No corresponding increase in NO_3^- accompanied the second N topdress application. This was not unexpected since denitrification rates increase only under more favorable reducing conditions.

Salts in Soil Solution

As indicated in the section on soil solution sampling, the highly impermeable soil caused difficulty in obtaining an adequate solution sample. Where samples were obtained, the analyses varied tremendously within replications. Thus, inadequate sample volume and variability with replications made it difficult to obtain and interpret the data. The primary purpose of this phase was to evaluate nutrient losses by percolation through the soil. It was evident from the inability to obtain soil solution samples, and from the water balance studies that very little water moved below into the profile below the root zone.

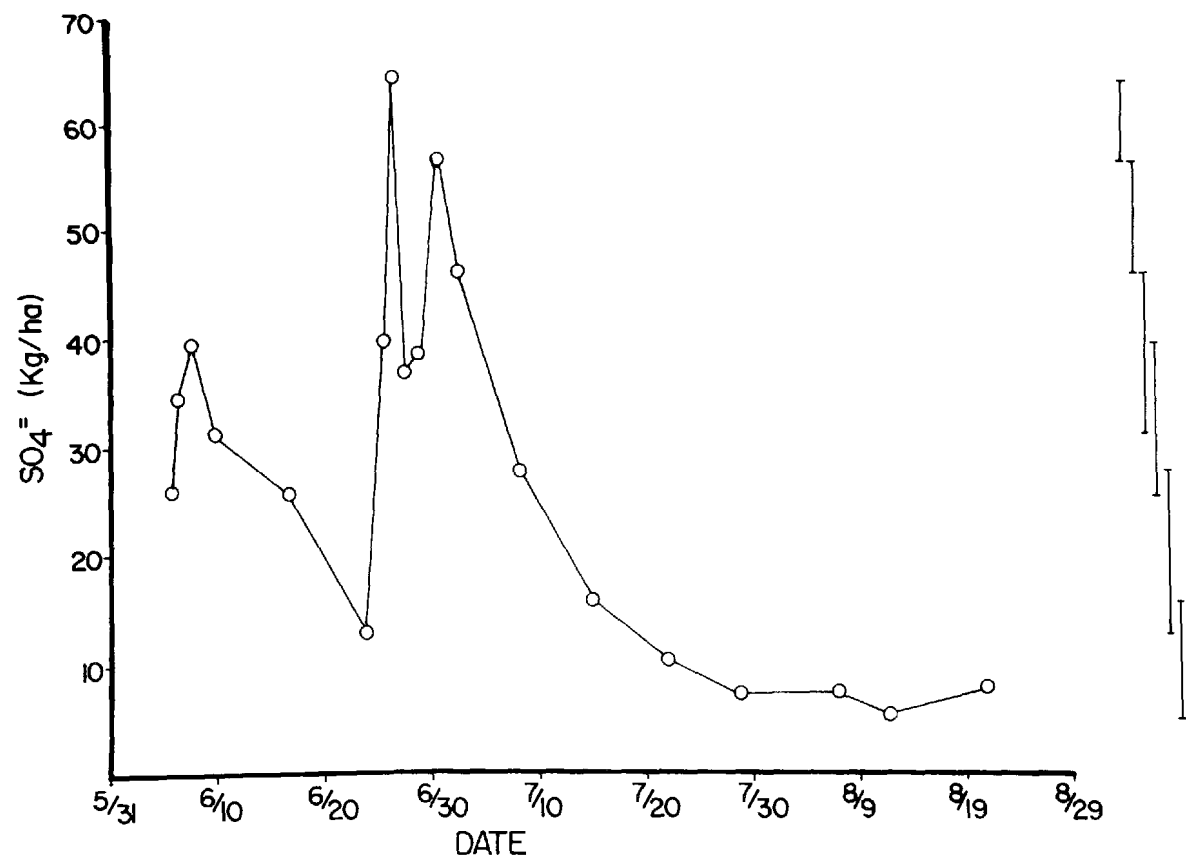


Figure 68. The amount of SO_4^{2-} per hectare in the floodwater during 1974. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

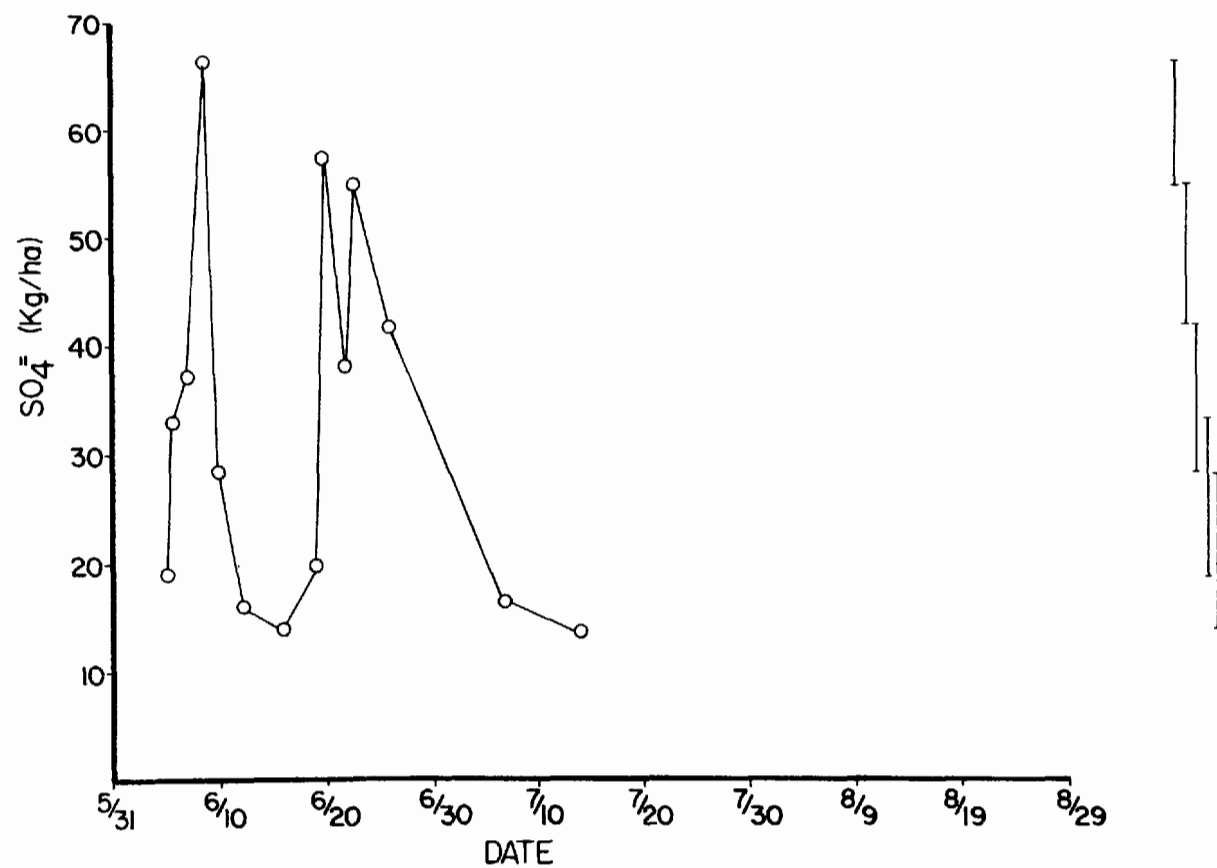


Figure 69. The amount of SO_4^{2-} per hectare in the floodwater during 1975. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

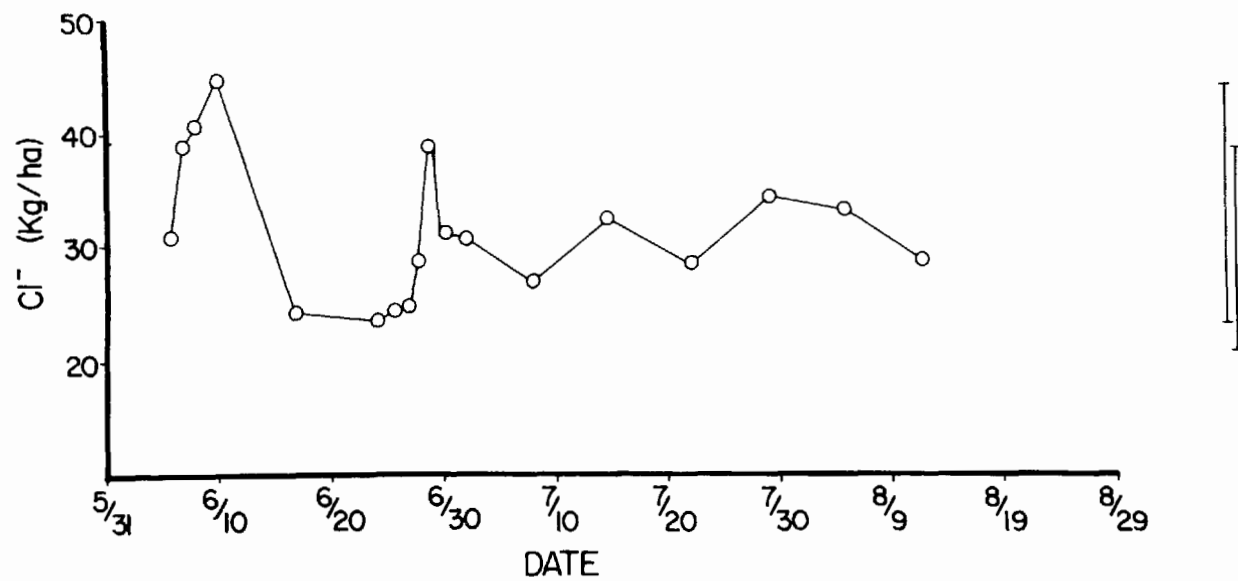


Figure 70. The amount of Cl^- per hectare in the floodwater during 1974. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

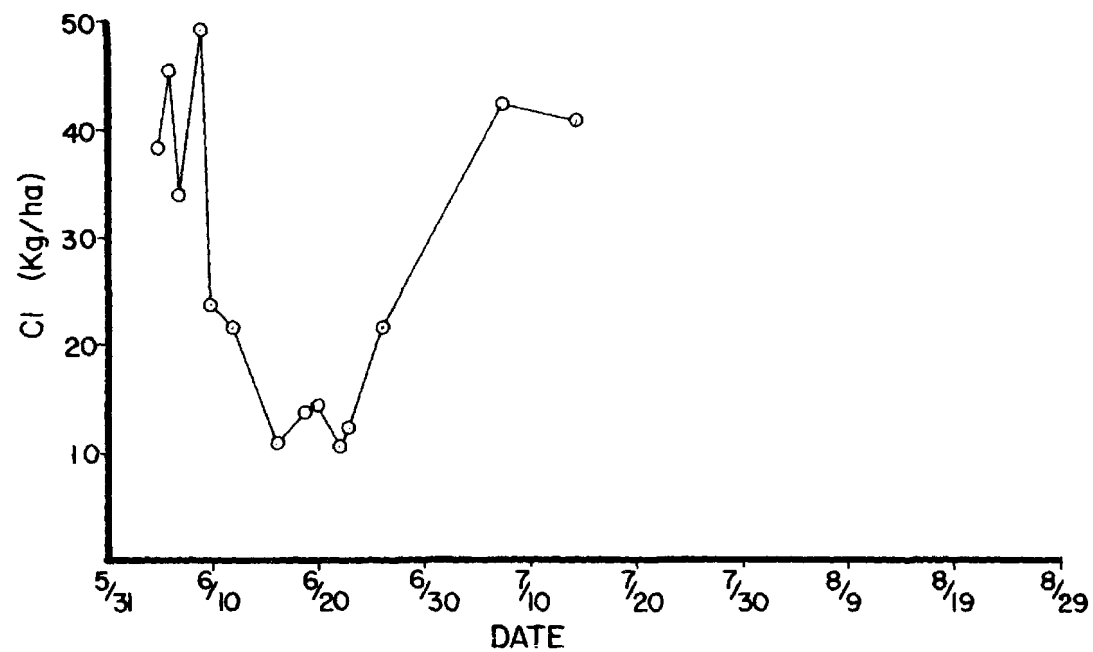


Figure 71. The amount of Cl^- per hectare in the floodwater during 1975. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

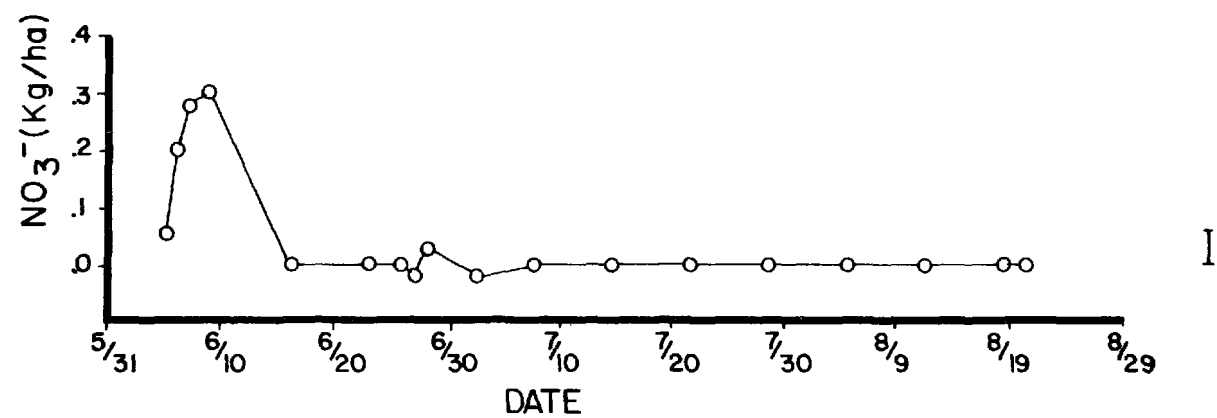


Figure 72. The amount of NO_3^- per hectare in the floodwater during 1974. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

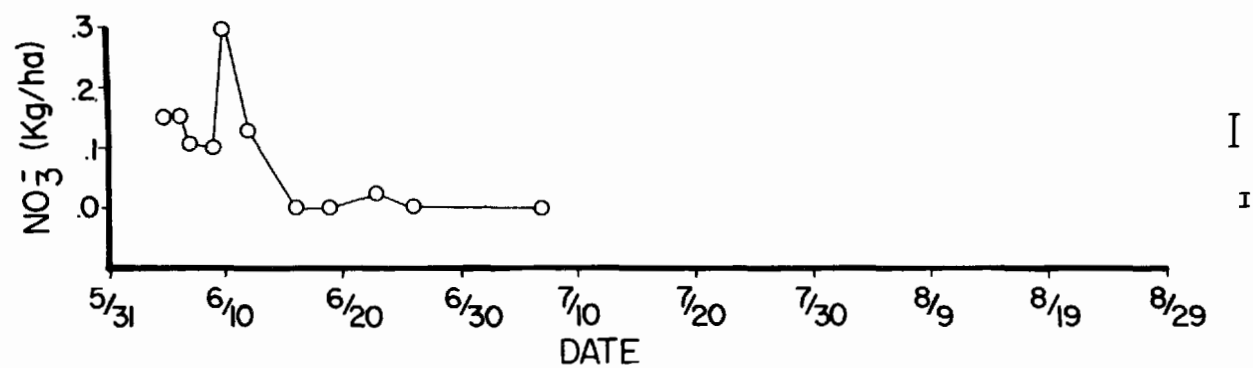


Figure 73. The amount of NO_3^- per hectare in the floodwater during 1975. The vertical bars represent the results of Duncan's Multiple Range Test at a 5% level of significance.

TABLE 18. ASSOCIATED IONS ADDED WITH FERTILIZERS
DURING THE THREE YEARS.

Growth stage of rice	Fertilizer element	Associated anion/cation	Associated ion added	
			Recommended rate	Excessive rate
Preplant	NH_4^+	$\text{SO}_4^{=}$	184	246
	K^+	Cl^-	16	64
	H_2PO_4	Ca^+	13	33
		$\text{SO}_4^{=}$	3	7
Preflood	NH_4^+	$\text{SO}_4^{=}$	184	246
Panicle Differentiation	NH_4^+	$\text{SO}_4^{=}$	92	121

Dialysis tubes containing distilled water were placed at 1 cm in each plot on the respective sampling dates, and allowed to equilibrate 24 hours to assess the NH_4^+ and NO_3^- levels of the soil solution in 1974 (Table 19). Calcium was measured in the dialysate in 1975 in addition to NH_4^+ and NO_3^- (Table 20). Soil solution concentrations generally reflect that of the bulk paddy water previously discussed. The higher $\text{NH}_4\text{-N}$ levels correspond to the preflood and panicle differentiation N topdressings. There was no discernible difference in the preflood application with respect to the amount applied, whereas the concentrations reflected the amounts applied at panicle differentiation. This indicates that much of the $\text{NH}_4\text{-N}$ applied preflood was leached below the soil solution - plot water equilibria level and/or tightly adsorbed by the soil. Ammonium levels 4 days after the first sampling period are much higher in 1975 compared to the same time interval in 1974. This may have been related to the interim 22 cm rain.

The averaged NO_3^- levels never exceeded 0.20 ppm indicative of low nitrification and high denitrification rates.

Calcium soil solution concentrations were similar in magnitude to that

TABLE 19. IONIC CONCENTRATION OF DIALYSATE AVERAGED WITHIN
TREATMENTS FOLLOWING THE 24-HOUR EQUILIBRATION
PERIOD IN TOP 1 CM OF THE SOIL IN 1974

Treatment*	Date	Ionic Concentration (ppm)	
		NH ₄ -N	NO ₃ -N
I ₁ R ₁	6/10/74	6.45	0.03
I ₁ R ₂		8.01	0.02
I ₂ R ₁		7.83	0.19
I ₂ R ₂		8.67	0.20
I ₁ R ₁	6/14/74	0.15	0.03
I ₁ R ₂		0.17	0.04
I ₂ R ₁		0.05	0.03
I ₂ R ₂		0.21	0.10
I ₁ R ₁	6/28/74	4.61	0.03
I ₁ R ₂		8.08	0.02
I ₂ R ₁		4.28	0.03
I ₂ R ₂		6.18	0.06
I ₁ R ₁	7/5/74	0.36	0.00
I ₁ R ₂		0.19	0.00
I ₂ R ₁		0.13	0.00
I ₂ R ₂		0.21	0.00
I ₁ R ₁	7/26/74	0.09	0.00
I ₁ R ₂		0.11	0.00
I ₂ R ₁		0.14	0.00
I ₂ R ₂		0.12	0.00

*I₁ and I₂ correspond to continuous flow and impoundment irrigation, respectively; R₁ and R₂ correspond to recommended and excessive application rate, respectively.

TABLE 20. IONIC CONCENTRATION OF DIALYSATE AVERAGED WITHIN
TREATMENTS FOLLOWING THE 24-HOUR EQUILIBRATION
PERIOD IN TOP 1 CM OF THE SOIL IN 1975

Treatment*	Date	Ionic Concentration (ppm)		
		NH ₄ -N	NO ₃ -N	Ca++
I ₁ R ₁	6/9/75	4.88	0.06	16.60
I ₁ R ₂		8.57	0.05	32.70
I ₂ R ₁		8.38	0.05	32.00
I ₂ R ₂		8.57	0.06	22.70
I ₁ R ₁	6/13/75	3.42	0.05	19.20
I ₁ R ₂		2.95	0.01	18.30
I ₂ R ₁		2.19	0.06	19.00
I ₂ R ₂		3.03	0.00	22.60
I ₁ R ₁	6/20/75	8.92	0.00	14.50
I ₁ R ₂		15.70	0.00	34.80
I ₂ R ₁		11.15	0.00	49.00
I ₂ R ₂		12.05	0.00	62.20
I ₁ R ₁	6/30/75	0.08	0.00	20.80
I ₁ R ₂		0.19	0.00	22.70
I ₂ R ₁		0.08	0.00	22.50
I ₂ R ₂		0.08	0.00	22.00
I ₁ R ₁	7/10/75	0.18	0.00	15.73
I ₁ R ₂		0.12	0.00	4.15
I ₂ R ₁		0.16	0.00	4.07
I ₂ R ₂		0.16	0.00	4.30
I ₁ R ₁	7/25/75	0.14	0.00	21.50
I ₁ R ₂		0.27	0.00	23.60
I ₂ R ₁		0.11	0.00	30.00
I ₂ R ₂		0.18	0.00	21.23

* I₁ and I₂ correspond to continuous flow and impoundment irrigation;
R₁ and R₂ correspond to recommended and excessive application rates,
respectively.

of the paddy water. Unlike NH_4^+ , Ca^{++} remained at a relatively high concentration up to the July 10, 1975 sampling date. The small, but frequent rain prior to this sampling date probably significantly curtailed the amount of irrigation water needed to maintain the desired plot depth. The July 25, 1975 sampling date was preceded by several canal water irrigations and the concentrations reflect that of the irrigation supply suggesting that the flux is from the water to the soil.

Salts in the Soil Samples

Surface soil samples were collected prior to the preplant fertilizer applications and following the rice harvest in 1973, 1974 and 1975. These were extracted and analyzed for NH_4^+ , Ca^{++} , Mg^{++} , Na^+ , K^+ , Cl^- , PO_4^{--} and NO_3^- (Table 21). Due to the accelerated water sampling schedule adopted early in the 1973 season, time did not permit processing the soil samples collected at the different soil depths. It was evident that the floodwater was not percolating through the soil profile, so efforts were directed towards analysis of the floodwater.

It is evident from the soil data obtained that the difference in CEC between soils used for the 1973 field experiment and that employed for the 1974 and 1975 field experiment, was largely reflected in the amounts of Ca^{++} in the soil. Furthermore, the salts were evidently adsorbed and not readily solubilized since the floodwater in no way reflected the magnitudes of salt in the soil. This is further substantiated by the rather tenuous equilibria between canal water and surface soil solution which fluctuated with comparatively small fertilizer inputs, rainfall, and the colloidal loads of the irrigation supply. The point being that the soil served more as a sink rather than as a source.

The rice plant must also be considered as a sink. Although yields were lower in the excessive rate plots in 1974 and 1975 (Table 22), the difference in fertility rates was small and could have been reflected in the vegetative matter produced. The lower rice yields incurred in the excessive rate plots during 1974 and 1975 may have been induced by the untimely application of an excessive rate of molinate. Flinchum et al. (1973) reported that 10 kg molinate/ha applied in the floodwater within 4 days of the panicle differentiation growth stage reduced yields by 1000 kg/ha. Yields were not affected in 1973 when molinate was applied 11 days prior to panicle differentiation. Correspondingly, there was a much greater net decrease in ionic soil constituency in the 1973 growing season, as indicated by the preplant and post-harvest analyses (Table 21).

Salt Balance

The water balance data was utilized with the electrical conductivity to calculate the overall salt balance for the two irrigation treatments from the time of seeding to the drainage at the end of the season. For purposes of the calculation, a conversion factor of 640 mg/l per 1000 μmhos was used. The salt load of each irrigation and all runoff was calculated for both continuous and impounded irrigation. The results are shown in Table 22.

TABLE 21. INORGANIC IONS EXTRACTED FROM THE 0-5 CM SURFACE SOIL SAMPLED PREPLANT
AND FOLLOWING THE HARVEST IN 1973, 1974, AND 1975

Sampling Date	Year	NH ₄ ⁺ ppm	Cationic Constituency				Anionic Constituency		
			Ca ⁺⁺ ppm	Mg ⁺⁺ ppm	Na ⁺ ppm	K ⁺ ppm	Cl ⁻ ppm	PO ₄ ppm	NO ₃ ⁻ ppm
Preplant	1973	10.78	6003	722	163	53.11	552.6	0.89	4.14
Post Harvest		7.35	5172	489	170	38.22	447.9	1.15	2.76
Preplant	1974	11.40	3840	487	228	126.00	144.0	1.43	0.90
Post Harvest		8.71	3900	660	276	112.00	193.0	1.28	0.90
Preplant	1975	7.14	3500	345	238	92.00	196.0	2.65	0.90
Post Harvest		5.83	3268	411	280	121.00	190.0	2.63	-

TABLE 22. SALT BALANCE DURING THE RICE GROWING SEASON DURING 1974 AND 1975.

Year	Irrigation technique	Salt applied in Irrigation water	Salt lost in runoff	Salt gained by flood
		kg/ha	kg/ha	kg/ha
1974	Impounded	528	559	-31
1974	Continuous	993	575	417
1975	Impounded	428	433	-5
1975	Continuous	712	587.9	124

During 1974, the rainfall was less, and the salt concentration in the irrigation water was greater than during 1975. During both years, the salt uptake and outflow for the impounded plots were nearly identical. More salt was applied to the impounded plots during 1974 than in 1975, but the greater concentration of salts in the runoff during 1974 resulted in more salt being removed from the impounded plots during 1975. The continuous flow plots received much more water than the intermittent irrigated plots during both years. Consequently, the amount of salt added to these plots was greater. A total of 993 kg/ha was applied during 1974 again as a result of the greater concentration of salts in the irrigation water. The salt loss in the outflow from the continuous flow plots during 1974 and 1975 was nearly identical, resulting in a net gain of 417 kg/ha during 1974 and 124 kg/ha in 1975. Individual runoff-producing storms during both years contributed significantly to the salt losses. The salt concentrations decreased sharply in the paddies during a heavy rain, but the large values of runoff conveyed large amounts of salt from the field. Rainfall induced runoff which occurred before the permanent flood was established, indicates that salt residues from irrigation could be removed from the fields in the runoff of a few storms each year.

Since more salt-bearing water is added to the continuous flow plots than is removed in the outflow during the growing season, it is apparent that this management practice could lead to excess salt in the soil during years which do not receive much rainfall between growing seasons. On the other hand, the concentrations of salts in the outflow from these plots are less and the water would more easily meet rigid quality standards. The final release water before harvesting carried only a small fraction of the cumulative salt lost during the entire season; therefore, termination of irrigation several weeks before harvest to minimize outflow from the fields would not greatly increase the salt residue in the field.

FATE OF PESTICIDES

Much has been done to elucidate the fate of several of the infamous chlorinated hydrocarbon pesticides in soils, aquatic environments, plants, and other bio-systems. Persistence has been measured in years for this class of pesticides, whereas persistence in most other classes of pesticides is measured in months or weeks (Kearney et al., 1969).

Perhaps a better indication of persistence is the half-life, or time required for a 50% decrease of the applied material. This is a better measurement of residue because many compounds degrade most rapidly at first, but may linger for a considerable period of time at insignificant levels. Johnson and Stansbury (1965) reported the half-life of carbaryl to be approximately eight days with complete degradation in 40 days. Tanji and his co-workers (1974) reported that molinate incorporated in dry soil persisted for only about three to five days in the subsequently applied flood water. However, molinate persisted in seepage waters in small quantities for at least four months.

The production of toxic metabolites upon degradation of the parent pesticide must also be considered when one evaluates persistence of some particular compound. Some metabolites can have a deleterious effect on non-target organisms more striking than the original pesticide (Corke and Thompson, 1970). Whatever the effect, metabolites can, under some conditions, extend the residual life of a pesticide (Burge, 1972; Chisaka and Kearney, 1970; Karinen et al., 1967).

There are several modes by which the bioactivity of a pesticide is diminished in a target zone. They include: volatilization, leaching, adsorption by soil colloids, chemical alteration or decomposition, microbial degradation, and absorption by non-target organisms (Bailey and White, 1970; Edwards, 1966; Newman and Downing, 1958; Reed and Orr, 1943; Valentine and Bingham, 1974). These processes interact creating very complex systems by which pesticides are dissipated. Due to the complexity of the systems, pathways of degradation are very difficult to elucidate, making it very difficult to predict how a compound will react under a given set of conditions.

Volatilization is generally important for those chemicals with vapor pressures greater than 10^{-3} mm Hg at room temperature (Weber, 1972). Variables affecting volatility are soil moisture, formulation, wind speed, turbulence, temperature, and time (Farmer et al., 1972). Other processes such as adsorption, greatly affect volatility (Ashton and Sheets, 1959).

Leaching of pesticides is of particular importance in sandy soils low in organic matter. High solubilities in water and low adsorptivities are characteristics of compounds susceptible to leaching (Newman and Downing, 1958).

Bailey and White (1970) reported that soil adsorption was largely dependent upon the properties of the adsorbate molecule. Some of these properties are: acidity or basicity (pK_a or pK_b), water solubility, molecular size, and polarizability. However, the clay and organic humus fraction gen-

erally determines the adsorptive capacity of a soil. Martin and Haider (1971) reported that humic acid is generally the most important constituent of soil humus. Several authors (Bartha, 1971; Chisaka and Kearney, 1970; Getzin, 1973; Helling et al., 1971; Kazano et al., 1972; Martin and Haider, 1971) have related adsorption to the humus fraction of the soil. They have demonstrated that an actual chemical bond may be formed between the carboxyl group of humic acids and the adsorbate molecule. While an important mechanism in soils in general, many soils have very low organic matter content limiting its impact on the total amount adsorbed. These soils would favor adsorption by the clay fraction of the soil. Amounts adsorbed in the clay fraction are governed largely by the total percentage of clay and dominant clay minerals. Clay minerals are comprised mainly of 1:1 and 2:1 type clays. The 1:1 type clays (e.g. kaolinites, halloysites) are comprised of an octahedral sheet and a tetrahedral sheet. They are characterized as non-expanding, low in cation exchange capacity (CEC) and low in total surface area. The 2:1 type clays (e.g. micas, vermiculites, montmorillonites) are comprised of an octahedral sheet sandwiched between two tetrahedral sheets. They are characterized by their higher CEC and higher surface area. Some are classed as expanding, such as the montmorillonites, while others are non-expanding such as the micas. The vermiculites are intermediate in that they do expand to some degree but not nearly as much as montmorillonites. Perhaps the most important property with respect to adsorbance is their well defined interlayer spacing. Swoboda and Kunze (1968) have shown that there are different types of sites available for adsorption of organic molecules at the surface of clays. Much of the surface of 2:1 clays is exposed within the associate interlayer. A small interlayer spacing could exclude large pesticide molecules from a considerable portion of the available adsorption sites, due to steric hindrances.

Weber (1972) defined a distribution coefficient for adsorbance of pesticides in the two phase soil:water system as given in the equation below:

$$K_d = \frac{\text{amount adsorbed/kg of soil}}{\text{amount in solution/liter}} \quad (3)$$

He pointed out that this was a relative value certainly dependent upon the available sites, competition of water for the sites, concentration of the adsorbate, and other chemical and physical properties. Generally, a large K_d value indicates removal of the pesticide from solution by adsorbance to soil colloids.

Adsorbance is integrally related to microbial degradation of pesticides in that it tends to reduce the amounts available for degradation, particularly when a compound is chemisorbed in the interlayer or bonded to the organic fraction (Bartha, 1971; Chisaka and Kearney, 1970; Karinen et al., 1967; Swoboda and Kunze, 1968). Newman and Downing (1958) and Edwards (1966) reported that loss rate of pesticides following application was rapid at first due to overlapping processes of volatilization, leaching, adsorption, etc., but that in the long term the loss rate was principally due to microbial decomposition.

Microbial degradation is a very complex process influenced by many

variables. Aldrich (1953) reported that small differences within the structure of otherwise similar pesticides affected microbial degradation. Other authors (Audus, 1951; Engvild and Jensen, 1969; Newman et al., 1952; Patrick and Mikkelsen, 1971) have demonstrated that previous treatment with a particular pesticide affected the microbial decomposition rate of succeeding treatments. Newman and his co-workers (Newman et al., 1952) showed that the enrichment effect can carry over from one year to the next. Generally, microbial decomposition increases with temperature, substrate level, and moisture increases. As the soil becomes saturated with water, a condition created by flooding in rice culture, the biological activity changes. Patrick and Mikkelsen (1971) have demonstrated that flooding quickly reduces the oxygen content of the soil, since the diffusion of oxygen in air is much greater than its diffusion in water. The oxygen profile in a flooded soil is given in Figure 74. As the redox potential decreases in the soil, the aerobic bacterial count decreases, and the anaerobic bacteria count increases. Generally, any treatment to the flooded soil that stimulates microbial activity tends to decrease the oxygen content even more, resulting in lower redox potentials. This could reduce the oxidized layer at the surface of the soil shown in Figure 74. Numerous changes occur in the chemical nature of the flooded soil and perhaps the most important with respect to pesticides, is the change in soil reaction. Acid soils become neutral to slightly alkaline, and alkaline soils tend toward a neutral pH after submergence. Soil reaction has been shown to greatly affect the process of chemical alteration (Caro et al., 1973; Wauchope and Haque, 1973). According to Faust (1964), photodecomposition would be insignificant under flooded soil conditions due to the scattering of ultraviolet light by the water and suspended colloids.

Propanil

Propanil (3',4'-dichloropropionanilide) is a postemergence herbicide used in rice cultivation to control barnyardgrass and other annual weeds (Hodgson, 1971; Smith, 1965). Several researchers have shown that biological degradation is the principal mode of dissipation of propanil from soils (Bartha et al., 1967; Bartha and Prammer, 1967; Bordeleau and Bartha, 1972a; Burge, 1972; Burge, 1973; Plimmer et al., 1970; Rosen and Siewierski, 1971). Two toxic metabolites, DCA (3,4-dichloraniline) and TCAB (3,3',4,4'-tetrachlorazobenzene); are formed from the biological degradation of propanil (Bartha and Prammer, 1967; Corke and Thompson, 1970; Weisburger and Weisburger, 1966). Propanil is biologically hydrolyzed to the aniline moiety and further transformed to TCAB. Other complex products derived by the metabolism of chloranilines have been isolated in soil cultures under laboratory conditions (Plimmer et al., 1970; Rosen and Siewierski, 1971). However, TCAB is the only complex aniline derivative isolated from field soils treated at normal application rates of propanil (Kearney et al., 1970).

Bordeleau and Bartha (1972a and b) determined that the biological transformations of propanil involved microorganisms with peroxidase and aniline oxidase enzymatic activity. Peroxidase was found to have the greatest effect in soil cultures. The occurrence of substantial cell-free peroxidases in natural soils has been documented (Bartha and Bordeleau, 1969). Burge (1973) reported that propanil could be converted to TCAB, and that the condensation of two DAC molecules to TCAB was not necessarily dependent upon peroxidase

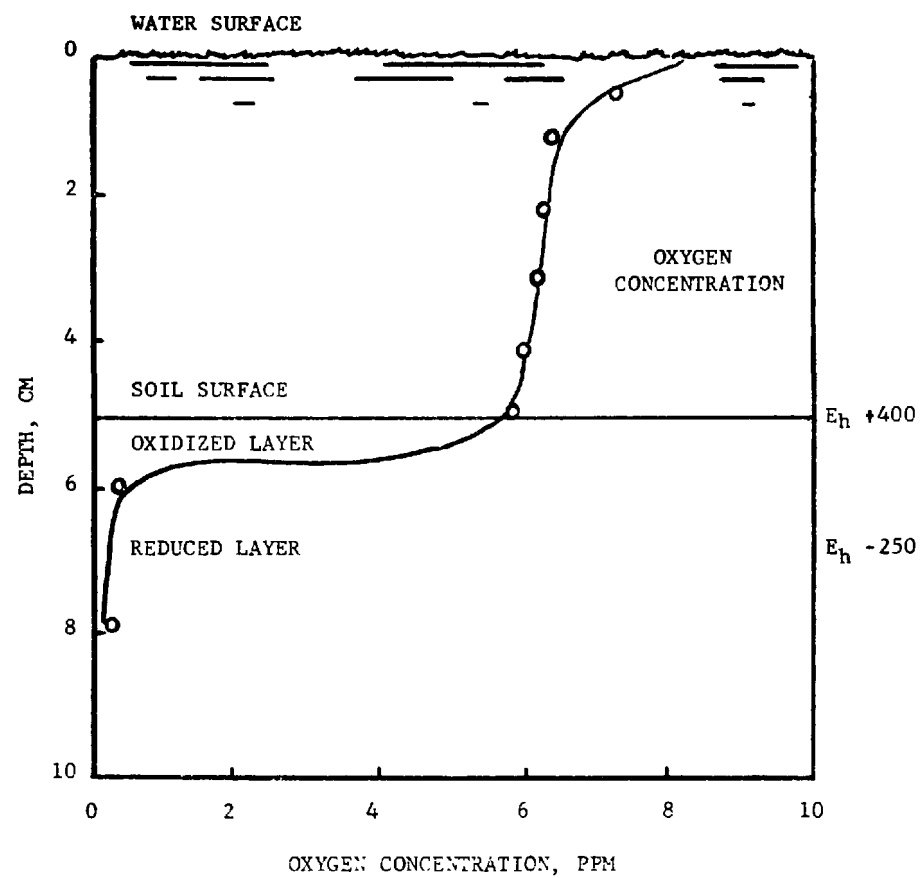


Figure 74. Oxygen profile in flooded soil [Patrick and Mikkelsen (1971)].

activity.

Chisaka and Kearney (1970) recovered a maximum of 41% of the activity from soils treated with ^{14}C -labeled DCA. They concluded that binding with soil components depended on the soil type as well as the physical-chemical nature of the chloraniline. Others (Bartha, 1971; Chisaka and Kearney, 1970; Kearney et al., 1970) have reported difficulty in recovering DCA from the soil, indicating that adsorption is an important reaction involving chloranilines and pathways of degradation.

Considerable work has been done to elucidate the nature of propanil residues in soils under aerobic conditions, and it has been found that acyl-anilides are generally bio-degraded rapidly in soils (Bartha, 1971; Burge, 1972; Chisaka and Kearney, 1970; Helling et al, 1971; Kearney et al., 1970; Plimmer et al., 1970). However, it is not known what effect anaerobic conditions of a flooded soil regime may have on the half-life of propanil or its toxic metabolites. Bordeleau and Bartha (1972a and b) demonstrated that the oxygen content has a pronounced effect on the peroxidase and aniline oxidase enzymatic activity. Also, it is not known to what extent the heavy montmorillonitic clay soils common to the Texas rice belt would affect the degradation of propanil, or if irrigation management practices currently employed would affect degradation rates. The extremes in irrigation management practices are impoundment (a static condition) and continuous flow systems.

Residue Levels in the Paddy Water--

Concentrations of propanil in the plot water sampled in 1973 indicated that it was dissipated within 24 hours following the flood application (Table 23). Propanil was not detected in the 48-, 96-, and 152-hour water samples. A more rigorous sampling schedule was employed in 1974 and 1975 to determine the rapidity with which propanil was dissipated in the plots (Tables 24 and 25). The data were normalized to kg/ha to eliminate the influence of variable plot water depths and impaired any meaningful statistical interpretation of the results.

Analyses of variance for the 1973, 1974 and 1975 data indicated that time had a significant effect upon the concentration of propanil in the plot water. A Student-Newman-Keul's range test (Steel and Torrie, 1960) as employed to determine the statistical significance between average concentrations with respect to time for the 1974 and 1975 data (Tables 24 and 25). Although the propanil concentration was about constant or increased over the first 12 hours, it did not persist at significant levels 24 hours following the flood application. A zero residue level was used as the lower limit of the range test in computing the persistence at 24 hours alluded to in the above statement.

The concentration of propanil was generally higher in those plots which received the 6.8 kg/ha treatment. Differences between the normal and excessive rates were significant at the 1% level in 1974 and 1975.

Analyses of variance did not reflect discernible differences between the irrigation schemes tested. This was probably due to the rapidity with which propanil was dissipated from the flooded rice plots. No first order inter-

TABLE 23. PROPANIL RECOVERED IN WATER FROM TREATED RICE PLOTS
SAMPLED 0 AND 24 HOURS FOLLOWING THE FLOOD IN 1973

<u>Treatments</u>		<u>Hours Following Flood</u>	
Water mgt.	kg/ha propanil	0	24
		kg/ha†	
Impounded	3.4	1.608	0.001
Impounded	6.8	2.210	0.001
Flowing	3.4	1.442	0.002
Flowing	6.8	2.343	0.002
Experiment Ave*†SNK(p=2), 0.692		1.901 _a	0.002 _b

†Values represent mean of three replications.

*†Averages over entire experiment not followed by the same letter are significantly different at the 5% level using a Student-Newman-Keul's range test.

TABLE 24. PROPANIL IN WATER FROM TREATED RICE PLOTS SAMPLED 0, 3, 6,
12 AND 24 HOURS FOLLOWING THE FLOOD IN 1974

<u>Treatments</u>		<u>Hours Following Flood</u>				
Water mgt.	kg/ha propanil	0	3	6	12	24
		kg/ha†				
Impounded	3.4	0.136	0.070	0.041	0.167	0.008
Impounded	6.8	0.330	0.242	0.249	0.105	0.008
Flowing	3.4	0.078	0.090	0.087	0.091	0.011
Flowing	6.8	0.322	0.249	0.236	0.241	0.005
Experiment Ave*†SNK(p=5) 0.113		0.217 _a	0.163 _a	0.153 _a	0.151 _a	0.008 _b

†Values represent mean of three replications.

*†Averages over entire experiment not followed by the same letter are significantly different at the 5% level using a Student-Newman-Keul's range test.

TABLE 25. PROPANIL RECOVERED IN WATER FROM TREATED RICE PLOTS
SAMPLED 0, 3, 6, 12, AND 24 HOURS FOLLOWING THE FLOOD IN 1975

Treatments		Hours Following Flood				
Water mgt.	kg/ha propanil	0	3	6	12	24
		kg/ha†				
Impounded	3.4	0.817	0.176	1.267	0.822	0.061
Impounded	6.8	1.036	1.203	1.310	1.671	0.056
Flowing	3.4	0.440	0.466	1.327	0.989	0.075
Flowing	6.8	1.108	1.036	2.525	2.306	0.208
Experiment Ave*† SNK(p=5) 0.560		0.850 _a	0.720 _a	1.607 _b	1.447 _b	0.100 _c

†Values represent mean of three replications.

*† Averages over the entire experiment not followed by the same letter are significantly different at the 5% level using a Student-Newman-Keul's range test.

actions involving time, application rate and/or irrigation scheme were found to be statistically significant, although these sources of variation were extracted from the error term. Hierarchical interactions involving replications were not subtracted from the error term since differences between replications were not found to be significant.

Propanil recovered from the rice foliage just prior to flooding was linearly correlated to that recovered in the water just after flooding in both 1974 and 1975 (Figures 75 and 76). The amount of propanil in the plot water in 1974 (Table 24) was considerably lower than in 1973 and 1975 (Tables 23 and 25). The lower values in 1974 were attributed in part to the 0.63-cm rain, which washed the propanil from the plants about five hours following application. Propanil, which was washed from the foliage samples collected prior to flooding and 24 hours after the application, was significantly lower than that washed from the foliage immediately following the spray in 1974 (Table 26). Differences were not detected in 1975 at the corresponding time interval (Table 27). Not all of the propanil dissipated from the foliage between the two sampling periods in 1974 can be attributed to the rain, since a 28% decrease in concentration was found on the foliage sampled within the plot frames which were protected from rain (Figure 77). There was an additional 52% decrease in the amount of propanil recovered in the foliar rinses over the next four days, during which no rain reached the plots. The analysis of variance of the foliar data in the 1975 experiment indicated that the propanil concentrations were not significantly different at a 5% level between the two sampling periods (Table 27).

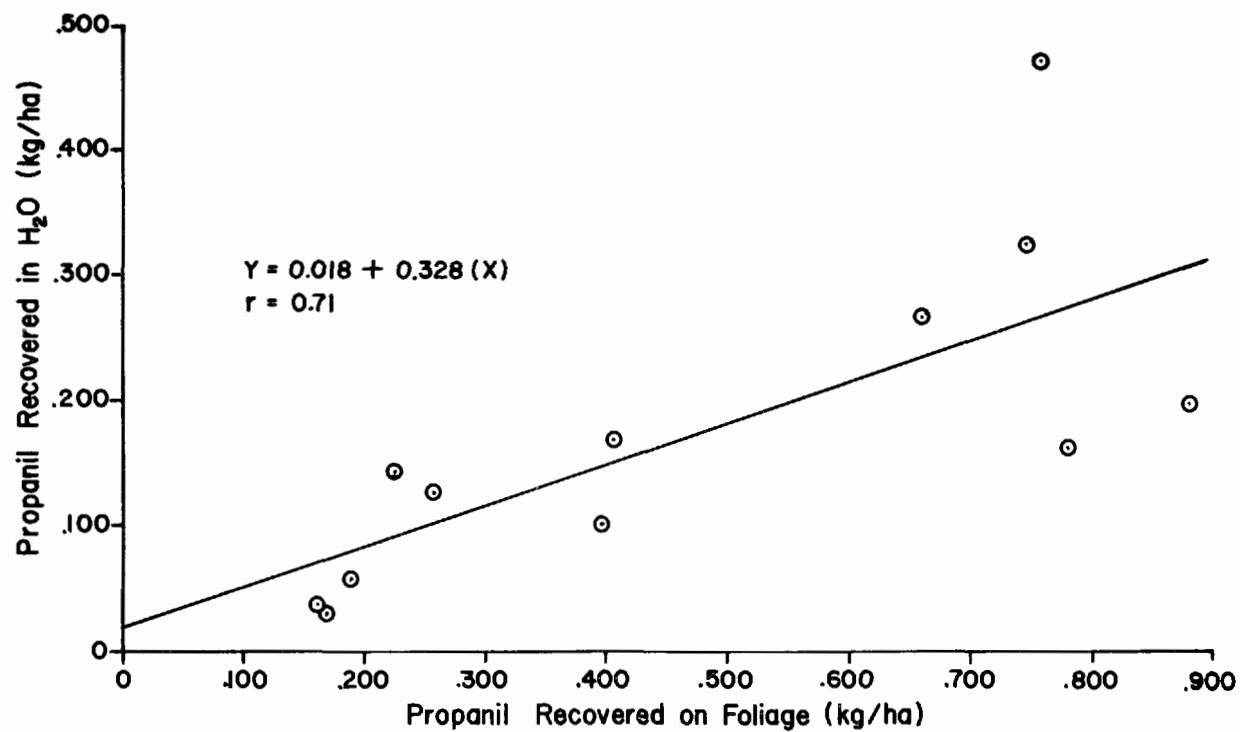


Figure 75. Propanil recovered in the water immediately following the flood as affected by the adsorbed foliar concentration prior to the flood application in 1974.

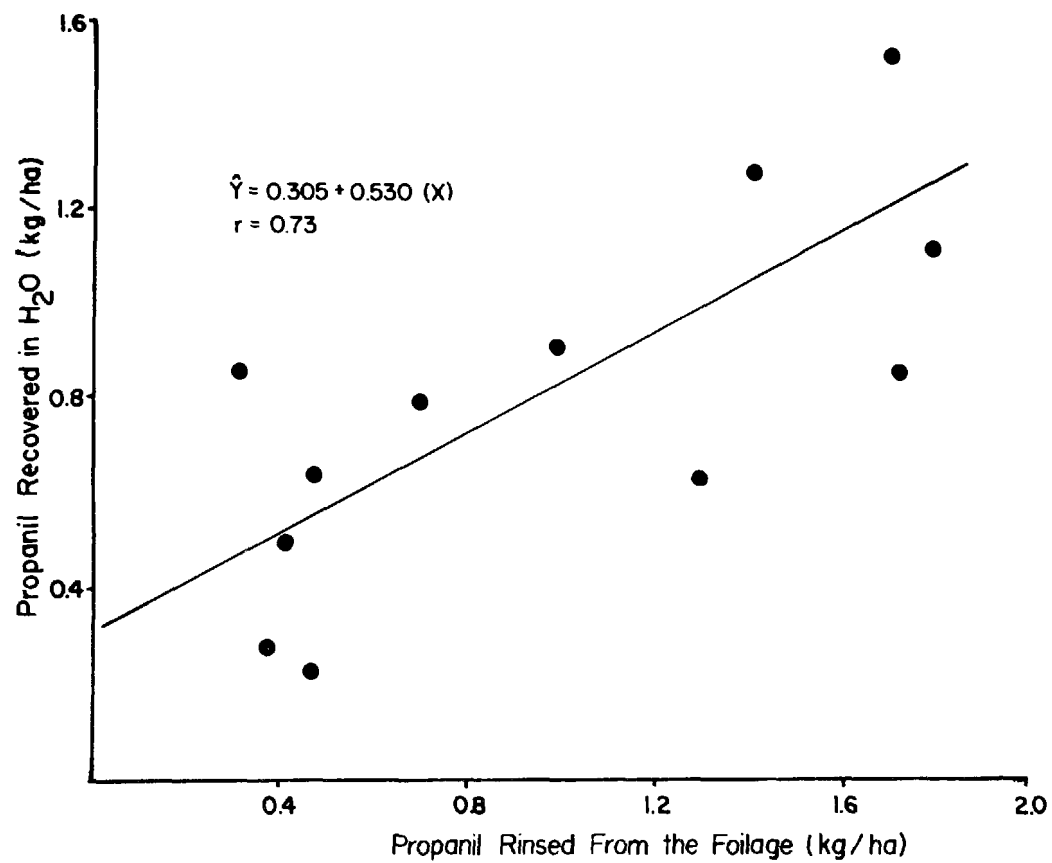


Figure 76. Propanil recovered in the water immediately following the flood as affected by the adsorbed foliar concentration prior to the flood application in 1975.

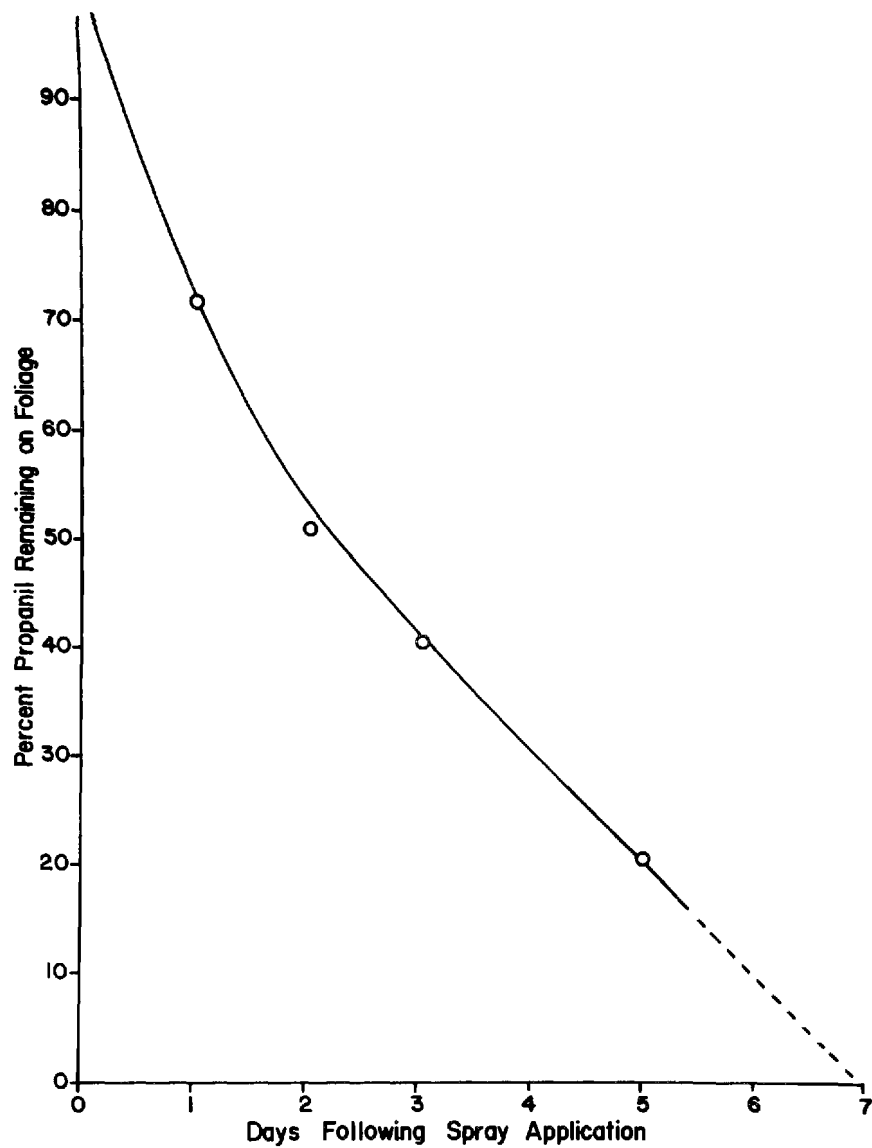


Figure 77. Percent propanil remaining on rice foliage sampled in protected plots at 0, 1, 2, 3, and 5 days following the application.

TABLE 26. PROPANIL RECOVERED ON FOLIAGE SAMPLED FROM TREATED RICE PLOTS
0 AND 24 HOURS FOLLOWING APPLICATION IN 1974

Water mgt.	Treatments kg/ha propanil	Hours Following Application	
		0	24
		kg/ha†	
Impounded	3.4	0.609	0.213
Impounded	6.8	1.599	0.601
Flowing	3.4	0.636	0.254
Flowing	6.8	1.902	0.806
Experiment Ave* SNK (p=2) 0.272		1.582 _a	0.625 _b

†Values represent mean of three replications.

* Averages over entire experiment not followed by the same letter are significantly different at the 5% level using a Student-Newman-Keul's range test.

TABLE 27. PROPANIL RECOVERED ON FOLIAGE SAMPLED FROM TREATED RICE PLOTS
0 AND 24 HOURS FOLLOWING APPLICATION IN 1975

Water mgt.	Treatments kg/ha propanil	Hours Following Application	
		0	24
		kg/ha†	
Impounded	3.4	0.453	0.433
Impounded	6.8	1.930	1.233
Flowing	3.4	0.590	0.333
Flowing	6.8	1.483	1.306
Experiment Ave* SNK (p=2) .360		1.114 _a	0.826 _a

† Values represent mean of three replications.

* Averages over entire experiment not followed by the same letter are significantly different at the 5% level using a Student-Newman-Keul's range test.

The trend indicated a decrease with time. Foliar absorption probably accounts for the losses where rain was not a factor. Absorption studies in rice and other plants support this as a plausible explanation. Propanil absorbed by the plants would not have been washed off by the foliar rinses.

The quantity of propanil remained nearly constant during the first 12 hours following the flood in 1974 (Table 24). A statistically significant increase in propanil was found between the experimental averages computed for the three hour and six hour water samples in 1975 (Table 25). The increase corresponded to a statistically significant increase in plot water depth during the 12 hours following flooding (Table 28). Continuous flow plots were flooded to a greater depth in 1975 to further investigate the influence of plot water depth on the amounts rinsed from the foliage. The higher flood levels resulted in higher propanil concentrations at the 24 hour sampling period within the same application rate, although the differences were not significant at the 5% level (Table 25).

TABLE 28. AVERAGE PLOT DEPTHS WITHIN TREATMENT BLOCKS
WITH RESPECT TO TIME IN 1975

<u>Treatments</u>		<u>Plot Depth</u> <u>Hours Following Flood</u>				
Water mgt.	kg/ha propanil	0	3	6	12	24
				cm		
Impounded	3.4	11.92	11.52	11.34	11.22	10.80
Impounded	6.8	11.06	10.62	10.40	10.32	9.77
Flowing	3.4	10.86	12.71	14.44	17.21	15.15
Flowing	6.8	12.52	13.62	15.06	17.28	17.47
Experiment Ave*SNK (p=5) 2,10		11.59 _a	12.12 _{ab}	12.81 _{ab}	14.01 _b	13.29 _{ab}

*Averages over the entire experiment not followed by the same letter are significantly different at the 5% level using a Student-Newman-Keul's range test.

Approximately 82% of the 6.8 kg/ha propanil application was recovered on the soil and foliar surfaces sampled from the border plot immediately following the spray application in 1974. Propanil recovered on the soil surface and foliar canopy was 3.5 and 2.1 kg/ha, respectively. The low levels of propanil recovered in the water immediately following the flood (Table 24) suggests little contribution from that which had been sprayed onto the soil surface and that which had been washed onto the soil surface by the rain.

This is substantiated by the low numerical value of the Y intercept obtained from the linear regression of propanil recovered on the rice foliage and that recovered in the flood water in 1974 (Figure 75). The very dry soil surface conditions, which occurred at the time of propanil application in 1975, may have retarded its dissipation since more than 50% of that intercepted by the soil surface remained in the 0.0 to 0.5 cm soil samples collected 20 hours after the application (Figure 78). The Y intercept for the linear regression of propanil recovered in the water was 0.31 kg/ha (Figure 76) which was substantially larger than the corresponding value for the 1974 data. This indicates that soil-borne propanil may have contributed significantly to the flood water concentration in 1975.

Propanil was not detected in the soil samples collected at 2.5 to 5.0 and 17.5 to 20.0 cm depths 24 hours following the flood water application.

Residue Levels of Metabolites--

DCA--DCA could not be quantitatively recovered from fortified soil and canal water samples using the following extractants: 95% ethanol, benzene, hexane, acetone, acetone-water, dichloromethane, diethyl ether, and combinations of the above. However, the chromatograms of 1:1 acetone:benzene extracts for propanil showed that a small peak, analogous to the retention time of the DCA standard, occurred in all of the 24-hour water samples in 1973 and 1974.

A steam distillation technique for DCA analyses in soil and water was developed prior to the 1975 experiment. The distilling apparatus consisted of a Friedrichs condenser equipped with a 34/45 ground glass joint and an accompanying 750 erlenmeyer flask. A 10-g soil sample and 150 ml of water was added to the flask, followed by 30 ml 6 N KOH. It was necessary to add 150 ml distilled water to the soil samples. The sample flask, with attached condenser, was heated on a combination magnetic stirrer-hot plate until 100-ml distillate was collected. The distillate was extracted with three, 25-ml volumes of hexane. Extracts were combined, dehydrated with anhydrous Na₂SO₄ and reduced to a suitable volume for GC analysis. Generally 100% of the DCA was recovered from fortified canal water samples. DCA recovered from fortified soil samples ranged between 91 and 100%.

The above method may not be suitable for soils and water levels with appreciable propanil levels. Burge (1973) employed an alkaline hydrolysis to convert propanil to DCA in the procedure he used for propanil analysis. Interference from propanil was indicated in the present study. The mean DCA concentration (Figure 78) of the surface soil samples collected from the six high rate plots immediately following the propanil application, was 32 ppm, or 20 ppm when the background level was subtracted. The propanil concentration determined on separate sub-samples was 58 ppm. This suggests that DCA was 34% contaminant of the spray formulation relative to the propanil concentration. Laboratory analysis of the propanil formulation used in 1975 showed DCA to be less than a 2% contaminant. No attempt was made to remove propanil prior to the DCA steam distillation procedure. It appears that the alkaline conditions of the procedure employed resulted in a 32% conversion of propanil to DCA. The mean DCA concentration (Figure 78) reported for the soil sediment sampled 24 hours after the flood was valid, since very little propanil was present in the sample to interfere with the DCA analysis.

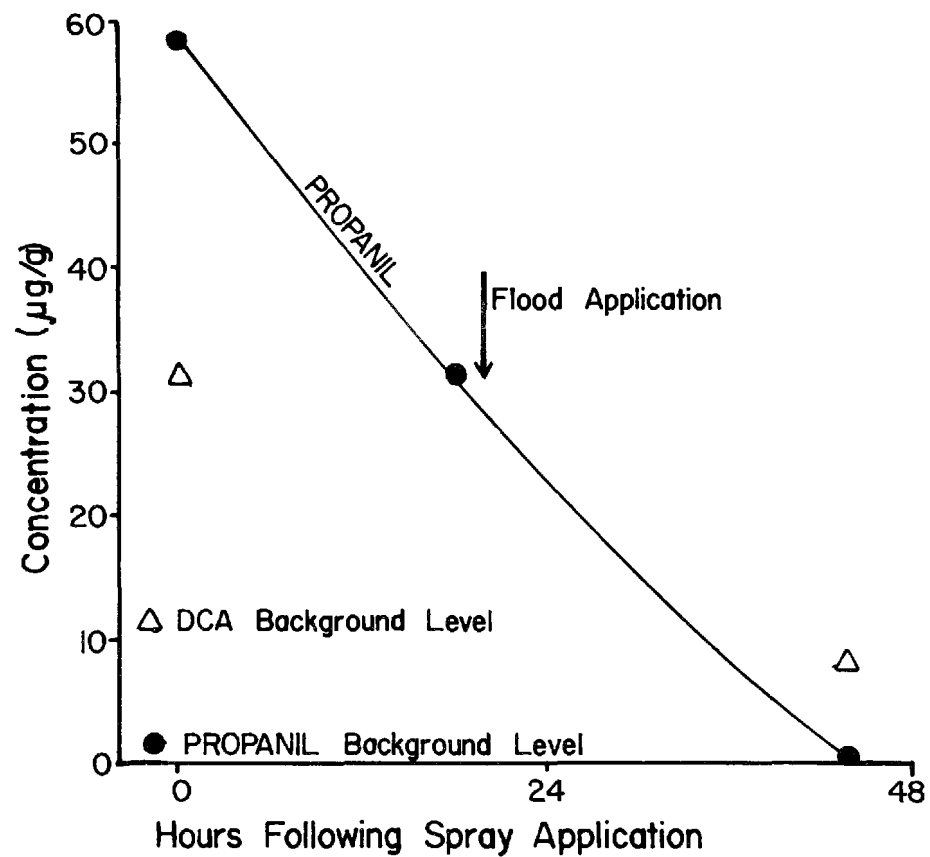


Figure 78. Concentration of propanil and DCA in soils sampled from high rate plots immediately following the spray application, just prior to flood, and 24 hours following the flood application in 1975.

DCA levels in the plot water sampled 24 hours following the flood application were linearly correlated to propanil dissipated between the 12 and 24 hour sampling periods (Figure 79). Generally, the propanil concentration 24 hours after the flood was small compared to the DCA concentration, suggesting that only a small positive error would have been incurred by the propanil in the distillation procedure.

The relatively high background level of DCA probably came from the degradation of a uniform 3.4 kg/ha propanil application made two weeks prior to the replicated experiment for weed control in the plots. The flood applied 24 hours following the propanil was drained after 24 hours, and the surface was allowed to dry. The drier surface condition may have retarded the microbial decomposition of DCA.

Although propanil was rapidly dissipated in the surface soil samples (Figure 78), there was no corresponding increase in the DCA concentration. A marked increase in the mean DCA concentration of the surface sediment of the six high rate plots was observed 72 hours following the permanent flood application in 1975 (Figure 80). There was a corresponding decrease in the DCA concentration of the plot water sampled, which suggests that a large portion of the DCA in the H₂O was adsorbed to the suspended colloidal load, and the surface sediment concentration increased as the suspended particles settled. The average suspended sediment concentration was 0.53 g/l 24 hours following the permanent flood application (Figure 81). This was diminished to 0.18 g/l 72 hours following the permanent flood application. Subsequent variations from one sampling date to another did not appear to be associated with heavy rainfall or irrigations.

DCA was not detected in the soil sampled at 2.5 to 5.0 cm and 17.5 to 20.0 cm depths 24 hours following the flood water application.

TCAB--The biological condensation of DCA → TCAB did not occur to any appreciable extent, as only trace levels were found in the 24 hour samples collected in 1973, and none were detected in any of the samples collected in either 1974 or 1975. The probability of two DCA molecules and the right organisms coming together was perhaps a factor lessened greatly by the dispersal of soil sediments and dilution created by the flood.

Modes of Dissipation--

Volatilization and photodecomposition--It has been shown that the variable and relatively high levels of propanil found in the water immediately following the flood reflected the quantities washed from the leaf canopy. Significant losses by photodecomposition and volatilization were not indicated by the data. The driest year with respect to leaf and soil surface prior to application resulted in the greatest concentration present in the flood. Propanil concentrations present in the water had remained almost constant or increased during mid-afternoon heat and sunlight intensities, with most of the loss incurred during the night. No propanil was lost from the spiked distilled water samples placed in the laboratory, or those exposed to direct sunlight for four days. This further indicates that photodecomposition and vaporization are not predominant factors in the dissipation.

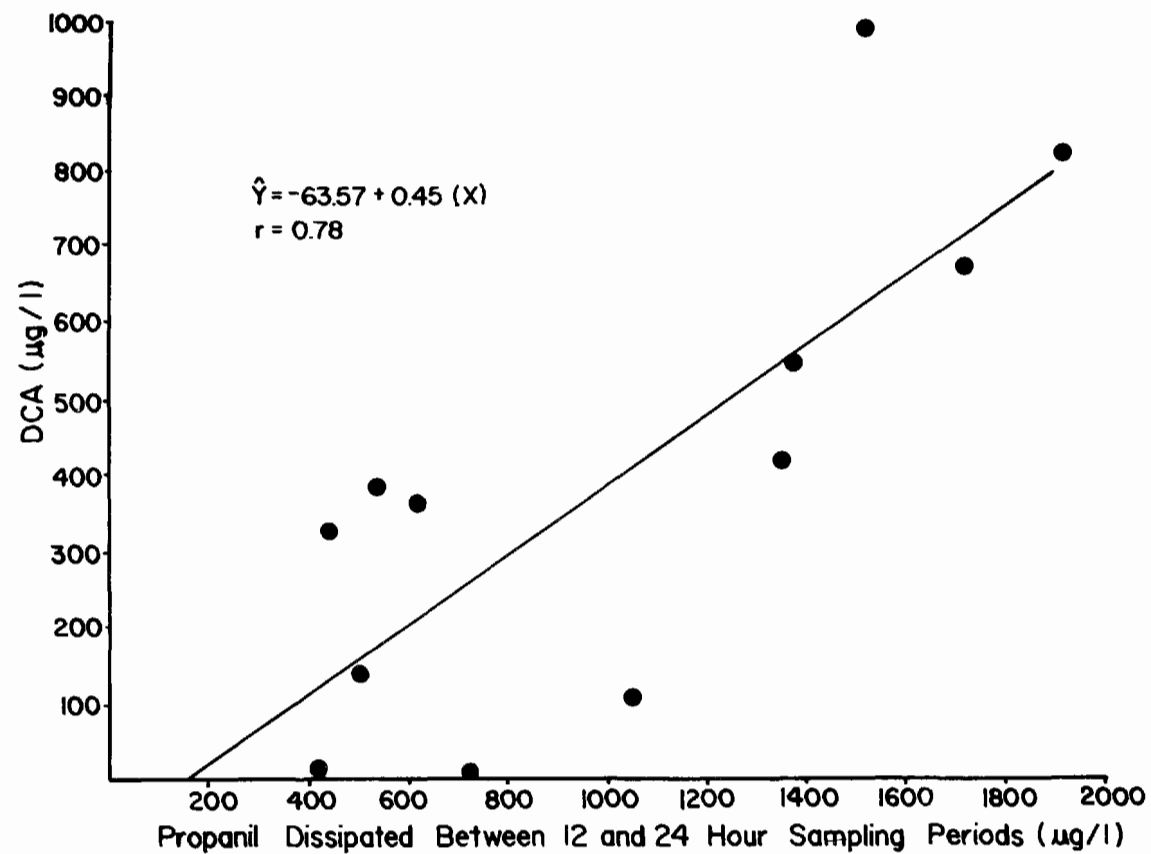


Figure 79. Levels of DCA in rice paddies sampled 24 hours following the flood application as affected by the dissipation of propanil between the 12 and 24 hour sampling periods in 1975.

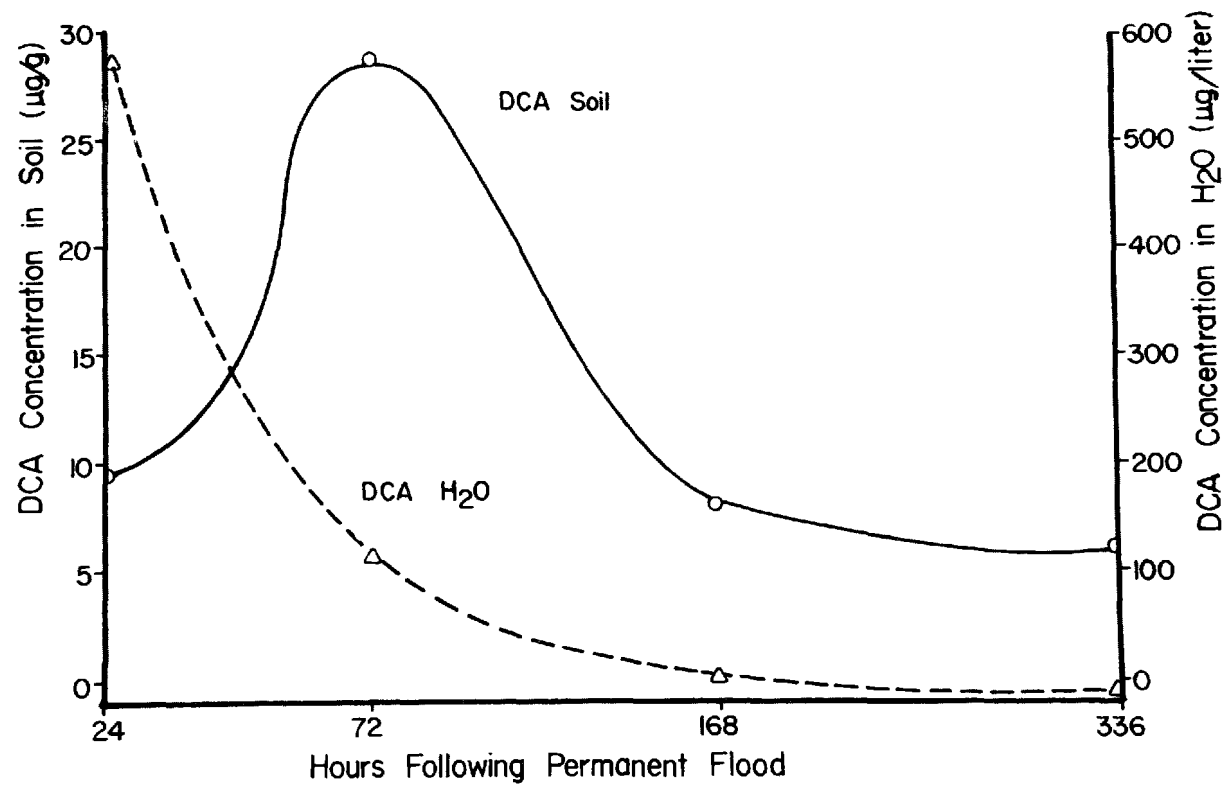


Figure 80. Average DCA concentrations of the surface sediment and flood water sampled from the 6 high rate plots at 24, 72, 168, and 336 hours following the permanent flood application in 1975.

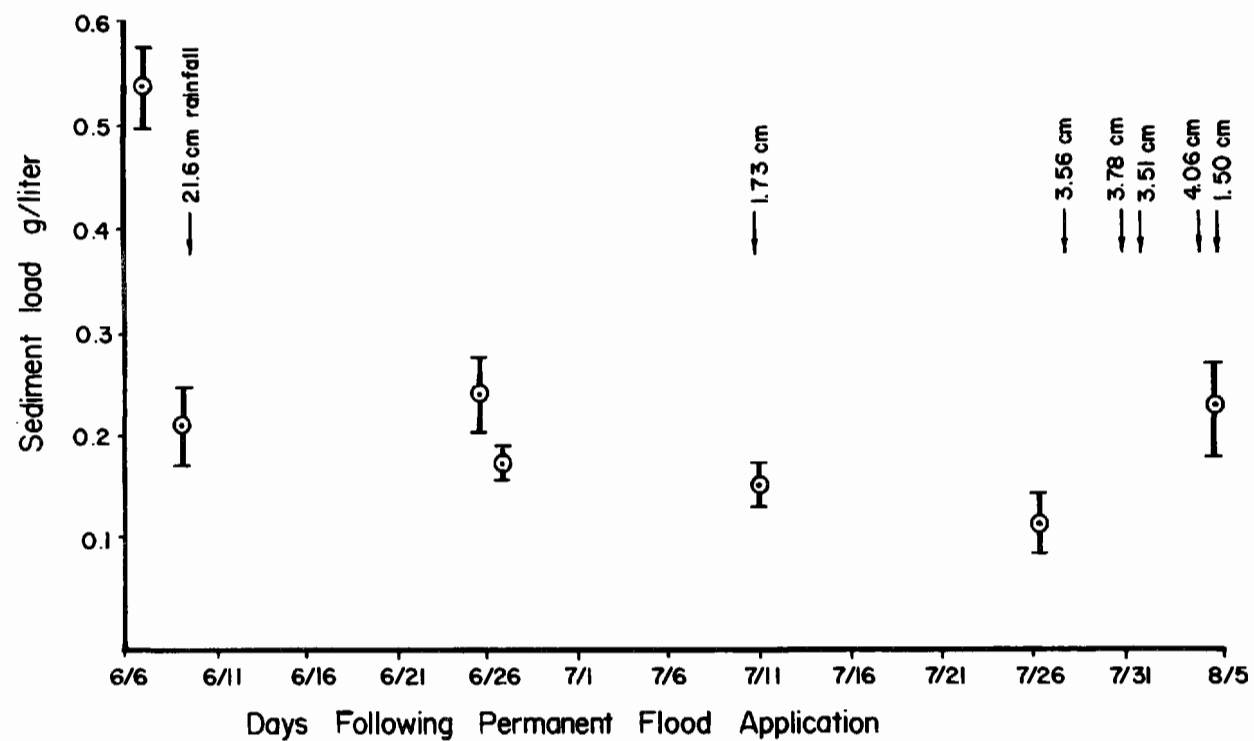


Figure 81. Sediment load with respect to time following the permanent flood application in 1975.

Adsorption--Adsorption coefficients (K_d) were determined for propanil, DCA and TCAB at different sediment loads (Figure 82). The K_d was found to increase sharply at sediment loads less than 10 g/l. This was attributed to a surface area increase resulting from dispersion of the clay fraction into individual particles, exposing sites within the interlayer space. The TCAB K_d values ranged from 200 to 600 and, consequently, are not shown in Figure 82. The relationship between K_d and percent pesticide in solution is graphically depicted in Figure 83. Adsorption coefficients determined at 50 g l⁻¹ sediment load and corresponding percent pesticide (propanil, DCA, carbofuran, 3-keto, and 3-Hydroxy-carbofuran, molinate, carbaryl, 1-naphthol) in solution were found to be negatively correlated, $r^2 = 0.87$, using an exponential function. Generally, the higher the K_d value, the lower the percent pesticide in solution. Concentration did have some effect on the K_d values determined for propanil and DCA (Figure 82). Values determined at 0.5 ppm pesticide were generally greater than those determined at 0.2 ppm, especially at the lower sediment loads. This is possibly due to the increased probability of the pesticide being at a specific adsorption site at the higher concentration.

Biological degradation--The authors submit that biological degradation was the primary mode by which propanil was dissipated from the rice plots. Propanil was probably adsorbed by the colloidal load of the water and brought into contact with the soil microorganisms which degraded it to DCA.

Molinate

Residue Levels in the Paddy Water--

Molinate (S-ethylhexahydro-1H-azepine-1-carbamate) is a herbicide commonly used to control broadleaved weeds in rice after the permanent flood. Kaufman (1967) proposed that the degradation of thiocarbamates may proceed by an initial hydrolysis at the ester linkage with the formation of mercaptan, CO₂, and an alkylamine. Hydrolysis is followed by the subsequent degradation of the mercaptan and alkylamine formed.

Molinate may be subject to volatilization due to its high vapor pressure (10⁻³ mm Hg) and high water solubility (Ashton and Sheets, 1959; Weber, 1972).

Tanji et al. (1974) recently reported their results on experiments conducted to determine the persistence and movement of molinate in field plots under static, flow-through, and recycled water management systems. Molinate applied in a preflood, preplant treatment was found to persist in the water for about three to five days. Much of that lost appeared to have been leached in the subsequent flood, as indicated by the much higher initial concentrations which resulted from the postflood application. Molinate persisted for at least four months in seepage water, which suggested to the authors that anaerobic conditions induced by submergence of the plots may have retarded microbial degradation. Molinate applied as a post-flood treatment in the static water management system remained at relatively high concentrations for more than 10 days following the application. It was not determined what effect a granular application would have in a post-flood water treatment.

Molinate in commercially available granular form was applied by broadcast over the entire plots. Applications succeeded the permanent flood by

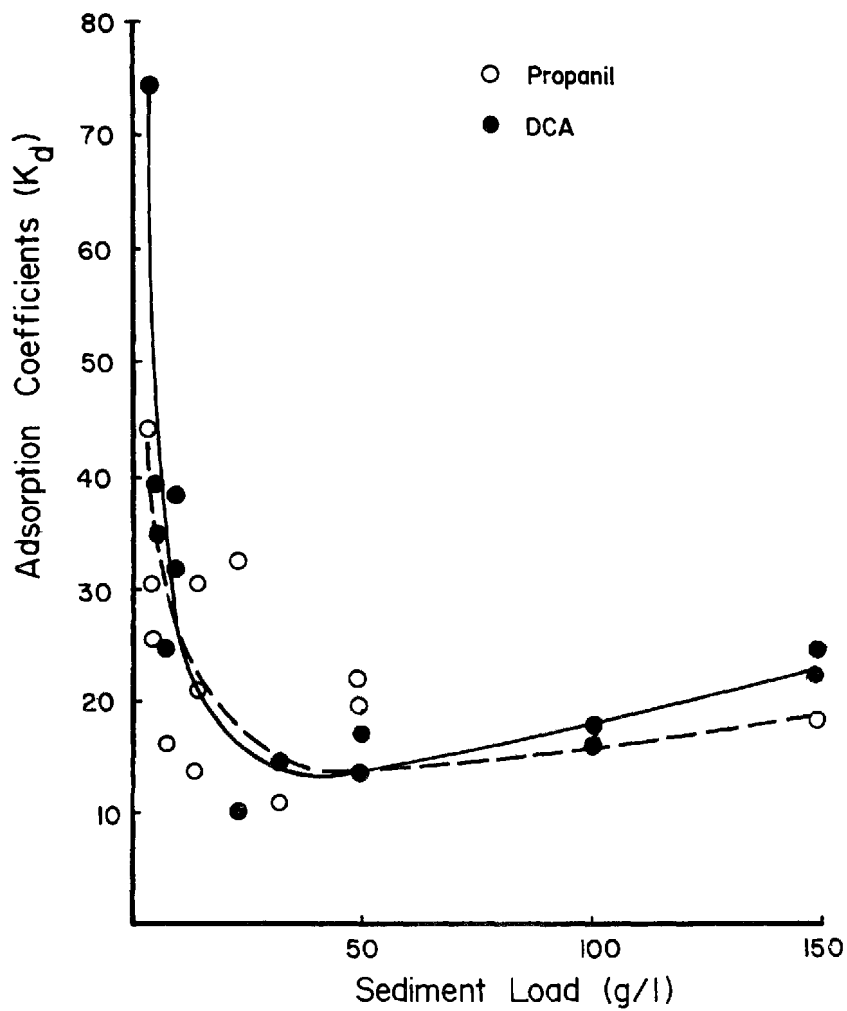


Figure 82. Adsorption coefficients of propanil and DCA calculated at the corresponding sediment loads.

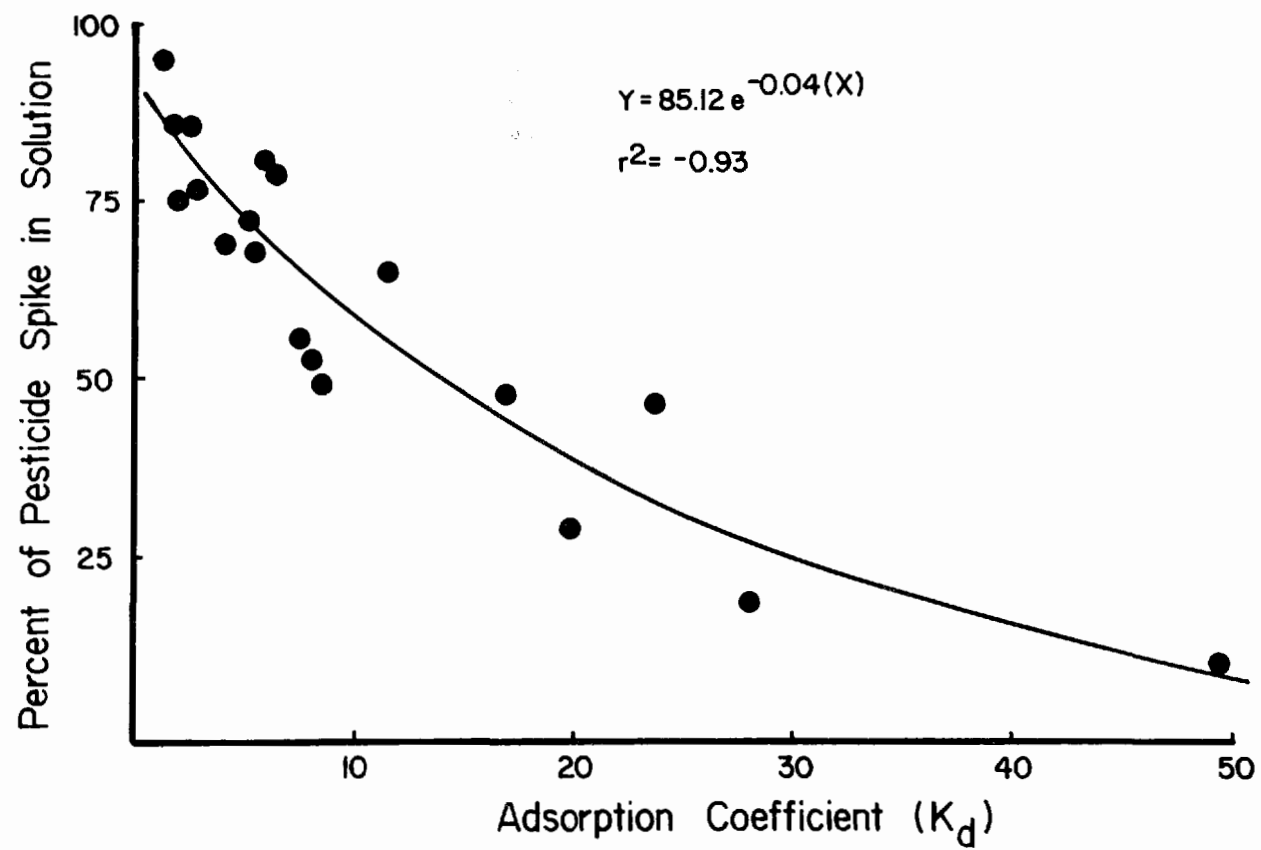


Figure 83. Correlation of percent pesticide in solution and K_d values determined at a sediment load of 50 g/l.

10 days in 1973, and by 18 days in 1974 and 1975 (Appendix A).

The amounts of molinate in the rice paddy water averaged within each treatment block with respect to time are shown in Figures 84, 85, and 86, for 1973, 1974, and 1975, respectively. The data were converted to kg/ha to account for the variable plot water depths which influenced the concentrations and impaired any meaningful statistical interpretation of the field results. Concentrations in the flood water were approximately proportional to the application rates (Tables 29, 30, and 31). The plots receiving excessive rates contained about three times that found in the plots receiving the recommended rate.

Maximum molinate concentrations were obtained at the 0-hour sampling period in 1973 and 1974. However, the maximum occurred at the 24-hour sampling period in 1975. The apparent disparity in the data may have resulted from the shorter time differential between application and zero sample collection in 1975.

Analyses of variance for the data collected in 1973, 1974 and 1975 are given in Appendix I. Concentrations of molinate were significantly different with respect to time at better than a 1% level in each of the three years tested. A Student-Newman-Keul's range test (Steele and Torrie, 1960) was employed to determine the statistical significance of differences between average concentrations within treatment (Tables 29, 30, and 31). Molinate did not persist at significant levels in any of the treatments after the 96 hour sampling period in 1973. The 768 hour average concentration was used as the lower limit of the range test for computing persistence on a significant basis. For practical purposes, it was essentially 0 since the maximum average concentration at the 768 hour sampling period was 5 ppb in 1973. Generally, persistence was two to four times longer in the 1974 and 1975 field experiments.

Application rate was found to have a highly significant influence on plot water concentrations all three years. Molinate persisted longer in plots treated at the excessive rate, as indicated by the highly significant first order interaction between time and rate of application (Appendix I, Tables I1, I2, and I3).

Concentrations of molinate were generally higher under the impounded irrigation management scheme all three years, but the difference was statistically significant only in 1973. Correspondingly, a highly significant interaction was noted between time and irrigation treatments in 1973; whereas, the interaction was not statistically significant in 1974 or 1975.

A first order, three-way interaction between time, irrigation treatment, and application rate was significant at the 5% level in 1973. This interaction was not significant in 1974 or 1975. Since differences due to replications were not significant in 1973 or 1974, and only barely significant at the 5% level in 1975, one would not expect higher order interactions involving replications to be significant.

The rainfall which occurred during the period when measurements were

TABLE 29. CONCENTRATION OF MOLINATE IN PADDY WATER FOLLOWING ITS APPLICATION IN 1973, AND STATISTICAL SIGNIFICANCE WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application						
		0	24	48	96	192	384	768
I ₁ R ₁	1	1.055	0.977	0.535	0.228	0.331	0.000	0.000
	2	1.239	0.617	0.396	0.362	0.193	0.011	0.003
	3	1.104	0.704	0.191	0.049	0.068	0.001	0.001
	ave**	1.133a	0.766ab	0.374bc	0.231bc	0.197bc	0.004c	0.001c
I ₁ R ₂	1	3.319	2.248	1.238	0.500	0.081	0.006	0.000
	2	4.128	3.363	1.574	0.613	0.083	0.005	0.000
	3	3.064	2.795	1.438	0.604	0.052	0.000	0.000
	ave	3.504a	2.802b	1.417c	0.572d	0.072d	0.004d	0.000
I ₂ R ₁	1	1.383	1.023	0.902	0.553	0.216	0.038	0.000
	2	1.638	1.642	1.319	0.934	0.301	0.026	0.005
	3	1.660	1.523	1.250	0.904	0.235	0.045	0.008
	ave	1.560a	1.396a	1.157ab	0.797bc	0.251c	0.036c	0.004c
I ₂ R ₂	1	6.638	4.545	3.978	2.165	0.699	0.076	0.004
	2	4.213	4.225	3.000	1.541	0.544	0.094	0.006
	3	7.234	5.960	4.000	2.810	0.398	0.035	0.004
	ave	6.028a	4.910b	3.659c	2.172d	0.547e	0.068e	0.005e

* I₁ and I₂ indicate continuous flow and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

TABLE 30. CONCENTRATION OF MOLINATE IN PADDY WATER FOLLOWING ITS APPLICATION IN 1974, AND STATISTICAL SIGNIFICANCE WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application					
		kg/ha					
		0	24	96	192	384	768
I ₁ R ₁	1	1.967	2.466	1.672	0.538	0.000	0.000
	2	2.607	1.801	1.768	0.403	0.052	0.000
	3	<u>2.443</u>	<u>1.924</u>	<u>1.386</u>	<u>0.342</u>	<u>0.010</u>	<u>0.000</u>
	ave**	2.339a	2.064ab	1.609b	0.428c	0.021c	0.000
I ₁ R ₂	1	8.363	7.000	4.749	0.819	0.028	0.001
	2	5.663	4.333	2.456	0.669	0.070	0.000
	3	<u>3.757</u>	<u>4.343</u>	<u>3.561</u>	<u>1.412</u>	<u>0.110</u>	<u>0.004</u>
	ave	5.928a	5.225a	3.589b	0.967c	0.069d	0.002d
I ₂ R ₁	1	0.588	0.800	0.008	0.329	0.017	0.000
	2	2.731	1.680	0.754	0.982	0.141	0.000
	3	<u>1.397</u>	<u>0.973</u>	<u>0.202</u>	<u>0.450</u>	<u>0.026</u>	<u>0.000</u>
	ave	1.572a	1.151a	0.321b	0.587b	0.061c	0.000
I ₂ R ₂	1	8.504	6.000	2.261	1.984	0.819	0.093
	2	5.756	4.672	6.305	1.828	0.370	0.009
	3	<u>6.463</u>	<u>5.967</u>	<u>2.611</u>	<u>2.012</u>	<u>0.403</u>	<u>0.056</u>
	ave	6.908a	5.546b	3.726c	1.941d	0.531e	0.053e

* I₁ and I₂ indicate continuous flow and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

TABLE 31. CONCENTRATION OF MOLINATE IN PADDY WATER FOLLOWING ITS APPLICATION IN 1975, AND STATISTICAL SIGNIFICANCE WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application						
		0	24	48	kg/ha 96	192	384	768
I ₁ R ₁	1	.000	1.814	1.535	.859	.569	.003	.000
	2	.001	1.235	.983	.715	.032	.000	.000
	3	.019	2.289	1.446	.809	.105	.049	.000
	ave**	.007d	1.780a	1.321b	.794c	.235d	.017d	.000d
I ₁ R ₂	1	.030	4.853	4.917	3.549	1.053	.385	.005
	2	.000	6.755	4.217	3.177	1.224	.029	.000
	3	.027	4.186	4.660	3.272	2.130	.459	.001
	ave	.019d	5.265a	4.598a	3.333b	1.469c	.291d	.002d
I ₂ R ₁	1	.000	1.758	1.756	1.544	.958	.159	.035
	2	.001	1.461	1.162	.802	.484	.052	.006
	3	.000	1.659	1.691	1.516	.716	.093	.000
	ave	.0003c	1.626a	1.536a	1.287a	.719b	.101c	.014c
I ₂ R ₂	1	.000	6.756	5.857	5.023	2.062	.960	.113
	2	.001	4.416	4.403	3.408	2.138	.726	.099
	3	.001	3.309	3.254	2.923	1.569	.914	.037
	ave	.001c	4.827a	4.505a	3.785a	1.923b	.867bc	.083c

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

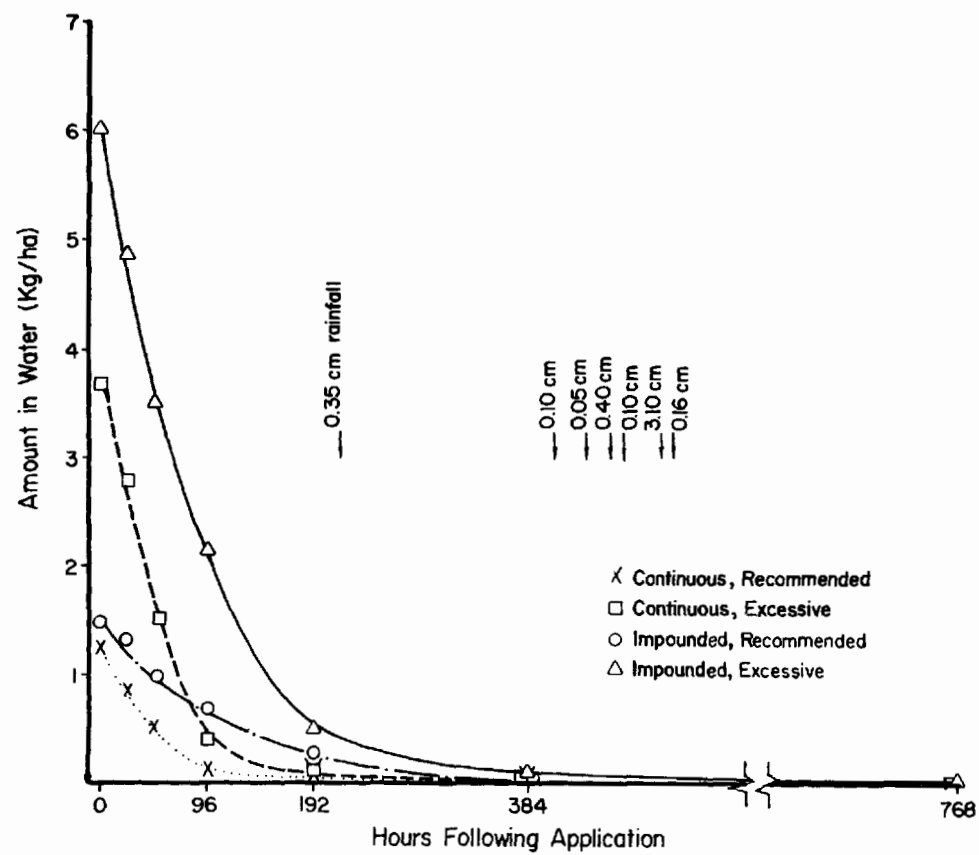


Figure 84. Average concentration of molinate in rice paddy water sampled in 1973.

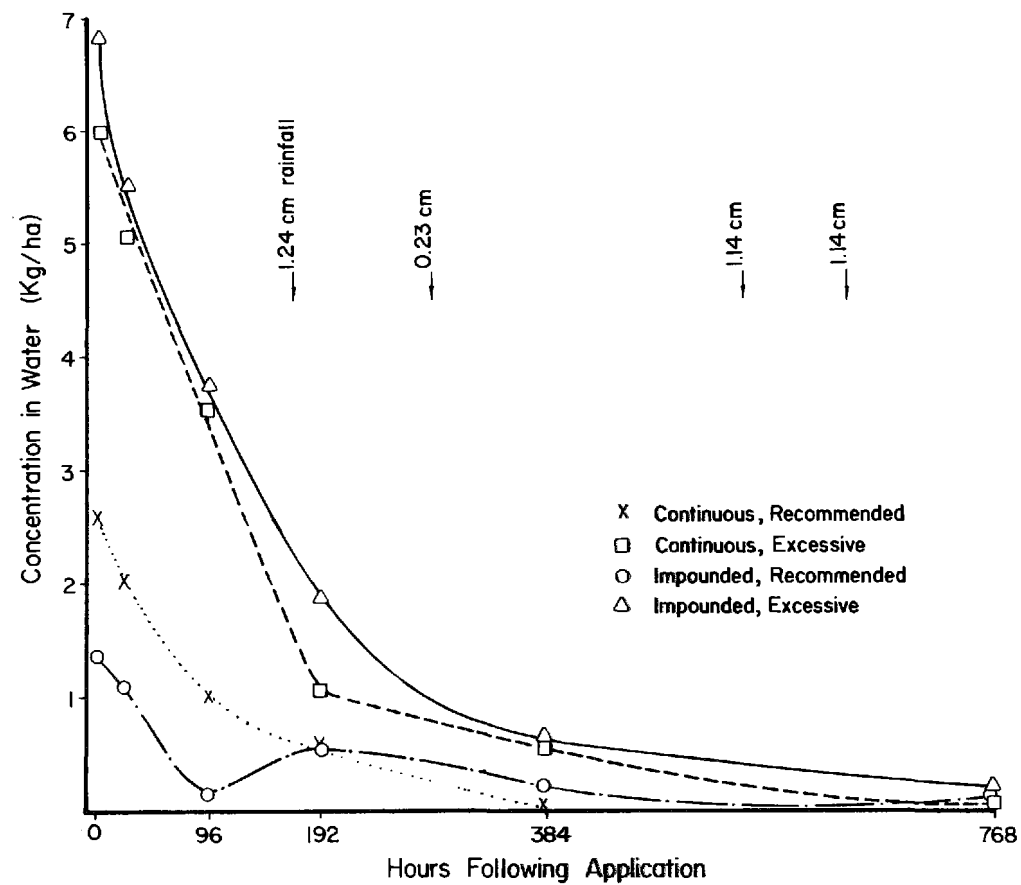


Figure 85. Average concentration of molinate in rice paddy water sampled in 1974.

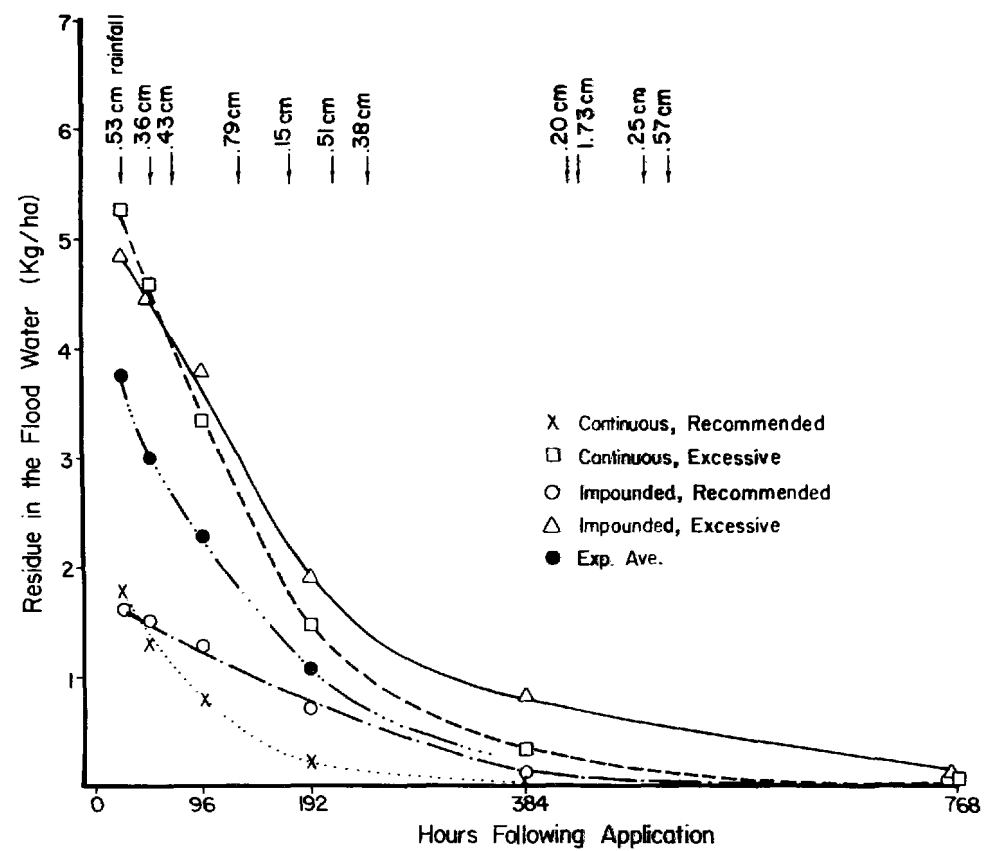


Figure 86. Average concentration of molinate in rice paddy water sampled in 1975.

taken had no apparent influence on the concentration of molinate in the flood water. Both molinate and carbofuran were applied as granular materials. The greater solubility of molinate may have resulted in a more rapid dissolution of that held in the sheath, diminishing the probability of secondary plot water concentration peaks, as were observed for carbofuran.

Modes of Dissipation--

Molinate dissipation rates within the paddy water were approximately the same for continuous flow and impounded irrigation schemes. The rate of loss was about 20% per day corresponding to a half-life of about $2\frac{1}{2}$ days. Since some water flowed out of the continuous flow system lots each day, one would expect an inherently higher dissipation rate for this management scheme. The apparent incongruity may have induced greater dissipation rates by other modes negating the effect of the flushing mechanism under continuous flow.

Volatilization--An experiment was conducted in the laboratory to evaluate volatilization as a potential mechanism for loss of molinate from the plot water (Table 32). Very little difference was found between the vapor flux using air saturated with water vapor and unsaturated air, suggesting that co-distillation with water was minimal. Little difference was noted in the vapor flux with an almost four-fold increase in the molinate concentration. However, the vapor flux was diminished considerably when soil was placed in the flask prior to the molinate spike.

TABLE 32. VOLATILIZATION OF MOLINATE FROM WATER AT
27°C AND AIR FLOW RATE OF 8 ML/SEC

<u>Sample</u>	<u>Concentration</u>	<u>Vapor Flux*</u>	<u>Volatilization</u>
	$\mu\text{g/ml}$	$\mu\text{g/cm}^2/\text{day}$	<u>Potential**</u> $\mu\text{g/plot/day}$
Distilled H_2O	2.0	1.6	4.8×10^6
Distilled $\text{H}_2\text{O}^\dagger$	2.0	1.7	5.1×10^6
Distilled H_2O	7.8	2.0	6.0×10^6
Distilled $\text{H}_2\text{O}^{\dagger\dagger}$	7.1	0.8	2.4×10^6

* Average of two determinations

** Calculated on the basis of a 300 m^2 plot water surface

† Air not saturated with H_2O prior to being passed into chamber

†† Ten g soil added to 100 ml water prior to molinate spike

The potential loss from a plot 300 m^2 was calculated using the vapor flux values determined empirically (Table 32). A maximum of 6 g/day would be lost from pure water under the conditions of the experiment. Only 2.4 g/day would be lost by vaporization from a surface the size of field plots with colloids in the water. Both rates are only a fraction of the 30 g/day

actually dissipated from the field plots. Temperatures in the water ranged between 35°C during the day and 25°C during the night. The high daytime water temperature would probably result in an increased vapor flux (Farmer et al., 1972). But it is doubtful that the increase would overcome the negative effect of the colloidal load of the plot water. Thus, vaporization would not be the primary mode of dissipation, but the cumulative loss over a period of time may be significant under hot, windy conditions.

Adsorption--To evaluate this mechanism, adsorption coefficients were measured at varying sediment loads (Figure 87). Molinate reacted similarly to propanil with respect to the rapid increase in K_d at sediment loads less than 10 g/liter. An extrapolation of the K_d obtained at 50 g/liter to the percent pesticide in solution curve given in Figure 83 indicates that molinate adsorption is reversible with water, since about 75% is in solution. The amount adsorbed (numerator in K_d equation) and K_d were measured at increasing concentrations of molinate at the 2.5 g/liter sediment load as shown in Figure 88. Amounts of molinate adsorbed increased linearly with increased concentration. However, K_d appears to have peaked at about 1 ppm molinate, suggesting that a partitioning mechanism with water may be occurring. It should be noted that only about 10% of the added molinate was adsorbed at the 2.5 g/liter sediment load, even at the higher K_d values. However, the percentage adsorbed increased with increased sediment load in the experiment summarized in Figure 87. This may have been the result of increased organic matter content with increased additions of soil to the centrifuge tubes.

A leaching experiment was conducted in which 20 g samples of a Beaumont clay soil were spiked with 87 ug of molinate, then leached with 100 ml distilled water (Table 33). The soil had been pre-wet with distilled water, and the molinate was applied evenly in 1 ml water after complete drainage of the pre-rinse. The Beaumont clay became very tight in the columns during wetting and it took more than 48 hours to leach 100 ml. The 70% of the molinate leached from the soils closely approximated the 67% in solution averaged for the adsorption experiment where 20 g of soil was thoroughly mixed with 200 ml of water for 30 min on a reciprocating shaker.

TABLE 33. COLUMN LEACHING OF A MOLINATE-SPIKED
BEAUMONT CLAY SOIL WITH DISTILLED WATER

Column	Molinate Recovered*	
	Soil ug	Leachate ug
1	17.9	62.4
2	16.6	60.0

* An 87 ug spike was added to each soil column.

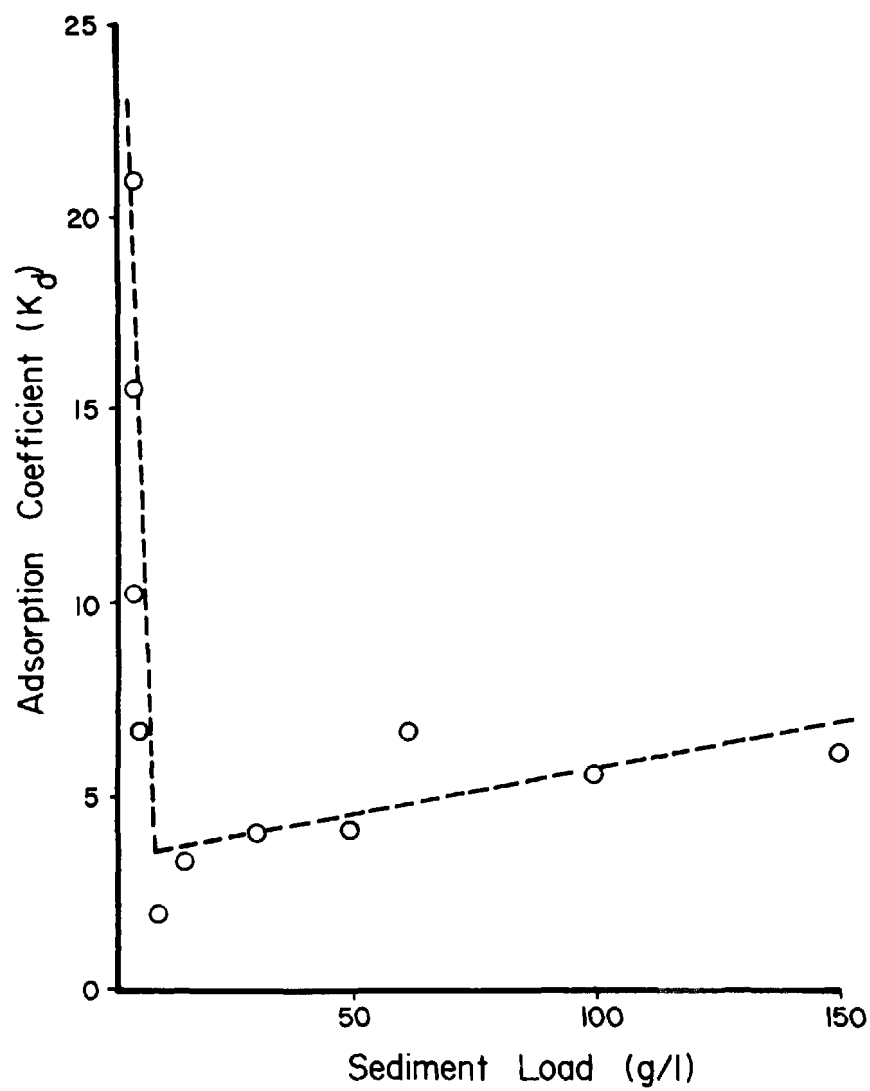


Figure 87. Adsorption coefficients of molinate at varying sediment loads.

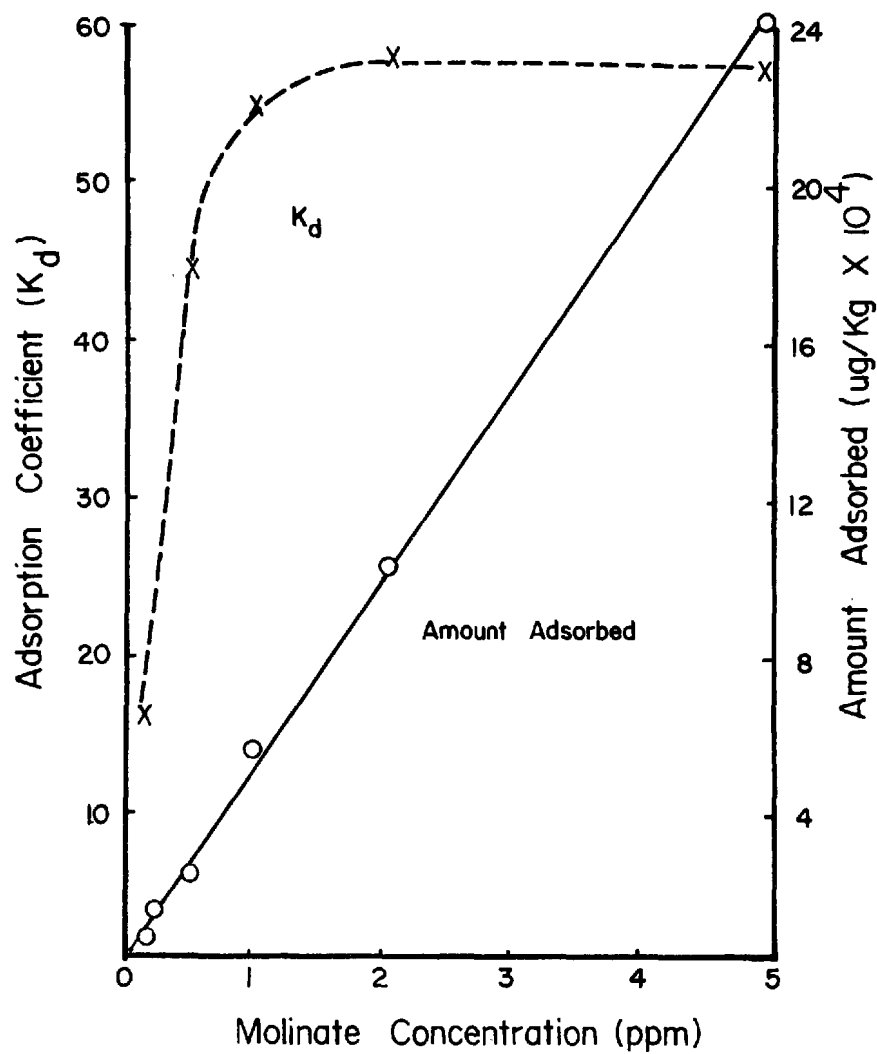


Figure 88. The amount adsorbed and K_d versus molinate concentration in water with a sediment load of 2.5 g/l.

Molinate would probably leach under conditions other than total saturation associated with the permanent flood in rice culture (Tanji et al., 1974). However, the downward net flux in most rice soils is essentially zero after establishment of the permanent flood. No molinate was found at either the 2.5 to 5.0 cm depth or the 17.5 to 20.0 cm depth sampled in the field experiment after the application. The leaching of molinate could be a problem if applied to a soil in which downward movement of water does occur. The hazard would become a function of distance between the surface and the ground water and the adsorptive capacity of the soil.

At the lower sediment loads, only 10% of the molinate was actually adsorbed. The net effect of the colloidal load may be precipitatory in nature. The adsorptive mechanism returns solubilized molinate to the soil surface where it may be trapped by other soil particles carried on sedimentation or adsorbed more tightly by humic acids associated with the organic fraction of the soil. Adsorption cannot account for the dissipation rates of molinate demonstrated in the field experiment, although chemical bonding to the organic fraction could have a significant influence on the amounts in solution. A precipitatory mechanism would tend to bring molinate into more intimate contact with the microorganisms proliferating at the soil surface (Patrick and Mikkelsen, 1971).

Biological dissipation--Soil samples were placed under flooded conditions and equilibrated for eight days prior to the molinate fortification to simulate field conditions. Molinate dissipation was generally greater for the most oxidized samples (Table 34). The redox range was not as encompassing as desired but resulted in some discernible differences in molinate recovered. Samples receiving no added substrate generally had the higher redox potential, but required a longer period of time to dissipate molinate. Those treated with 0.25 g sugar dissipated more molinate over an eight day period than those not treated with sugar. It is surmised that the 0.25 g treatment induced rapid proliferation of microbial growth followed by a depletion in the oxygen content. It appears that the depletion rate of oxygen was a function of the substrate level. Although decomposition of molinate was noted in only one of the 16 hour samples treated with 1 g sugar, the soils were definitely becoming more oxidized with time. No degradation was noted in the sterilized controls after the 16 day incubation period.

Results in the field experiment are consistent with those obtained in the laboratory experiment. Field plots were flooded eight days prior to the molinate application in 1973; whereas, the plots were flooded 18 days prior to the application in 1974 and 1975. The longer half-life of molinate in 1974 and 1975 may be due to a more reduced environment attained in the longer interval between permanent flood and molinate application.

Carbofuran

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-N-methyl carbamate) is a broad spectrum insecticide belonging to the N-methyl carbamate family of pesticides. The two toxic metabolites reported for carbofuran are 3-keto carbofuran (2,3-dihydro-2,2-dimethyl-3-keto-7-benzofuranyl-N-methyl carbamate) and 3-hydroxy carbofuran (2,3-dihydro-2,2-dimethyl-3-hydroxy-7-benzo-

TABLE 34. EFFECTS OF TIME, SUBSTRATE LEVEL, AND REDOX POTENTIAL
ON THE DISSIPATION OF MOLINATE IN FLOODED SOIL SAMPLES
UNDER LABORATORY CONDITIONS*

<u>Incubation Period</u>	<u>Soil Preparation</u>	<u>Sucrose Added</u>	<u>Rep</u>	<u>Molinate Recovered</u>	<u>Redox Potential</u>
Days		g		ug	mv
1	Not Sterilized	none	1	89.1	- 75
			2	98.4	- 98
	Not Sterilized	0.25	1	99.5	-425
			2	97.8	-418
	Not Sterilized	1.00	1	96.7	-450
			2	91.5	-485
	Sterilized	1.00		94.3	+ 10
8	Not Sterilized	none	1	92.9	-155
			2	85.2	-120
	Not Sterilized	0.25	1	77.2	- 75
			2	72.9	- 68
	Not Sterilized	1.00	1	88.3	-330
			2	92.8	-285
	Sterilized	1.00		89.7	+150
16	Not Sterilized	none	1	30.8	-145
			2	69.2	-170
	Not Sterilized	0.25	1	85.7	-190
			2	52.9	-175
	Not Sterilized	1.00	1	90.0	-260
			2	58.9	-175
	Sterilized	1.00		89.1	+ 60

* All flasks including controls were spiked with 100 mg molinate.

furanyl-N-methyl carbamate) (Butler and McDonough, 1971).

Caro et al. (1973) followed the degradation of carbofuran in an actual field experiment. They found that carbofuran disappeared from the soil by first-order kinetics, the half-life ranging from 46 to 117 days in the broadcast and in-furrow applications, respectively. Degradation was greatly accelerated in several localized areas within the treated watersheds. These areas were found to have higher soil water contents, a generally higher pH level, and a more clayey texture. The field receiving the broadcast application had an average soil pH of 6.3, and the field employed for the in-furrow treatment averaged pH 5.2. Although circumstantial, the data certainly indicate that pH may drastically affect the dissipation rate of carbofuran. From 0.5 to 0.2% of the carbofuran applied was lost in runoff water. Of that lost, more was in solution than in the suspended soil particles. About 5 to 10% of the carbofuran applied was converted to 3-keto carbofuran, which disappeared at about the same rate as the parent compound. Only sporadic trace levels of 3-hydroxy were found in the soil samples.

Getzin (1973) determined the persistence of ^{14}C carbonyl-labeled carbofuran and ^{14}C ring-labeled carbofuran phenol on four soils ranging in pH from 7.8 to 5.9. The soil with pH 5.9 was an organic muck soil with 40% organic matter. The half-life varied from three weeks in the pH 7.8 to more than 50 weeks in the organic muck soil. $^{14}\text{CO}_2$ was evolved in both sterilized and non-sterilized soils fortified with 20 ppm of the carbonyl-labeled carbofuran suggesting that hydrolysis was not due only to metabolic processes of microorganisms under the oxidized conditions of these experiments. Evolution of $^{14}\text{CO}_2$ proceeded at a considerably slower rate using ring-labeled carbofuran phenol. Approximately 25% of the carbofuran phenol was degraded within the 32-week experimental period. However, carbofuran was almost completely hydrolyzed within 32 weeks in the two soils used in the ring-labeled phenol experiment. Soil-bound residues of ring-labeled carbofuran phenol reached a 70 to 80% maximum within two weeks after treatment. Thus, it appears that carbofuran may be chemically altered to its phenol which is immediately bound to soil constituents and slowly metabolized by microorganisms. Getzin (1973) made no attempt to identify metabolites other than carbofuran phenol.

It is not known how carbofuran would react under the anaerobic conditions of flooded rice culture. The half-lives reported in the experiment above suggest that carbofuran may be a problem in rice culture.

Residue Levels in the Paddy Water--

The residual amounts of carbofuran found for the various treatments with respect to time following application are plotted in Figures 89, 90, and 91 for the 1973, 1974, and 1975 data, respectively. Residual levels were highest initially and decreased rapidly to less than 50% of the initial concentration within 24 hours in 1973. Carbofuran residues in the water followed a different dissipation pattern in 1974 and 1975. The amounts in the water were low initially and highest in the 24-hour samples. It is possible that a time differential between application and the zero-hour sampling period could explain the discord in the data initially. Carbofuran was applied in the flood water in a commercially available granular form, and sufficient time may not have elapsed for dissolution in 1974 and 1975. However, a time differential

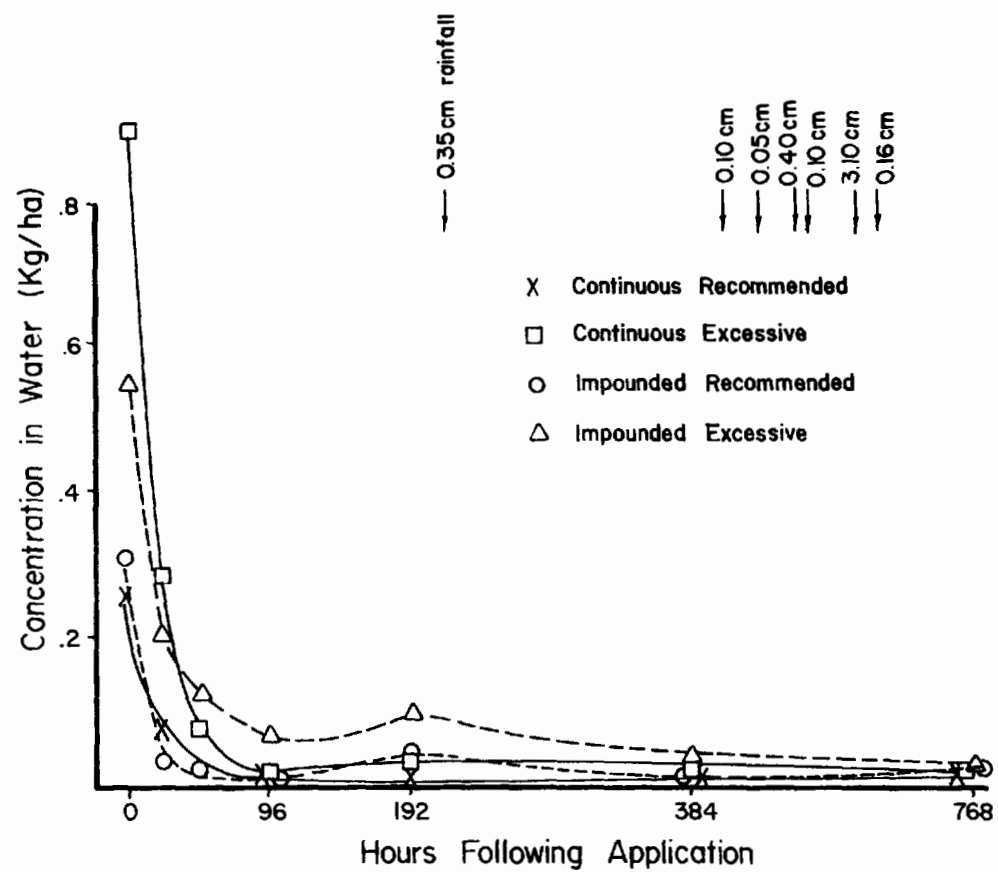


Figure 89. Average concentrations of carbofuran in rice paddy water sampled in 1973.

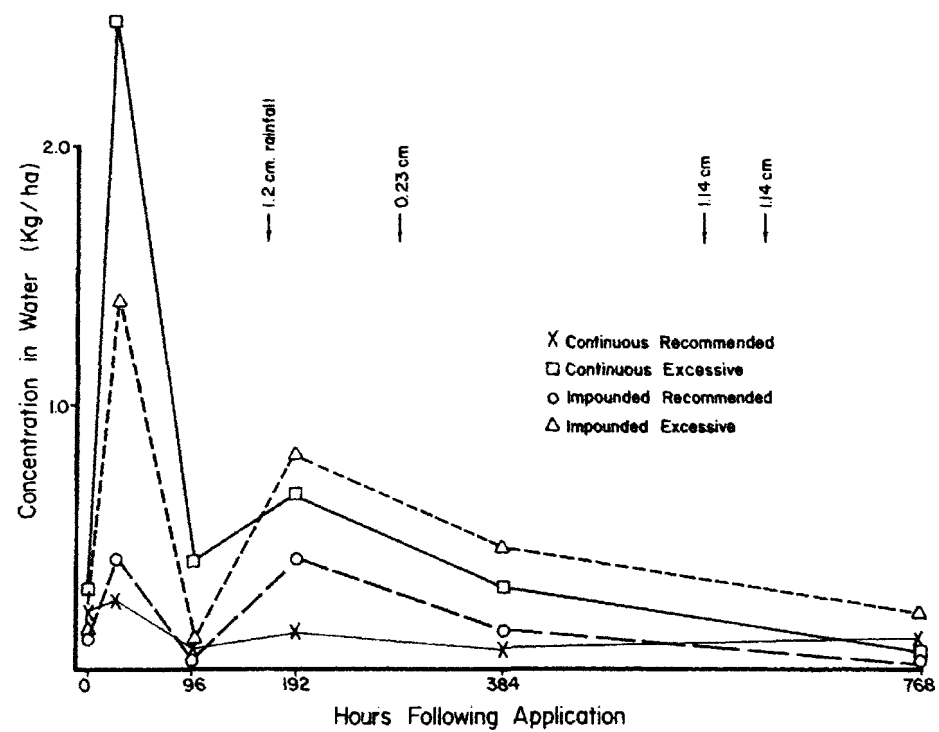


Figure 90. Average concentrations of carbofuran in rice paddy water sampled in 1974.

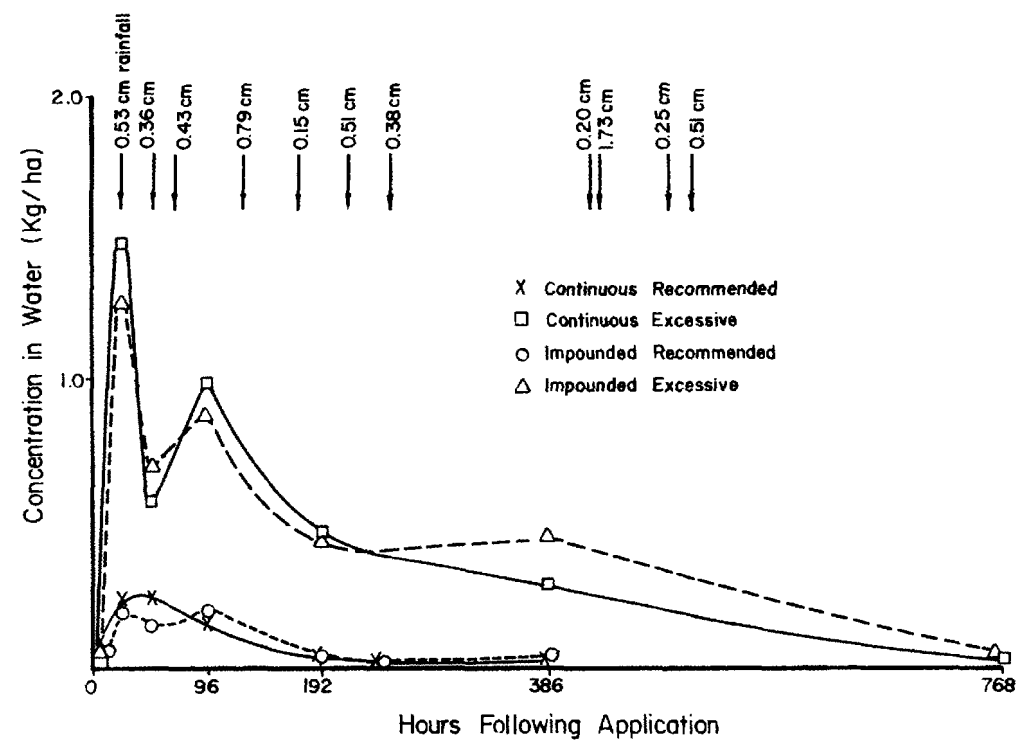


Figure 91. Average concentrations of carbofuran in rice paddy water sampled in 1975.

cannot explain the anomaly in the 24-hour samples. As much as 60% of that applied at the excessive rate could be accounted for in 1974, 24 hours later. Conversely, only about 30% of that applied in 1973 was present in the water, and this maximum occurred in the zero-hour samples. Error in application could perhaps account for the disparity in amounts recovered but cannot explain the trend noted in the 24-hour sample.

During 1973, no rain fell until later than 192 hours after application. This and subsequent rains had little effect on the amount of carbofuran in the flood water. This most likely occurred because the amount of carbofuran on the foliage had decreased, and because the rains fell just after sampling, allowing considerable time for dissipation before the next sampling. During 1974, a 1.24 cm rain fell just before the 192-hour sampling causing a second peak in concentration. Subsequent rainfall resulted in no increase in the amounts in the floodwater. In 1975 a 0.53 cm rain fell just before the 24-hour sample was collected. Those samples had the greatest concentrations. The concentration decreased markedly between the 24- and 48-hour samples. Two rains totaling 0.79 cm were recorded between the 48- and 96-hour sampling which may have washed additional material into the water resulting in a second peak in three of the four treatments at 96 hours. The influence of subsequent rainfall was again not evident.

The carbofuran had been applied as granular material, a fraction of which may have lodged in the sheath of the rice foliage. The data presented here indicates that some of the material probably dissolved in the rainfall and washed into the plots.

Deviations between replications within treatments were not statistically significant at the 0.05 level or better during any of the three years (Appendix I, Table I4, I5, and I6). No significant difference was found between irrigation treatments. Application rate and time were found to have a highly significant influence on the amounts of carbofuran in the paddy water in each of the three years tested. The only significant interaction found was that between application rate and time. As expected, higher rates resulted in longer persistence of significant residue levels.

A Student-Newman-Keul's range test (Steel and Torrie, 1960) was employed to determine which average residue level concentrations were significantly different with respect to time (Tables 35, 36, and 37). Only the zero-hour concentrations were significantly different from that measured in the 768-hour samples in 1973, with the exception of the excessive rate treatments. For this treatment significance was extended into the 24-hour samples.

No significant difference was found with respect to time in the treatment receiving the recommended application rate in 1974 (Table 36). The 24-hour level and the peak at 192 hours were found to be significant at the 5% level in the excessive application rate treatments in 1974.

Trends in the 1975 data corresponded well with those observed for the 1974 data. However, the peak occurred at 96 hours in 1975 (Table 37). Residue levels in the 192-hour samples were not significantly higher than the minute quantities obtained at 768 hours. Relatively higher levels were ob-

TABLE 35. CONCENTRATION OF CARBOFURAN IN PADDY WATER FOLLOWING ITS APPLICATION IN 1973, AND STATISTICAL SIGNIFICANCE WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application						
		0	24	48	96	192	384	768
I ₁ R ₁	1	0.317	0.044	0.009	0.002	0.002	0.002	0.001
	2	0.159	0.052	0.008	0.001	0.002	0.006	0.001
	3	0.205	0.090	0.050	0.014	0.030	0.024	0.016
	ave**	0.227a	0.062b	0.022b	0.006b	0.011b	0.011b	0.006b
I ₁ R ₂	1	0.547	0.186	0.076	0.011	0.008	0.005	0.000
	2	1.130	0.302	0.058	0.021	0.029	0.003	0.004
	3	1.050	0.263	0.079	0.025	0.003	0.002	0.001
	ave	0.909a	0.250b	0.071c	0.019c	0.024c	0.014c	0.007c
I ₂ R ₁	1	0.206	0.098	0.052	0.050	0.037	0.029	0.016
	2	0.312	0.093	0.040	0.058	0.004	0.009	0.007
	3	0.405	0.103	0.069	0.025	0.014	0.055	0.005
	ave	0.308a	0.098b	0.054b	0.044b	0.018b	0.031b	0.009b
I ₂ R ₂	1	0.500	0.200	0.117	0.072	0.072	0.023	0.016
	2	0.990	0.275	0.102	0.069	0.074	0.068	0.010
	3	0.954	0.191	0.098	0.041	0.039	0.013	0.003
	ave	0.815a	0.222b	0.106bc	0.061c	0.062c	0.035c	0.010c

* I₁ and I₂ indicate continuous flow and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

TABLE 36. CONCENTRATION OF CARBOFURAN IN PADDY WATER FOLLOWING ITS APPLICATION IN 1974, AND STATISTICAL SIGNIFICANCE WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application					
		kg/ha					
		0	24	96	192	384	768
I ₁ R ₁	1	0.043	0.197	0.051	0.118	0.015	0.000
	2	0.407	0.286	0.025	0.147	0.032	0.000
	3	<u>0.232</u>	<u>0.229</u>	<u>0.094</u>	<u>0.176</u>	<u>0.123</u>	<u>0.000</u>
	ave**	0.227a	0.237a	0.057a	0.147a	0.057a	0.000a
I ₁ R ₂	1	0.188	3.906	0.384	0.890	0.124	0.001
	2	0.012	1.462	0.121	0.536	0.513	0.019
	3	<u>0.080</u>	<u>1.901</u>	<u>0.063</u>	<u>0.467</u>	<u>0.108</u>	<u>0.002</u>
	ave	0.093a	2.423b	0.189a	0.631c	0.248a	0.007a
I ₂ R ₁	1	0.468	0.263	0.004	0.328	0.026	0.012
	2	0.012	0.262	0.024	0.467	0.137	0.049
	3	<u>0.050</u>	<u>0.540</u>	<u>0.004</u>	<u>0.525</u>	<u>0.094</u>	<u>0.001</u>
	ave	0.101a	0.355a	0.011a	0.440a	0.086a	0.021a
I ₂ R ₂	1	0.224	1.939	0.013	1.280	0.843	0.202
	2	0.077	0.738	0.029	0.495	0.267	0.067
	3	<u>0.251</u>	<u>1.235</u>	<u>0.069</u>	<u>0.583</u>	<u>0.229</u>	<u>0.195</u>
	ave	0.184a	1.304b	0.037a	0.786c	0.446a	0.155a

* I₁ and I₂ indicate continuous flow and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

TABLE 37. CONCENTRATION OF CARBOFURAN IN PADDY WATER FOLLOWING ITS APPLICATION IN 1975, AND STATISTICAL SIGNIFICANCE WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application						
		0	24	48	96	192	384	768
I ₁ R ₁	1	.001	.260	.344	.142	.126	.002	.001
	2	.001	.240	.142	.094	.003	.002	.000
	3	.001	.173	.204	.190	.007	.056	.000
	ave**	.001b	.224a	.230a	.142a	.045b	.020b	.0003b
I ₁ R ₂	1	.000	1.814	.913	.941	.423	.018	.002
	2	.000	1.210	.506	.443	.472	.450	.000
	3	.001	1.425	.279	1.572	.516	.246	.035
	ave	.0003c	1.483a	.566bc	.985ab	.470bc	.238c	.012c
I ₂ R ₁	1	.000	.192	.188	.198	.172	.118	.052
	2	.001	.102	.019	.089	.093	.045	.007
	3	.001	.250	.205	.291	.091	.096	.000
	ave	.0007c	.181a	.137ab	.193a	.030bc	.086abc	.020bc
I ₂ R ₂	1	.000	1.124	.552	.489	.309	.700	.004
	2	.000	2.072	.875	.670	.397	.324	.006
	3	.000	.587	.649	1.476	.630	.375	.003
	ave	.000b	1.261a	.692ab	.878ab	.445ab	.466ab	.004b

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.05 level.

tained in the I₂R₂ block 768 hours in 1974 as compared to 1975, although the plot water residues were comparable at corresponding sampling periods. Two heavy rains in excess of 2.5 cm fell on the plots just three and four days prior to the 768-hour sampling period in 1975, which may have resulted in the difference.

Residue Levels of Metabolites--

Small amounts of 3-keto carbofuran were detected in the plot water sampled following the application of carbofuran (Tables 38, 39, and 40). The time lag between application of carbofuran and detection of the 3-keto carbofuran suggests the latter to be a dissipation product rather than a contaminant of the former. However, the minute amounts detected (less than 0.05 ppm even of the excessive application rate) indicate that the 3-keto moiety would not enhance the residual life of carbofuran to an appreciable extent under flooded rice culture. Concentrations of 3-hydroxy carbofuran were never detected in excess of minute trace levels.

Modes of Dissipation--

Volatilization--Neither carbofuran nor 3-keto carbofuran were found to volatilize to any appreciable extent in the laboratory. The 3-hydroxy metabolite of carbofuran had a vapor flux of $1.8 \mu\text{g cm}^{-2} \text{ day}^{-1}$ in unsaturated (with respect to water) air. However, when the air was saturated with water vapor prior to being passed into the volatilization chamber, the vapor flux was diminished to $0.3 \mu\text{g cm}^{-2} \text{ day}^{-1}$ from distilled water at 27°C, with air flow rate of 8 ml/sec. No relevance was attached to the vapor flux obtained due to the low value in moist air and the fact that only trace levels of 3-hydroxy were ever detected in the plots. It is doubtful that significant amounts of carbofuran or 3-keto carbofuran would be dissipated from the paddy water via a volatilization mechanism.

Adsorption--Carbofuran and 3-keto carbofuran reacted similarly to molinate in that the K_d increased rapidly at sediment loads less than 10 g/l, but greater than 90% of the pesticide was in solution (Figure 92). Carbofuran and 3-keto carbofuran were different in that the K_d did not increase at increasing sediment loads greater than 10 g/l. This suggests that carbofuran was not adsorbed at specific sites and/or did not interact appreciably with the organic fraction. Lack of adsorption was evidenced by the fact that greater than 80% remained in solution at the highest sediment load of 150 g/l. The 3-hydroxy metabolite was adsorbed more tightly than carbofuran or 3-keto carbofuran. It is doubtful that adsorption had more than a precipitatory function in the dissipation of carbofuran from the field plots.

No carbofuran, 3-keto, or 3-hydroxy carbofuran was detected in the soils sampled at 2.5 to 5.0 and 17.5 to 20.0 cm depths one, three, and five weeks following its application.

The data collected in the field experiments in 1973, 1974, and 1975 suggest that carbofuran was rapidly dissipated to some degradation product other than 3-keto or 3-hydroxy carbofuran. It is surmised that chemical alteration may be the major mode of dissipation of carbofuran from the flooded Beaumont clay soil, with biological degradation important over a longer time span.

TABLE 38. CONCENTRATION OF 3-KETO CARBOFURAN WITH RESPECT TO TIME IN RICE PADDY WATER SAMPLED IN 1973

Treatment Block*	Rep	Hours Following Application kg/ha			
		96	192	384	768
I ₁ R ₁	1	ND**	ND	trace†	ND
	2	ND	ND	ND	trace
	3	ND	ND	trace	ND
	ave	ND	ND	trace	ND
I ₁ R ₂	1	ND	ND	ND	trace
	2	ND	trace	trace	.001
	3	ND	ND	ND	trace
	ave	ND	ND	ND	trace
I ₂ R ₁	1	ND	ND	trace	trace
	2	ND	.004	ND	trace
	3	ND	ND	trace	trace
	ave	ND	.001	trace	trace
I ₂ R ₂	1	.008	.010	.003	trace
	2	trace	.005	.004	.001
	3	.001	.003	trace	ND
	ave	.003	.003	.002	trace

* I₁ and I₂ indicate continuous and impoundment irrigation; R₁ and R₂ indicate recommended and excessive application rates of carbofuran, respectively.

** ND refers to none detected.

† Trace refers to those amounts detected but which were too close to the sensitivity limit to quantitate.

TABLE 39. CONCENTRATION OF 3-KETO CARBOFURAN WITH RESPECT
TO TIME IN RICE PADDY WATER COLLECTED IN 1974

Treatment Block*	Rep	Hours Following Application kg/ha	
		384	768
I ₁ R ₁	1	trace**	ND†
	2	trace	ND
	3	<u>0.001</u>	<u>ND</u>
	ave	0.001	ND
I ₁ R ₂	1	0.007	ND
	2	0.011	trace
	3	<u>0.017</u>	<u>trace</u>
	ave	0.012	<trace
I ₂ R ₁	1	0.004	trace
	2	0.002	ND
	3	<u>0.004</u>	<u>trace</u>
	ave	0.003	<trace
I ₂ R ₂	1	0.042	trace
	2	0.057	trace
	3	<u>0.044</u>	<u>0.002</u>
	ave	0.048	<0.001

* I₁ and I₂ indicate continuous and impoundment irrigation management schemes; R₁ and R₂ indicate the recommended and excessive application rates, respectively.

** Trace refers to those amounts detected but which were too close to the sensitivity limit to quantitate.

† ND refers to none detected.

TABLE 40. CONCENTRATION OF 3-KETO CARBOFURAN WITH RESPECT TO
TIME IN WATER SAMPLED FROM RICE PLOTS IN 1975

Treatment Block*	Rep	Hours Following Application kg/ha			
		48	96	192	384
I ₁ R ₁	1	ND**	trace†	trace	ND
	2	trace	ND	ND	ND
	3	trace	trace	ND	ND
	ave	trace	trace	ND	ND
I ₁ R ₂	1	ND	.003	.002	ND
	2	trace	.002	.002	trace
	3	.001	.005	.003	ND
	ave	trace	.003	.002	ND
I ₂ R ₁	1	ND	.001	trace	ND
	2	ND	trace	.002	ND
	3	ND	.002	.001	ND
	ave	ND	.001	.001	ND
I ₂ R ₂	1	.003	.006	.019	.006
	2	.002	.005	.006	.002
	3	.003	.011	.014	ND
	ave	.003	.007	.013	.003

* I₁ and I₂ indicate continuous and impoundment irrigation management schemes; R₁ and R₂ indicate recommended and excessive application rates of carbofuran, respectively.

** ND refers to none detected.

† Trace refers to those amounts detected but which are too close to the sensitivity limit to quantitate.

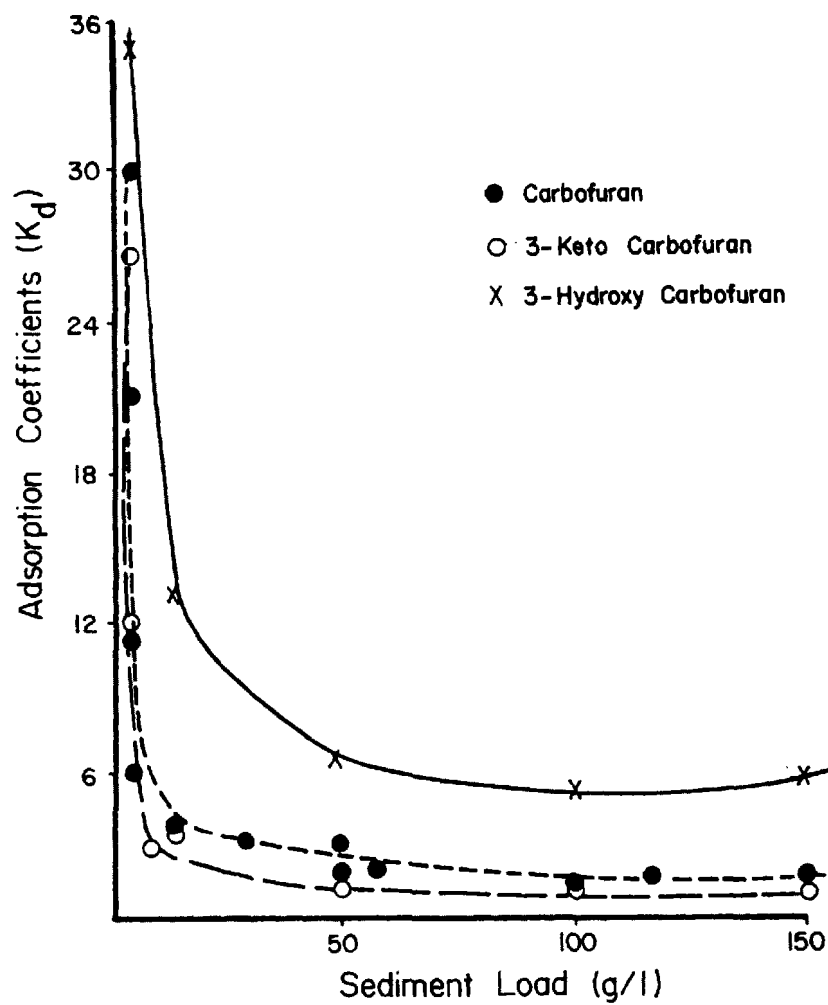


Figure 92. Adsorption coefficients of carbofuran, 3-keto and 3-hydroxy carbofuran at varying sediment loads.

Biological degradation--Very little degradation of carbofuran was observed in the unsterilized Beaumont clay soil samples incubated under flooded conditions for 96 hours (Table 41). However, more than 20% of the carbofuran could not be recovered in the sterilized soil samples. Steam autoclaving caused the Beaumont clay soil to disperse, creating a significant colloidal load. Since the entire contents of the flasks were extracted, the data suggested that carbofuran was non-biologically altered to some other moiety of carbofuran which was tightly bound to soil colloids. Others have recently reported on the importance of chemical alteration of carbofuran to carbofuran phenol with respect to soil adsorption (Caro et al., 1973; Getzin, 1973).

TABLE 41. CARBOFURAN RECOVERED FROM FLOODED BEAUMONT CLAY SOIL EQUILIBRATED 96 HOURS AT 27°C

Treatment*	Carbofuran Recovered**
	%
Unsterilized	95
Sterilized	79

* Sterilized samples, steam autoclaved prior to 100 µg carbofuran spike.

** Average of four determinations.

Another experiment was conducted with flooded soils to assess the effects of more reduced conditions than obtained in the above experiment. This was accomplished by allowing flooded Beaumont clay soil samples to equilibrate six weeks prior to the introduction of carbofuran and 3-keto carbofuran into the system. The data shown in Table 42 indicate that more reduced conditions favor the degradation of carbofuran and especially that of 3-keto carbofuran. Although the redox potentials were positive, it may be more a reflection on the length of equilibration than on oxidized conditions. Potentials were obviously much lower at some point in the six week equilibration period as evidenced by the rusty coating on the walls of the flasks. Perhaps the addition of carbofuran and 3-keto carbofuran tended to drive the highly equilibrated systems to a more oxidized state.

Carbaryl

Carbaryl (1-naphthyl-N-methyl carbamate) is a broad spectrum insecticide belonging to the N-methyl carbamate family of pesticides. Carbaryl has several metabolites associated with its degradation, but 1-naphthol is the most significant (Kazano et al., 1972; Wauchope and Haque, 1973). Bollag and Liu (1971) have demonstrated that soil microorganisms vary considerably in their ability to degrade carbaryl and 1-naphthol, and that some metabolites can be more deleterious to certain non-target organisms than the original pesticide. Kaufman et al. (1970) determined that methyl carbamate pesticides

TABLE 42. EFFECT OF REDUCING CONDITIONS ON THE DISSIPATION OF CARBOFURAN AND 3-KETO CARBOFURAN IN FLOODED SAMPLES OF A BEAUMONT CLAY SOIL

<u>Sample Spike</u>	<u>Aeration</u>	<u>Redox Potential</u>	<u>Pesticide Recovered</u>
80 ug		+mv	%
Carbofuran	Open	115	100
Carbofuran	Restricted	75	88
3-Keto*	Open	165	65
3-Keto	Restricted	130	11

* 3-Keto refers to 3-keto carbofuran.

are competitive inhibitors of soil microbial enzyme systems which hydrolyze other pesticides. It is not known if synergistic effects will occur between the pesticides to be used in this study.

Wauchope and Haque (1973) evaluated the effects of pH, light intensity, and temperature on carbaryl in the laboratory. They found the stability of carbaryl and 1-naphthol to be greatest in weakly acidic solutions. Marked decreases in the stability were noted with increases in pH. At a constant pH value of 10.0, first order half-lives were found to be 20 and eight minutes at 25° and 35°C, respectively. The 1-naphthol derivative was more susceptible to photodegradation than carbaryl. As indicated earlier, most rice soils would be well below the pH levels employed in their experiments. However, the pH of marine estuaries would be approximately that of sea water which has a pH of 8.

Karinen et al. (1967) did investigate the persistence of carbaryl and 1-naphthol in the marine estuarine environment. Their efforts indicated that carbaryl and 1-naphthol were greatly affected by temperature and the presence of mud. In plain sea water, the carbaryl concentration decreased 50% in 38 days at 8°C. Most of the decrease was accounted for by the production of 1-naphthol. In the presence of mud, both carbaryl and 1-naphthol were dissipated to less than 10% in the sea water in 10 days. They were found to be adsorbed by the mud where degradation continued at a slower rate. Radioactive carbon dioxide was produced in the aquaria spiked with ¹⁴C carbonyl-labeled and ring-labeled carbaryl, indicating decomposition by hydrolysis of the carbamate and oxidation of the ring had occurred. Some 60% of the total ¹⁴C activity could not be accounted for, which the authors believed to have been evolved as methane gas. Their primary evidence for this was the fact that carbaryl could be detected in the mud for 42 days at low concentrations, and the 1-naphthol persisted in significant quantities for only one day. It should be noted that their recovery was based upon a combustion method of their dichloromethane and acetone extracts. Their experiments with the aquaria containing mud indicate

that anaerobic conditions prevailed at some point in the experiment since the pH was 0.4 to 0.5 units lower than the control tank which contained only sea water. No attempt was made to correlate the seemingly increased persistence of carbaryl in the mud treated aquaria to the more reduced conditions. In a side experiment they showed that 93% of the carbaryl was hydrolyzed in four days at 28°C in sea water alone.

Kazano et al. (1972) conducted laboratory experiments with five acid Japanese rice soils treated with ^{14}C carbaryl-labeled carbaryl and ^{14}C -1, 4, 5, 8-ring-labeled 1-naphthol. Their soils were maintained at 80% of the field moisture capacity indicating aerobic conditions prevailed throughout the course of their experiment. The carbaryl experiment was conducted at 25°C with a 32 day incubation period. 1-Naphthol was incubated under the same conditions but for 60 days instead of 32 days. Persistence was found to be influenced by soil type. The $^{14}\text{CO}_2$ evolution ranged from 2.2 to 37.4% of initial radio-activity for carbaryl. The bulk of the remaining activity was found to be associated with the soil humus. The difficulty with which it was extracted indicated to the authors that it was more chemically bound than just adsorbed. They concluded that carbaryl was hydrolyzed to its phenol, 1-naphthol. $^{14}\text{CO}_2$ evolution in the 1-naphthol experiment followed the general scheme as that for carbaryl in that the soils degraded in 60 days incubation as compared to more than twice that for carbaryl in half the time. Once again the 1-naphthol was found to be immobilized on humic substances in the soil. The anomaly in their data was that the soil with the least amount of organic matter (1.5%) resulted in the least amount of $^{14}\text{CO}_2$ evolved in the 1-naphthol experiment. The soil with the lowest total CEC (9.8 meq/100g) and second lowest organic matter content (3.3%) had the lowest $^{14}\text{CO}_2$ evolved in the carbaryl experiment. This may have been a result of variable microbial populations.

Bollag and Liu (1971) reported that carbaryl could be degraded both chemically and biologically to 1-naphthol. A fungus, Fusarium solani, altered 1-naphthol rapidly under moist soil culture.

Residue Levels in the Paddy Water--

A commercially available formulation of carbaryl was foliarly applied approximately three weeks prior to harvest in 1973, 1974 and 1975 (Appendix A).

Generally, the amounts in the water were influenced by the rainfall distribution (Tables 43, 44, and 45). A 7.6 cm rain fell on the plots following the 24-hour sampling in 1973, washing the carbaryl from the foliage and, as a result, greatest amounts were measured in the 48-hour water samples. The peaks in plot water concentrations noted at 40 and 96 hours in 1974 also followed 8.6 and 0.5 rains, respectively. The carbaryl dispersed more evenly over the first four sampling periods in 1975 due to the corresponding rains incurred. Rains in excess of 7.0 cm were recorded between the 24 and 48 hour sampling periods in the regular field experiments in 1973 and 1974. Much of the residual material could have been flushed from the foliage into the plots by this rain. A rapid dissipation rate was indicated by the fact that the samples following the storms were much less than the concentration applied. The amount of carbaryl in the plot water sampled in 1975 peaked 28 hours following application, then was dissipated rapidly over the next 20 hours such that the 48 hour samples did not differ significantly from the 96 hour samples which were

TABLE 43. CONCENTRATION OF CARBARYL IN FLOOD WATER FOLLOWING
ITS APPLICATION IN 1973, AND STATISTICAL SIGNIFICANCE
WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application kg/ha					
		0	24	48	96	192	384
I ₁ R ₁	1	0.160	0.117	0.270	0.001	0.000	0.001
	2	0.055	0.031	0.124	0.001	0.000	0.000
	3	<u>0.095</u>	<u>0.034</u>	<u>0.321</u>	<u>0.000</u>	<u>0.001</u>	<u>0.000</u>
	ave**	0.103a	0.061a	0.238b	0.001a	0.000	0.000
I ₁ R ₂	1	0.119	0.073	0.650	0.000	0.001	0.002
	2	0.073	0.120	0.642	0.001	0.000	0.000
	3	<u>0.171</u>	<u>0.109</u>	<u>0.672</u>	<u>0.006</u>	<u>0.052</u>	<u>0.001</u>
	ave	0.121a	0.101a	0.655b	0.002a	0.027a	0.001a
I ₂ R ₁	1	0.085	0.047	0.563	0.001	0.000	0.002
	2	0.103	0.051	0.396	0.002	0.000	0.000
	3	<u>0.147</u>	<u>0.067</u>	<u>0.222</u>	<u>0.000</u>	<u>0.000</u>	<u>0.000</u>
	ave	0.112a	0.055a	0.394b	0.001a	0.000	0.001
I ₂ R ₂	1	0.119	0.121	0.815	0.573	0.000	0.001
	2	0.161	0.115	0.694	0.000	0.000	0.001
	3	<u>0.513</u>	<u>0.109</u>	<u>1.004</u>	<u>0.000</u>	<u>0.000</u>	<u>0.000</u>
	ave	0.264a	0.115a	0.851b	0.191a	0.000	0.001c

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

TABLE 44. CONCENTRATION OF CARBARYL IN PADDY WATER FOLLOWING
ITS APPLICATION IN 1974, AND STATISTICAL SIGNIFICANCE
WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application					
		kg/ha					
		0	24	40	96	168	240
I ₁ R ₁	1	0.198	0.051	0.498	0.251	0.000	0.000
	2	0.090	0.072	0.032	0.054	0.001	0.000
	3	<u>0.052</u>	<u>0.095</u>	<u>0.007</u>	<u>0.034</u>	<u>0.000</u>	<u>0.000</u>
	ave**	0.113a	0.073a	0.179a	0.113a	0.000a	0.000
I ₁ R ₂	1	0.034	0.125	1.291	0.433	0.000	0.000
	2	0.175	0.090	0.255	0.677	0.015	0.000
	3	<u>0.789</u>	<u>0.068</u>	<u>0.206</u>	<u>0.484</u>	<u>0.000</u>	<u>0.000</u>
	ave	0.333ab	0.094ab	0.584a	0.531a	0.005b	0.000b
I ₂ R ₁	1	0.104	0.039	0.161	0.496	0.000	0.000
	2	0.146	0.015	0.069	0.272	0.000	0.000
	3	<u>0.090</u>	<u>0.020</u>	<u>0.038</u>	<u>0.082</u>	<u>0.000</u>	<u>0.000</u>
	ave	0.113a	0.025a	0.089a	0.288a	0.000a	0.000
I ₂ R ₂	1	0.717	0.173	1.250	0.859	0.002	0.000
	2	1.140	0.659	0.820	0.623	0.000	0.000
	3	<u>1.875</u>	<u>1.807</u>	<u>0.003</u>	<u>1.534</u>	<u>0.473</u>	<u>0.001</u>
	ave	1.244a	0.880ab	0.691b	1.005ab	0.158c	0.000c

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

TABLE 45. CONCENTRATION OF CARBARYL IN PADDY WATER FOLLOWING ITS APPLICATION IN 1975, AND STATISTICAL SIGNIFICANCE WITH RESPECT TO TIME

Treatment Block*	Rep	Hours Following Application				
		kg/ha				
		0	21	28	48	96
I ₁ R ₁	1	0.102	0.490	0.038	0.065	0.000
	2	0.033	0.437	0.232	0.204	0.000
	3	0.029	0.056	0.127	0.090	0.000
	ave**	0.055ab	0.328a	0.132ab	0.120ab	0.000b
I ₁ R ₂	1	0.079	3.513	7.722	0.242	0.000
	2	0.132	1.407	2.644	0.194	0.000
	3	0.112	0.937	1.110	0.201	0.000
	ave	0.108b	1.950ab	3.832a	0.212b	0.000b
I ₂ R ₁	1	0.025	0.181	1.320	0.056	0.000
	2	0.027	0.249	0.024	0.196	0.001
	3	0.011	0.611	0.102	0.134	0.000
	ave	0.021a	0.347a	0.482a	0.129a	0.000a
I ₂ R ₂	1	0.220	2.368	2.927	0.670	0.006
	2	0.170	0.871	0.927	2.119	0.000
	3	0.066	4.476	0.300	1.760	0.625
	ave	0.152b	2.572a	1.385ab	1.516ab	0.210b

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Averages with different letter subscripts are significantly different at the 0.01 level.

essentially zero.

The results of the rainfall simulation experiment are shown in Figure 93 for the 2.5 cm per hour test conducted in 1975. Results of 1974 followed similar trends but were less complete. The initial concentrations represent the residuals in the water at the specified time intervals after application. All concentrations at this point were between 50 and 100 ppm. They were generally ranked such that those with large intervals between application and rainfall had the lowest background levels at the start of the tests. The concentration of carbaryl increased rapidly after rainfall started in the plots which had been sprayed the same day. Within four minutes the concentrations had reached their maximum, after which they remained relatively constant indicating that washoff had been completed. By the end of four minutes, less than two millimeters of rain had reached the plots. Thus, only a very small rainfall was necessary to rinse essentially all the carbaryl from the foliage. The concentration reached at the end of four minutes of rainfall represented approximately 10% of the carbaryl originally applied to the plots. Rainfall events occurring one, two, four, and seven days after application did not result in nearly as great a final concentration in the floodwater. In all cases complete washoff occurred within four to eight minutes after the beginning of the simulated storm. Although the concentrations resulting from washoff generally decreased as the interval between application and rainfall increased, the differences were small and resulted in no more than a doubling of the concentration found at the beginning of the storm. Although no rainfall reached the plots, very heavy dew was present on the plants each night, and it is possible that even after one night of dew, much of the residual pesticide may have already been washed from the foliage.

Analyses of variance indicated that time of sampling collection and application rate had a highly significant influence on carbaryl concentration measured in the water for each of the three years tested (Appendix I, Tables I7, I8, and I9). Residues of carbaryl were found to be greater in those plots under the impoundment irrigation scheme at a 5% level of significance in 1973 and at a 1% level of significance in 1974 (Appendix I). Irrigation treatment had no effect on carbaryl concentrations in 1975 (Appendix I, Tables I7, I8, and I9).

A second order interaction between time and rate of application was observed at a 1% level of significance in 1973 and at a 5% level of significance in 1975. This interaction simply suggests that residual carbaryl levels were greater with respect to time at the excessive application rate. Irrigation treatment and rate of application interacted to significantly affect the carbaryl concentration in 1974.

Residue Levels of Metabolites--

The 1-naphthol metabolite was determined in the paddy water in each of the samples collected in 1973, 1974 and 1975 (Tables 46, 47, and 48, respectively). Amounts present reflect the rate of carbaryl applied. However, the relatively high levels at the zero sampling period indicate that 1-naphthol was present initially as a contaminant. A peak in 1-naphthol levels was found corresponding to the carbaryl washed from the foliage after the rains. Thus, it appears that the 1-naphthol present was not produced as a metabolite of

TABLE 46. CONCENTRATION OF 1-NAPHTHOL IN THE
PADDY WATER IN 1973

Treatment Block*	Rep	Hours Following Application**				
		kg/ha				
		0	24	48	96	192
I ₁ R ₁	1	0.009	0.000	0.001	0.000	0.000
	2	0.004	0.000	0.003	0.000	0.000
	3	0.003	0.001	0.004	0.000	0.000
I ₁ R ₂	1	0.005	0.003	0.007	0.000	0.000
	2	0.020	0.003	0.004	0.001	0.000
	3	0.040	0.001	0.005	0.000	0.000
I ₂ R ₁	1	0.009	0.001	0.002	0.000	0.000
	2	0.017	0.003	0.007	0.000	0.000
	3	0.033	0.004	0.002	0.002	0.000
I ₂ R ₂	1	0.041	0.006	0.020	0.013	0.000
	2	0.008	0.002	0.033	0.000	0.000
	3	0.013	0.007	0.011	0.000	0.000

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Application is with respect to carbaryl.

TABLE 47. CONCENTRATION OF 1-NAPHTHOL IN THE PADDY
WATER SAMPLED IN 1974

Treatment Block*	Rep	Hours Following Application**		
		0	kg/ha 24	40
I ₁ R ₁	1	.001	.001	.003
	2	.002	.001	.002
	3	.004	.001	.000
I ₁ R ₂	1	.000	.001	.012
	2	.002	.002	.006
	3	.051	.001	.002
I ₂ R ₁	1	.001	.001	.011
	2	.005	.000	.001
	3	.005	.000	.000
I ₂ R ₂	1	.013	.008	.001
	2	.110	.010	.000
	3	.001	.005	.003

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Application is with respect to carbaryl.

TABLE 48. CONCENTRATION OF 1-NAPHTHOL IN THE PADDY
WATER SAMPLED IN 1975

Treatment Block*	Rep	Hours Following Application**			
		kg/ha			
		0	21	28	48
I ₁ R ₁	1	.001	.001	.000	.000
	2	.000	.001	.001	.002
	3	.001	.001	.001	.000
I ₁ R ₂	1	.001	-	.009	.006
	2	.000	.021	.091	.000
	3	.001	.044	.006	.001
I ₂ R ₁	1	.000	.004	.011	.000
	2	.001	.000	.000	.000
	3	.000	.001	.000	.001
I ₂ R ₂	1	.014	.019	.035	.000
	2	.000	.005	.012	.010
	3	.001	.065	.009	.009

* I₁ and I₂ indicate continuous and impoundment irrigation treatments, respectively. R₁ and R₂ indicate recommended and excessive application rates, respectively.

** Application is with respect to carbaryl.

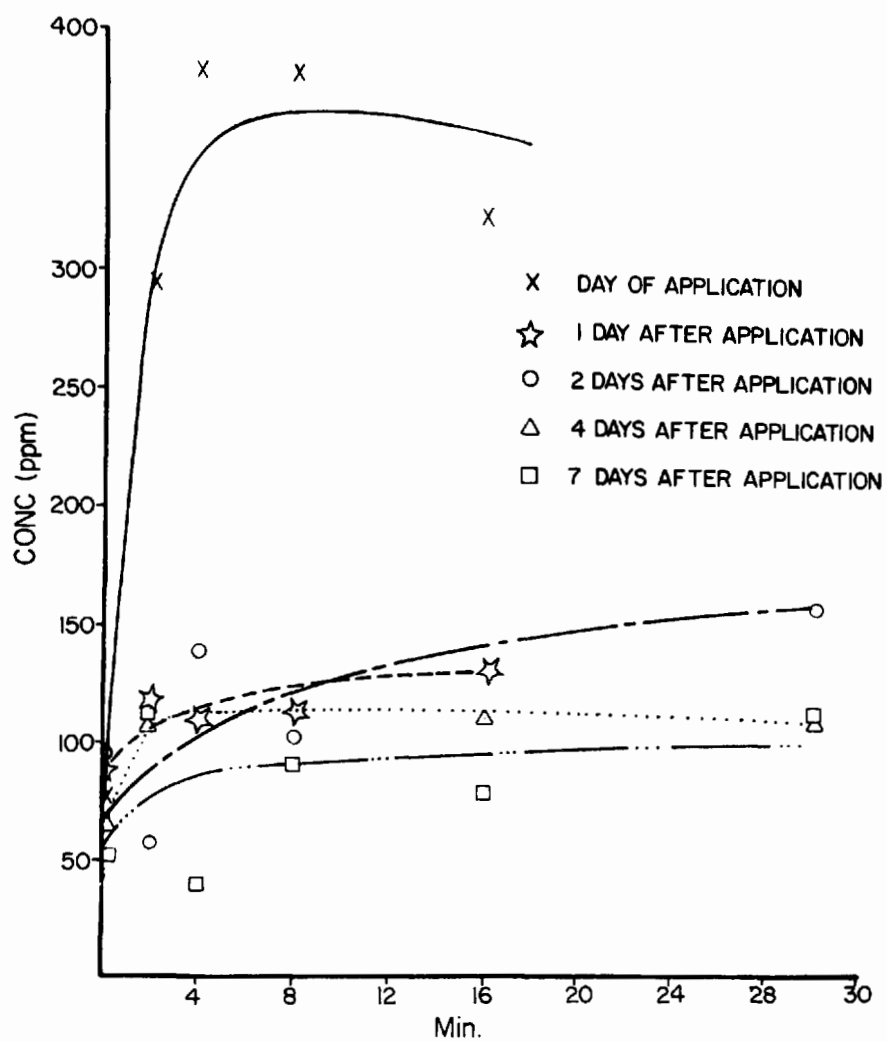


Figure 93. Carbaryl concentrations in the flood water just before and at a series of times following a simulated rainfall of 2.5 cm/hour.

carbaryl in the plots but was about a 2% contaminant of the commercial material. 1-Naphthol was rapidly dissipated in the paddy water and probably would not extend the residual life of carbaryl under flooded conditions even if metabolically produced.

Modes of Dissipation--

Volatilization--No measurable vapor flux was found for carbaryl or 1-naphthol from distilled water at 27°C and air flow rate of eight ml/min. This indicates that little would be lost by volatilization in the field.

Photodecomposition--This mechanism may account for some degradation of carbaryl exposed to direct sunlight on the leaf canopy, but cannot account for the dissipation from the plot water due to the protection of the rice canopy, and the diffraction of the incident radiation by the colloidal material in the plot water.

Adsorption--As demonstrated for the other chemicals, the K_d for carbaryl and 1-naphthol increased sharply at sediment loads less than 10 g/liter (Figure 94), which proves rather conclusively that the observed increase is not dependent upon the properties of the adsorbate molecule but is a function of some physical property associated with the sediment. Carbaryl and 1-naphthol were adsorbed tightly at even the lowest sediment load with only 85 and 73% in solution, respectively. This is similar to the tenacity demonstrated for DCA, which may suggest a chemical type adsorptive mechanism.

Three hundred ml distilled water was added to eight, 100-g samples of Beaumont clay soil previously spiked with 1 g sugar (Figure 95). Four of the flasks containing the soil samples were capped with a cotton plug and autoclaved for 30 minutes. All flasks were fortified with 100 ug carbaryl 48 hours later. Carbaryl was injected into the autoclaved sample flasks with a syringe to prevent contamination. Following a 96 hour incubation period, the soil and water samples were separated by filtration and analyzed separately for carbarul (Table 49). It should be noted that no attempt was made in this experiment to separate carbaryl and 1-naphthol from the respective soil and water samples extracted. More than twice as much carbaryl was recovered in the H₂O from the sterilized samples. This was possibly induced by the sterilization since the treatment dispersed the soil. The condition was noted throughout the 96 hour incubation. Most of the water in the non-sterilized samples was decanted prior to filtration, whereas all of the water in the sterilized samples had been filtered. The net results were enhanced conditions for soil adsorption in the sterilized samples, which suggests that the reduced conditions may have retarded biological dissipation. Ordinary laboratory light of between 10 and 15 microeinsteins had no discernible affect on the amounts of carbaryl recovered in the experiment.

No carbaryl was detected in the soils sampled in the plots at either the 2.5 to 5.0 cm or 17.5 to 20.0 cm depths following its application in 1973, indicating it had not moved to these zones in the soil profiles.

Biological degradation--Several flasks containing Beaumont clay soil were placed under reduced conditions by flooding and were allowed to equilibrate 10 days prior to the 100 ug spike of carbaryl and 1-naphthol. This was followed

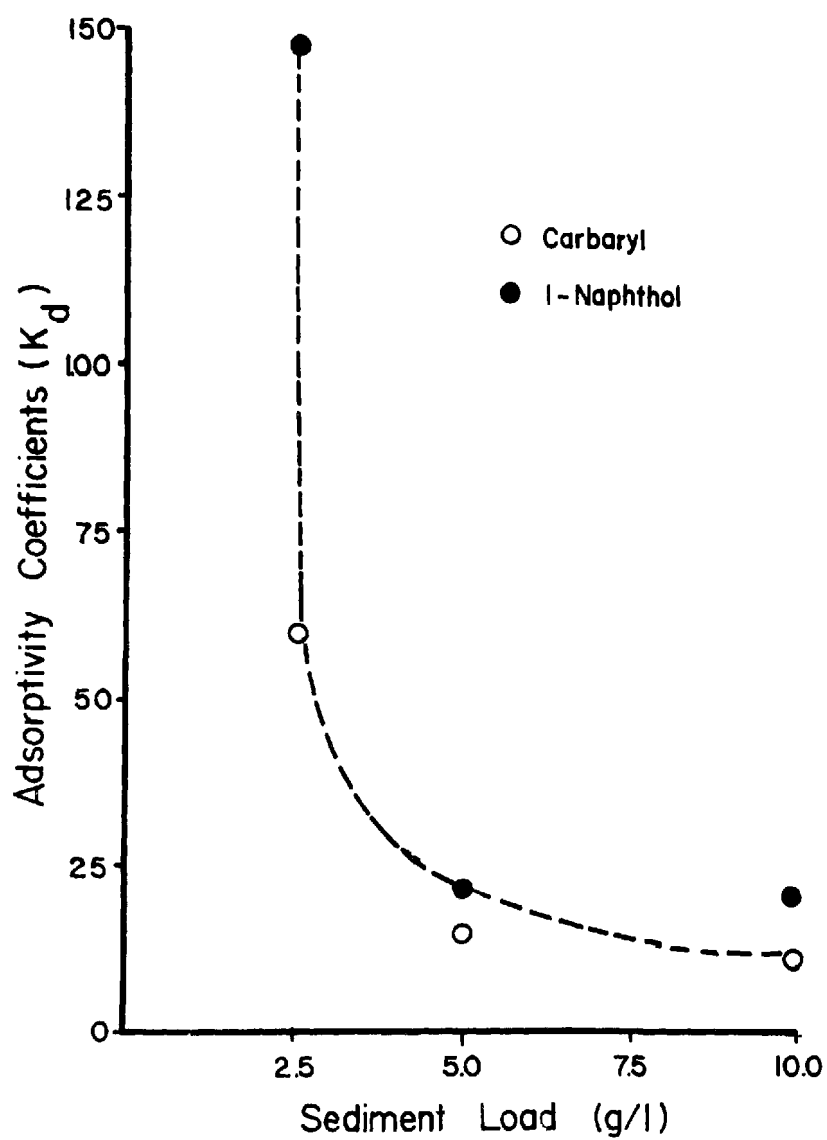


Figure 94. Adsorption coefficients of carbaryl and 1-naphthol at varying sediment loads.

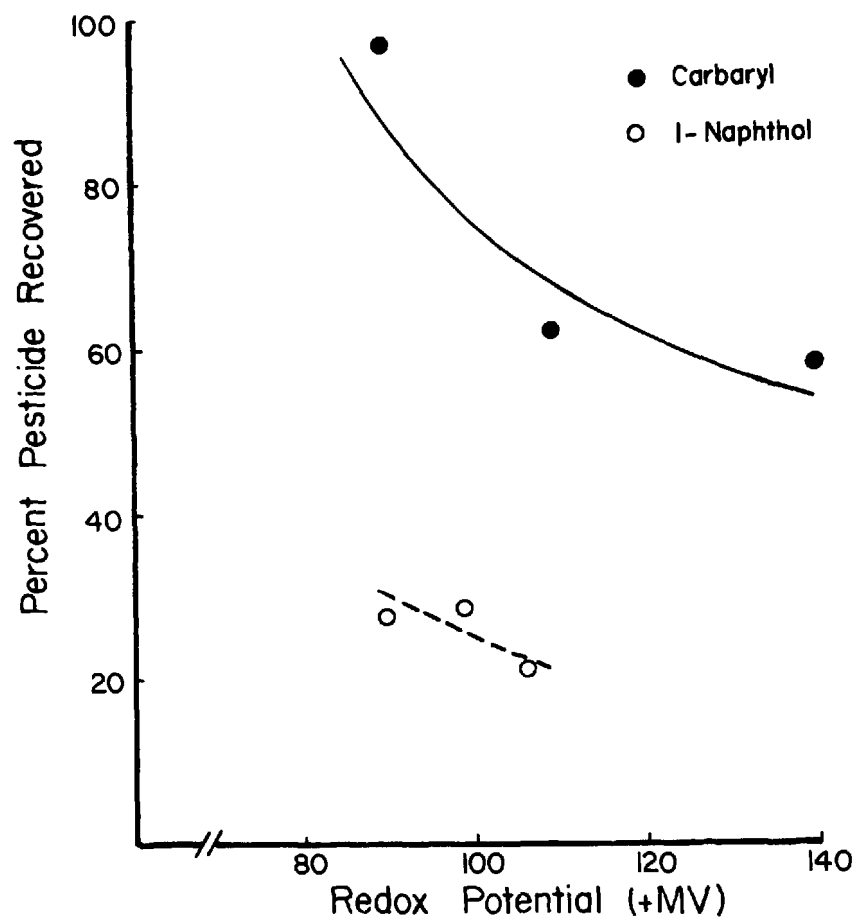


Figure 95. Percent recoveries of carbaryl and 1-naphthol from flooded Beaumont clay soil samples, and corresponding redox potentials.

TABLE 49. EFFECT OF STERILIZATION ON CARBARYL RECOVERED
FROM A BEAUMONT CLAY SOIL AND FLOOD WATER

Treatment*	Carbaryl Recovered	
	Soil	Water
	%	%
Sterilized Dark	50.5	21.5
Sterilized Light	57.7	20.0
Not Sterilized Dark	22.7	44.3
Not Sterilized Light	13.5	49.0

* Two of the sterilized and two non-sterilized samples were wrapped in tin-foil and placed in the dark for the 96 hour incubation period.

by an additional 12 day equilibration period and subsequent extraction of the contents of the flasks. Redox potentials were measured in the soil and flood water just prior to extraction. The amounts of 1-naphthol recovered ranged between 24 and 32% (Figure 95). Carbaryl recovered was higher and ranged between 61 and 98%. The 98% recovered indicates that no degradation of carbaryl occurred over the 12 day period at a redox value of +90 mv. The corresponding soil redox potentials ranged between -475 and -490 mv, indicative of very reduced conditions. Thus, it appears that the redox potentials of the water may be more of a governing factor in the dissipation of carbaryl than that of soil. 1-Naphthol dissipation did not appear to be hindered by the reduced conditions attained. Very low redox potentials could possibly retard the dissipation of carbaryl, but it is doubtful that the potentials were sufficiently low under the field conditions to retard degradation. The author submits that the high rainfall incidence and low substrate levels available in the plot water late in the season would favor more oxidized conditions.

Carbaryl Summary--

Carbaryl was washed from the foliage into the plots by the rain where it was dissipated in a relatively short period of time without the subsequent production of appreciable 1-naphthol levels. Carbaryl was found to be adsorbed to the colloidal fraction of the soil. The most significant toxic metabolite, 1-naphthol, was similarly adsorbed to the colloidal fraction of the soil. Adsorptivity coefficients were found to increase sharply at sediment loads less than 5.0 g/liter. The actual sediment load of the plot water was considerably lower than this (Figure 94) suggesting an even greater K_d value. It is not known if the actual amount of sediment in the plot water or the adsorptivity

of the pesticide determines the optimum amount adsorbed. Even if substantial conversion of carbaryl to 1-naphthol had occurred, it probably would not be reflected in the irrigation return flow from a Beaumont clay soil due to the adsorptive mechanism. The dissipation rate of 1-naphthol measured in the laboratory in flooded soil samples was greater than that of carbaryl, further suggesting that 1-naphthol would have little effect on the residual life of carbaryl under normal rice culture.

PESTICIDES IN CANAL WATER

The canal water collected each time pesticide samples were collected from the flood water was screened for the pesticides used in this study to determine background levels. Samples were collected from the feeder canal adjacent to the experimental plots in 1973. However, the main irrigation canal was sampled in 1974 and 1975. The concentrations following the applications of the pesticides are given in Tables 50, 51, and 52. Values in 1973 are biased by the drifts in application due to the close proximity of the feeder canal. Conversely, no appreciable background levels were found in 1974 and 1975, indicating that the materials which may have inadvertently reached the canal water applied further upstream were not contaminating the water supply used for the experiment.

TABLE 50. BACKGROUND LEVELS OF PESTICIDES IN CANAL H₂O USED TO FLOOD EXPERIMENTAL PLOTS IN 1973

Pesticide	Hours Following Application				
	0	96	192	384	768
Propanil	6.4	ND	-	-	-
DCA	ND	ND	-	-	-
TCAB	ND	ND	-	-	-
Molinate	0.6	Trace	ND	ND	ND
Carbofuran	5.5	1.4	0.8	1.3	0.9
3-keto	ND	ND	ND	ND	ND
3-hydroxy	ND	ND	ND	ND	ND
Carbaryl	78.2	11.0	Trace	ND	-
1-Naphthol	8.4	9.3	Trace	ND	-

TABLE 51. BACKGROUND LEVELS OF PESTICIDES IN CANAL H₂O USED
TO FLOOD EXPERIMENTAL PLOTS IN 1974

Pesticide	Hours Following Application				
	0	96	192	384	768
Propanil	4.4	-	-	-	-
DCA	ND	-	-	-	-
TCAB	ND	-	-	-	-
Molinate	ND	ND	ND	ND	ND
Carbofuran	ND	ND	2.6	14.5	ND
3-keto	ND	ND	ND	1.2	ND
3-hydroxy	ND	ND	ND	ND	ND
Carbaryl	0.4	ND	ND	-	-
1-Naphthol	ND	ND	ND	-	-

TABLE 52. BACKGROUND LEVELS OF PESTICIDES IN CANAL H₂O USED
TO FLOOD EXPERIMENTAL PLOTS IN 1975

Pesticide	Hours Following Application				
	0	96	192	384	768
Propanil	11.6	-	-	-	-
DCA	ND	-	-	-	-
TCAB	ND	-	-	-	-
Molinate	ND	ND	ND	ND	ND
Carbofuran	ND	0.8	ND	Trace	ND
3-keto	ND	ND	ND	ND	ND
3-hydroxy	ND	ND	ND	ND	ND
Carbaryl	Trace	ND	ND	ND	-
1-Naphthol	ND	ND	ND	ND	-

TOXICITY OF PESTICIDES TO FISH

General

The toxicity of many pesticides to fish is well known and well documented. Some of the available data is summarized in Tables 53 to 56. This data, which has been taken on treated or clarified tap water, may not be transferable to rice paddy water which often contains particulate matter, microflora, nutrients, and salts. Few studies have been conducted, however, which evaluate the toxicity of pesticides in irrigation return flow from rice paddies.

In 24 hour and 96 hour acute toxicity tests on three species of fish (Mosquitofish, Channel catfish, and Bluegills), Carter and Graves (1973) found carbofuran four, five and 73 times as toxic as carbaryl. They reported 50% tolerance limits (TL50's) ranging from 0.08 ppm to 2.03 ppm for carbofuran, and TL50's from 1.4 to 11.5 ppm for carbaryl. The FMC Corporation (undated) reported 96 hour 50% lethal concentrations (LC50's) for carbofuran to Bluegill (.24 ppm), Channel catfish (.21 ppm) and Rainbow trout (.28 ppm).

Young fish have been reported to be dramatically more susceptible to carbaryl than are their elder counterparts. In two 96 hour tests on carbaryl's toxicity to Mosquitofish, 0.5 g (Carter and Graves, 1973), and 65 g (Chaiyara et al., 1975) the LC50's were found to be 1.4 ppm and 31.8 ppm, respectively.

Macek and McAllister (1970) conducted tests on the relative susceptibility of 12 fish species to nine insecticides. They found channel catfish among the least susceptible and carbaryl to be less toxic than the organochlorine or organophosphorus insecticides tested.

The effects of long-term exposure to fathead minnows in carbaryl were considered in tests run by Carlson (1972). He introduced the fish when they were one to five days old and held them at constant concentrations for nine months. His study showed the no-effect level of carbaryl to be .21 ppm while reproduction was disrupted at .68 ppm.

Korn (1973) studied the uptake and persistence of carbaryl in Channel catfish. Results indicated food-dosed fish eliminated residues rapidly, while the water-dosed fish had not eliminated residues by the end of the 28 day test. The water exposure levels were .25 ppm and 0.05 ppm. These levels produced residues in the fish of 0.011 ppm and 0.002 ppm, respectively. Statham (1975) studied biliary excretion products of carbaryl. He exposed rainbow trout to .25 ppm carbaryl and found that in 24 hours the concentration of carbaryl in the bile was 1000 times that in the water. Statham and Lech (1975) noted an increase in the acute toxicity of several pesticides and herbicides to rainbow trout by the addition of a sub-lethal concentration of carbaryl.

Chaiyara et al. (1975) determined the 96 hour LC50 for mosquitofish in the herbicides propanil (9.46 ppm) and molinate (16.4 ppm).

Fabacher and Chambers (1974) determined percent mortality of insecticide-susceptible mosquitofish when exposed for 24 hours to 10 ppm of various herbicides. They found 50 to 100% mortality in the fish exposed to 10 ppm propanil

TABLE 53. TOXICITY OF PROPANIL TO FISH REPORTED IN THE LITERATURE

Organism	Exposure Time	Exposure Type	Concen- tration	End † Point	Temp- erature	Weight	Source
	Hours		ppm				
Mosquitofish pub	24	S	11.3	LC50	-	15cm	Chaiyara (75)
	48	S	11.0	LC50	-	65g	Chaiyara (75)
	96	S	9.46	LC50	-		Chaiyara (75)
Lake emerald shiners	4	S	13.5	TLM	70°F	59mm	Swabey(1965)
	24	S	7.5	TLM	70°F	59mm	Swabey(1965)
	48	S	7.5	TLM	70°F	59mm	Swabey(1965)
	96	S	7.5	TLM	70°F	59mm	Swabey(1965)
Mosquitofish	24	S	10.0	50-100% Death	21°C		Fabacher(75)

†(LC50) Lethal Concentration to 50%
(TLM) Median Tolerance Limitation

TABLE 54. TOXICITY OF MOLINATE TO FISH REPORTED IN THE LITERATURE

Organism	Exposure Time	Exposure Type	Concentration	End + Point	Temperature	Weight	Source
	Hours		ppm				
Mosquitofish pub	24	S	30.7	LC50	-	3-4cm	Chaiyara (75)
	48	S	21.4	LC50	-	3-4cm	Chaiyara (75)
	96	S	16.4	LC50	-	3-4cm	Chaiyara (75)
Catfish	96	S	13.0	LC50	60-62°F	2g	McGowan(1972)
Bluegill	24	S	>37.0	TL50	18°C	1.5g	Sleight(1972)
Rainbow trout	24	S	>28.0	TL50	13°C	1.5g	Sleight(1972)
Flathead minnow	24	S	>42.0	TL50	18°C	.8g	Sleight(1972)
Bluegill	96	S	18.8	TL50	18°C	1.5g	Sleight(1972)
Rainbow trout	96	S	6.97	TL50	13°C	1.5g	Sleight(1972)
Flathead minnow	96	S	26.0	TL50	18°C	.8g	Sleight(1972)
Mosquitofish	24	S	10.0	0-10% Death	21°C		Fabacher(74)
Rainbow trout	48	S	.29	LC50	12.8°C		Crosby(1966)
Bluegill	48	S	.48	LC50	23.9°C		Crosby(1966)

+(TL50) Tolerance Limitation to 50%
 (LC50) Lethal Concentration to 50%

TABLE 55. TOXICITY OF CARBOFURAN TO FISH REPORTED IN THE LITERATURE

Organism	Exposure Time	Exposure Type	Concen- tration	End† Point	Temp- erature	Weight	Source
	Hours		ppm		°C		
Bluegill	96	S	.08	TL50	23	.5 g	Carter (1973)
Mosquitofish	96	S	.30	TL50	24	.5 g	Carter (1973)
Channel catfish	24	S	2.03	TL50	26	10 g	Carter (1973)
Bluegill	96	S	.24	LC50	-	-	FMC Corp.
Channel catfish	96	S	.21	LC50	-	-	FMC Corp.
Rainbow trout	96	S	.28	LC50	-	-	FMC Corp.

†(TL50) Tolerance Limitation to 50%

(LC50) Lethal Concentration to 50%

TABLE 56. TOXICITY OF CARBARYL TO FISH REPORTED IN THE LITERATURE

Organism	Exposure Time	Exposure Type	Concentration	End Point	Temperature	Weight	Source
	Hours		ppm		°C		
<i>Gambusia affinis</i> (Mosquitofish)	24	S	60.0	LC50	-	65 g	Chaiyara ('75)
	48	S	35.0	LC50	-	.65 g	Chaiyara ('75)
	96	S	31.8	LC50	-	65 g	Chaiyara ('75)
<i>Cyprinus carpio</i> (Carp)	24	S	13.51	LC50	28-32	7-9cm	Toor (1974)
	48	S	11.74	LC50	28-32	7-9cm	Toor (1974)
	72	S	10.36	LC50	28-32	7-9cm	Toor (1974)
Bluegill	96	S	5.9	TL50	23	.5 g	Carter (1973)
Mosquitofish	96	S	1.4	TL50	24	.5 g	Carter (1973)
Channel catfish	24	S	11.5	TL50	26	10 g	Carter (1973)
Channel catfish	96	S	15.8	TL50	18	.6-1.7g	Macek (1970)
Bullhead	96	S	20.0	TL50	18	.6-1.7g	Macek (1970)
Goldfish	96	S	13.2	TL50	18	.6-1.7g	Macek (1970)
Flathead minnow	96	S	14.6	TL50	18	.6-1.7g	Macek (1970)
Carp	96	S	5.3	TL50	18	.6-1.7g	Macek (1970)
Sunfish	96	S	11.2	TL50	18	.6-1.7g	Macek (1970)
Bluegill	96	S	6.8	TL50	18	.6-1.7g	Macek (1970)
Bass	96	S	6.4	TL50	18	.6-1.7g	Macek (1970)
Rainbow	96	S	4.3	TL50	18	.6-1.7g	Macek (1970)
Brown	96	S	1.9	TL50	18	.6-1.7g	Macek (1970)
Coho	96	S	.76	TL50	13	.6-1.7g	Macek (1970)
Perch	96	S	.74	TL50	18	.6-1.7g	Macek (1970)
Channel catfish	48	S	19.0	EC50	24	-	Cope (1964)
Bluegill	48	S	2.5	EC50	24	-	Cope (1964)
Rainbow	48	S	2.0	EC50	13	-	Cope (1964)
Bluegill	24	S	3.4	EC50	24	-	Cope (1964)
Longnose Killfish	24	S	1.75	TLM	-	-	Stewart (1967)
Shiner perch	24	S	3.9	TLM	-	-	Stewart (1967)
English sole	24	S	4.1	TLM	-	-	Stewart (1967)
White mullet	24	S	4.25	TLM	-	-	Stewart (1967)
3-spine stickleback	24	S	6.7	TLM	20	-	Stewart (1967)
Flathead minnow	96	S	13.0	TLM	-	-	Stewart (1967)
Harlequin fish	24	S	6.8	LC50	-	-	Alabaster (1963)
Longnose killfish	48	S	1.75	TLM	-	-	Butler (1963)
Goldfish	48	S	15.0	LC50	-	-	Hayne (1958)
Flathead minnows	96	S	9.0	TL50	-	-	Carlson (1973)
3-spine stickleback	96	S	3.99	TLM	20±.5°	22-44mm	Katz (1961)

† (TLM) Median Tolerance Limitation
 (TL50) Tolerance Limitation to 50%
 (LC50) Lethal Concentration to 50%
 (EC50) Effective Concentration to 50%
 (LD50) Lethal Dose to 50%

and 0 to 10% mortality with the fish in 10 ppm molinate. In the same report, LC50's were found on mosquitofish from pesticide-contaminated drainage canals adjacent to cotton, soybean, and rice fields. Their study indicated that through selective mortality from insecticide contamination of the environment, the toxic response of fish to other pollutants (such as herbicides) can change. More work is needed to develop an understanding of the possible effects of multibicide interactions and their alteration of toxic responses in exposed fish species.

Fish may be indirectly affected by any upset in the aquatic ecosystem. Herbicides were viewed as a danger to fish by Holden (1972) since they destroy the vegetation which is an important food. Holden also pointed out that the zooplankton and insect larvae which are important food sources for fish are often particularly susceptible to insecticides. Short duration exposure of fish to potentially lethal concentrations of a pesticide may have "delayed lethal effects." Alabaster (1969) exposed fish for 30 minutes to an herbicide concentration lethal in eight hours, and the fish died a week later.

This study was undertaken to evaluate the toxicity of the four pesticides used in the field and to fish in both filtered tap water and irrigation return flow water.

Bioassay Data

Three sources of water were used in the bioassays. Tap water was used in all tests, and water collected from two different paddys on different dates were also used. As will be discussed later, the presence of an unknown toxicant was suspected in paddy water I, while no such contaminate was suspected in the second collection of paddy water.

The 24, 48, and 96 hour TLM concentrations and the 95% confidence intervals for each pesticide in each water are given in Tables 57 to 59 and Figures 96 to 99.

The TLM concentrations for propanil were greater in the filtered tap water than in either of the paddy waters.

The TLM values for molinate at 24 hours did not differ between waters. After 96 hours of exposure, the values in the filtered tap water and the paddy water II were similar but had decreased substantially in paddy water I. Molinate was the least toxic of the pesticides tested as reflected by the TLM₉₆ values.

In all waters, carbofuran was the most toxic of the pesticides tested. The TLM concentrations for carbofuran were determined in both the static and intermittent flow systems. For the static tests with tap water, the TLM₉₆ values were greater than for the intermittent tests. No differences between static and intermittent test results were evident in the paddy water II.

The increased toxicity in the intermittent flow tests with carbofuran in filtered tap water may be attributed to the difference between constant toxicant concentration in the intermittent test as compared to the single dose

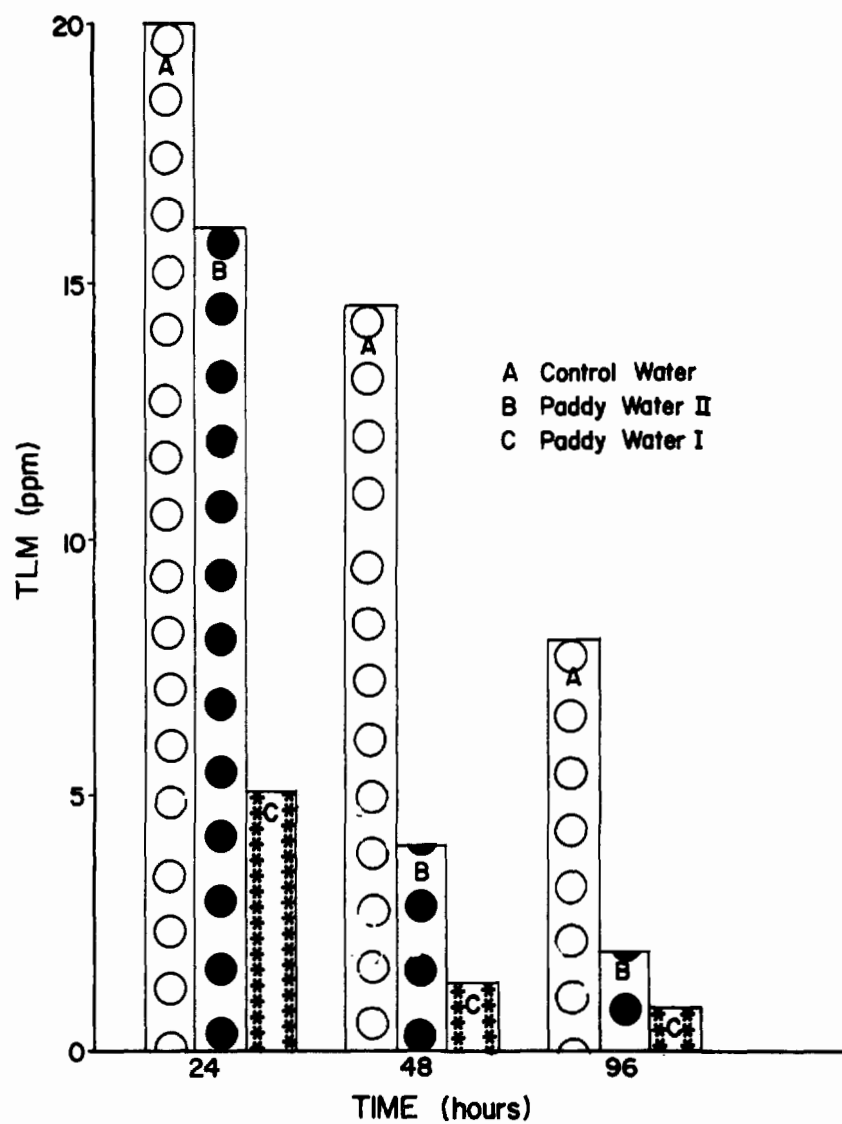


Figure 96. Median tolerance limitation for propanil in the three waters.

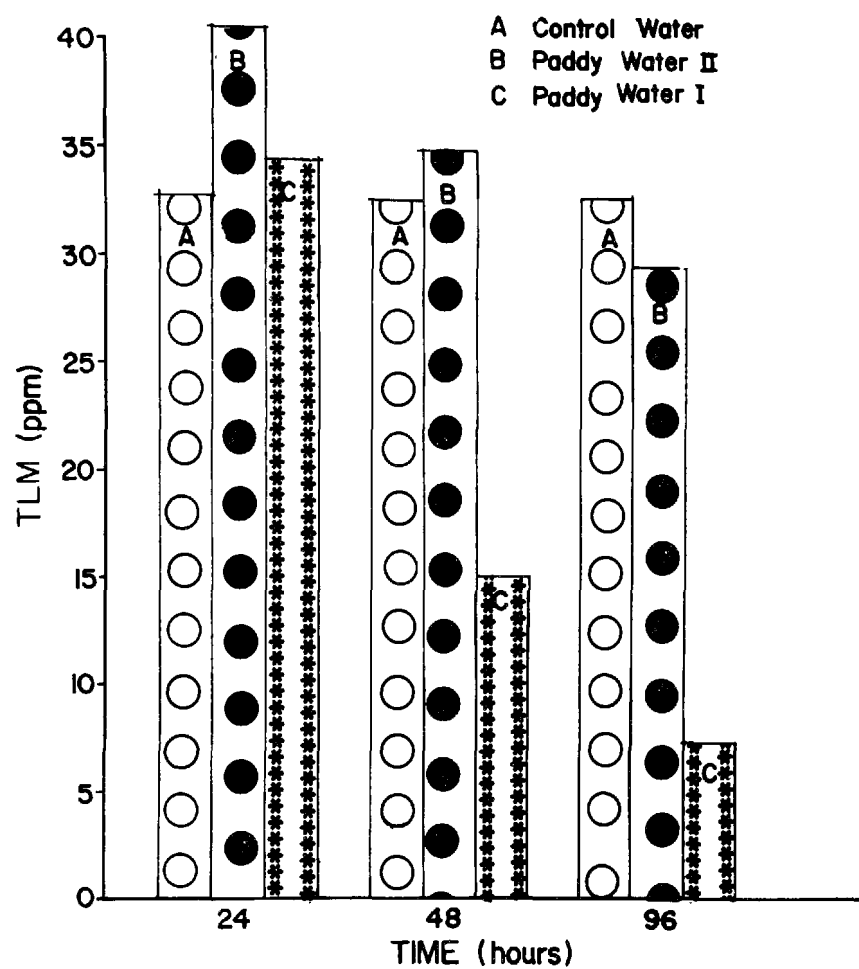


Figure 97. Median tolerance limitation for molinate in the three water.

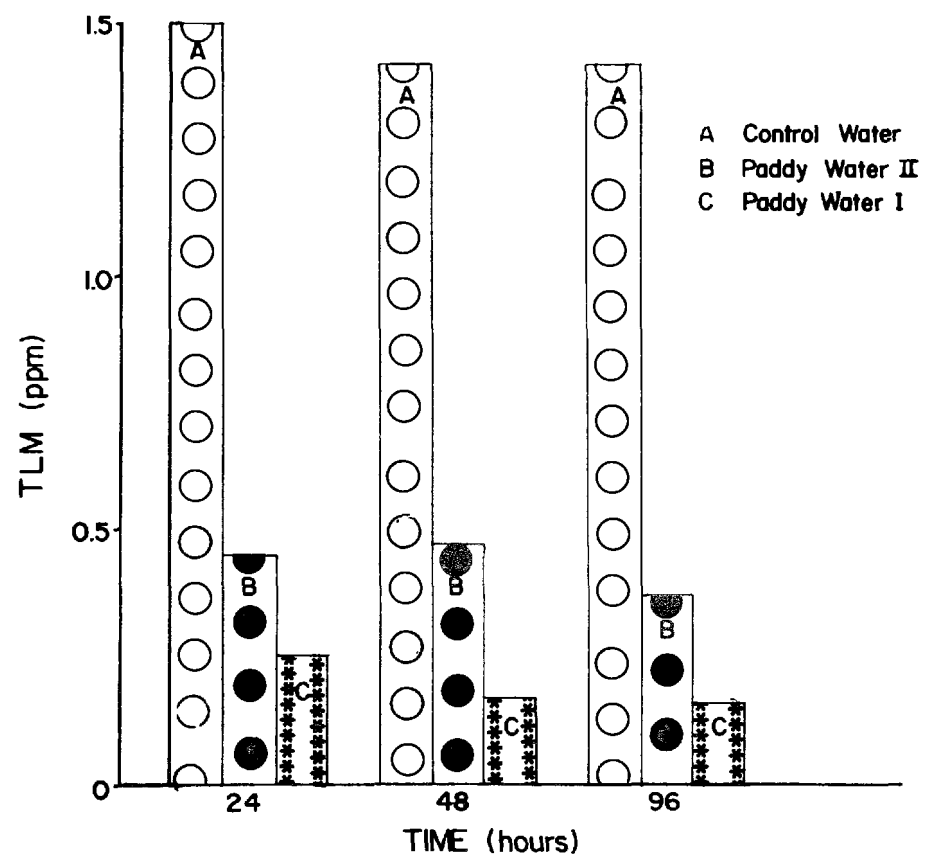


Figure 98. Median tolerance limitation for carbofuran in the three waters.

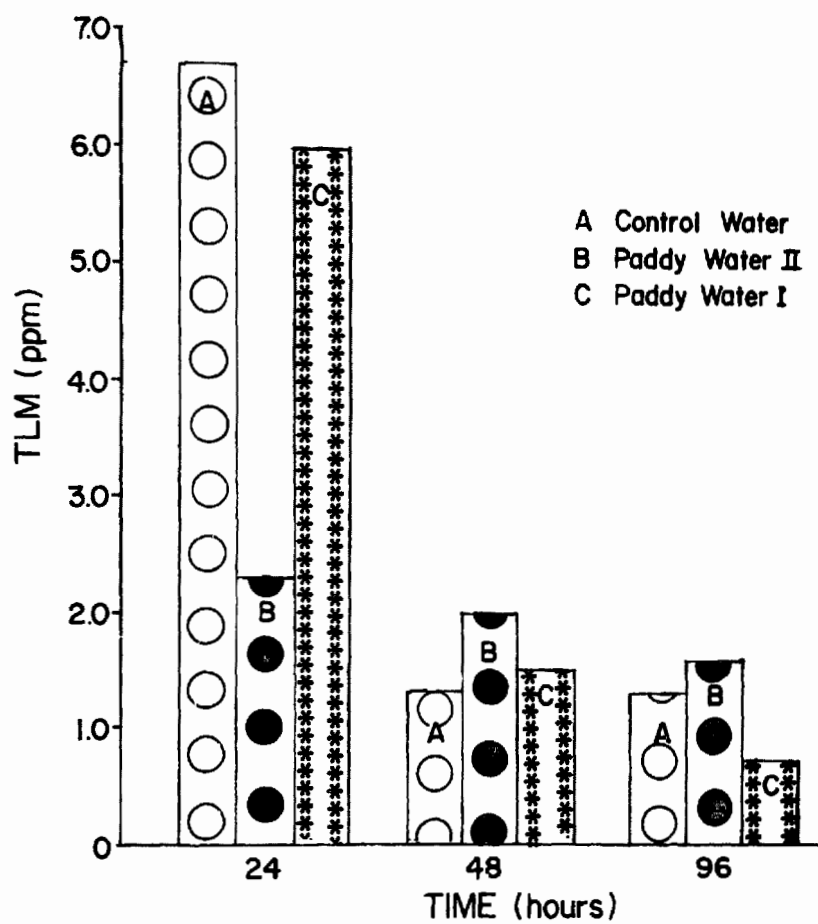


Figure 99. Median tolerance limitation for carbaryl in the three waters.

TABLE 57. THE 24, 48, 72, AND 96 HOUR TLM CONCENTRATION AND THEIR 95% CONFIDENCE INTERVALS IN PADDY WATER I IN STATIC TESTS GIVEN IN PPM

Pesticide	24-Hour	48-Hour	72-Hour	96-Hour
Propanil	>5.00 -	1.34 (1.01-1.99)	0.82 (.66-1.18)	0.43 (0-.59)
Molinate	34.01 (28.38-45.53)	15.67 (13.28-18.13)	7.21 (5.50-8.63)	>5.00
Carbofuran	.25 (.16-.33)	.17 (.07-.29)	.16 (.14-.17)	.13 (.11-.15)
Carbaryl	6.02 (5.20-6.71)	1.53 (1.27-1.94)	0.67 (.55-.83)	.14 (.08-.19)

TABLE 58. THE 24, 48 AND 96 HOUR TLM CONCENTRATIONS AND THEIR 95% CONFIDENCE INTERVALS IN FILTERED TAP WATER IN PPM

Pesticide	Flow	24-Hour	48-Hour	96-Hour
Propanil	Static	20.81 (19.68-22.44)	14.51 (13.33-15.65)	7.94 (6.99-8.85)
Molinate	Static	33.25 (31.82-34.96)	33.24 (31.82-34.96)	33.24 (31.82-34.96)
Carbofuran	Static	1.5 -	1.42 (1.33-1.80)	1.42 (1.29-1.70)
Carbofuran	Intermittent	>.56 (.50-.62)	.52 (.47-.58)	.51 (.46-.56)
Carbaryl	Static	6.71 (5.89-7.78)	1.30 (1.24-1.40)	1.30 (1.24-1.70)

TABLE 59. THE 24, 48 AND 96 HOUR TLM CONCENTRATIONS AND THEIR 95% CONFIDENCE INTERVALS IN PADDY WATER II IN PPM

Pesticide	Flow	24-Hour	48-Hour	96-Hour
Propanil	Static	16 ppm -	4.03 (2.39-12.36)	1.90 (1.63-3.24)
Molinate	Static	41 ppm -	35.47 (24.35-59.19)	29.41 (19.73-46.41)
Carbofuran	Static	.45 (.29-.62)	.45 (.29-.62)	.37 (.25-.51)
Carbofuran	Intermittent	1.60 (.67-1.99)	1.60 (.67-1.99)	.48 (.32-1.27)
Carbaryl	Static	2.27 (1.60-3.54)	2.00 (1.34-3.16)	1.56 (0.76-2.13)

of concentrated toxicant in the static test. However, the results in paddy water do not lend themselves to this explanation. Apparently the other factors in the paddy water are more influential on the 96 hour TLM than the decrease in toxicant concentrations in static systems.

The TLM's of carbaryl were nearly the same for the filtered tap water and for paddy water II. Much lower concentrations, however, were toxic to the fish in paddy water I.

In all cases, the TLM₉₆ values in paddy water I were less than those found in either the filtered tap water or paddy water II. In addition, an average of only 75% of the fish in the paddy water I controls survived for 96 hours. The reasons for the greater toxicity of the pesticides in this water and the loss of 25% of the fish in the controls was sought.

The presence of an unknown toxicant in paddy water I was suspected. An organic chloride pesticide scan (Environmental Protection Agency, 1971) showed no trace in paddy water I. The data presented elsewhere in this report suggest that the propanil and molinate applied early in the season (Appendix A, Table A3) would no longer be present in detectable amounts. Since benomyl had been applied most recently, it was suspected as the cause of the greater toxicity in paddy water I. Boiling paddy water I did not reduce the toxicity, thus, the toxicant was temperature stable and did not vaporize readily. Analysis of paddy water I for benomyl using a method capable of detecting levels of 0.5 ppm were negative. Since this is above the toxicity for rainbow trout reported by E. I. duPont de Nemours and Company, Inc. (1974), it is possible that the benomyl caused the loss of fish at 96 hours and the increased toxicity of the other pesticides in the water. More study is needed on the interactive

influences of pesticides and other chemical constituents of water on toxicity, especially since overlapping and often simultaneous applications are often made.

All fish survived 96 hours exposure to untreated paddy water II. Propanil and carbofuran pesticides had lower TLM's in this water, while carbaryl and molinate were not different from the filtered tap water. When both paddy waters are considered, it is evident that for static situations the TLM's are, on the average, lower than those in filtered tap water.

In the tap water, most of the mortality observed in tests with molinate and carbofuran occurred within 24 hours after exposure. The toxic effects continued to result in loss of fish through the 96 hour test for propanil and carbaryl. In paddy water I, the loss of fish in molinate treatments continued to increase with time of exposure. The mortality increases with time in paddy water I and II were greater for those treatments where they were observed than were found in the filtered tap water.

The coefficients of variability were generally greater in the paddy waters than in the filtered tap water. This may result from variability in suspended colloids.

The TLM values for molinate and propanil in the filtered water determined in this study are consistent with those reported in other publications (Tables 53 and 54). However, the bioassays of carbaryl in this study show it to be 10 times more toxic to catfish, and carbofuran to be five times less toxic than is reported in the literature (Tables 55 and 56). These differences may be a result of the different ages of the fish used in the tests reported in the literature.

ORGANIC LOAD

The values of TOC, COD, and BOD measured in the water at the end of each season are given in Tables 60, 61 and 62. During 1975 the intermittently irrigated plots were drained early to allow a study of the influence of water practices on the yield. As a result, there were no results on half of the plots. In lieu of this, the data from the border plots were used. For each parameter, no statistically significant figures were found between the replicated plots, and there is no indication that the volume in the release water differed from the canal water sample. The values of each parameter for both the plots and the canal water were nearly the same in 1973 and 1974, but the TOC and COD were only half as large during 1975, while the BOD averaged twice as much in 1975 as it did in 1973 and 1974. The difference from one year to the next appears to be reflected to the canal water. This may indicate that either the canal water is the source of the season-to-season change, or that the canals are in the same environment as the paddies and undergo the same microflora fluctuations as that when vegetation is blown down or the water level is raised due to rain. The influence of those factors on the average demand of the canals may be similar to those of the water in the paddies.

TABLE 60. AVERAGE TOC, COD AND BOD OF FLOOD WATER AND
CANAL WATER AT THE TIME OF FINAL DRAINAGE IN 1973*

Treatment	TOC mg/l	COD mg/l	BOD mg/l
Impounded irrigation recommended rates of pesticides and nutrients	28	61	2.2
Impounded irrigation recommended rates of pesticides and fertilizers	25.3	57	1.6
Continuous flow irrigation excessive rates of fertilizer and pesticides	29	45.7	2.2
Continuous flow irrigation excessive rates of fertilizer and pesticides	26.7	45	1.6
Canal water	28	55	1.0

* No significant differences between results were found in any year.

TABLE 61. AVERAGE TOC, COD AND BOD OF FLOOD WATER AND
CANAL WATER AT THE TIME OF FINAL DRAINAGE IN 1974*

Treatment	TOC mg/l	COD mg/l	BOD mg/l
Impounded irrigation recommended rates of pesticides and nutrients	29	47	2.1
Impounded irrigation recommended rates of pesticides and fertilizers	23	52	2.2
Continuous flow irrigation excessive rates of fertilizer and pesticides	27	57	1.7
Continuous flow irrigation excessive rates of fertilizer and pesticides	21	48	1.6
Canal water	21	47	2.3

*No significant differences between results were found in any year.

TABLE 62. AVERAGE TOC, COD AND BOD OF FLOOD WATER AND CANAL WATER AT THE TIME OF FINAL DRAINAGE IN 1975*

Treatment	TOC mg/l	COD mg/l	BOD mg/l
Impounded irrigation recommended rates of pesticides and fertilizers	11	28	5.3
Continuous flow irrigation excessive rates of fertilizer and pesticides	9.3	25.4	2.0
Border plots intermittent flow irrigation recommended rates of fertilizer and pesticides	13	29.5	6.4
Canal water	17	36	3.4

*No significant differences between results were found in any year.

In any event, more of the values are increased in the rice field, probably because of the large surface area to which the water is exposed. In addition, neither the BOD nor the COD exceeded the 30 mg/l level. During 1973 and 1974 the COD levels exceeded 30 mg/l, averaging 51. They did not exceed this level during 1975.

RICE YIELDS DURING THE STUDY

Effect of Designed Treatment

Irrigation treatment did not have a significant effect on rice yields during the three year evaluation, but the excessive rate of fertilizer and pesticide application did adversely effect yield in 1974 and 1975 (Table 63).

Yields from the plots receiving recommended rates of fertilizer and pesticides were on a par with the yield from adjacent plots in which optimum cultural practices were employed (the adjacent plots yielded 5500, 4652, 5043 kg/ha during 1973, 1974 and 1975, respectively). The lower rice yields incurred in the excessive rate plots during 1974 and 1975 may have been induced by the untimely application of an excessive rate of molinate. Flinchum et al. (1973) reported that 10 kg molinate/ha applied in the floodwater within four days of the panicle differentiation growth stage reduced yields by 1000 kg ha⁻¹. During 1974 and 1975 the excessive rate plots received 11.2 kg molinate ha⁻¹ (plus an excessive rate of carbofuran) within three days of panicle differentiation. Yields were not affected in 1973 when the molinate was applied 11

TABLE 63. RICE YIELDS DURING THE STUDY-AVERAGE OF THREE REPLICATIONS

Treatment		1973	1974	1975
Irrigation	Fertilizer and Pesticide	(Kg/Ha)	(Kg/Ha)	(Kg/Ha)
Continuous	Recommended	5658 a	3895 a	4745 a
Continuous	Excessive	5918 a	2561 b	3250 b
Intermittent	Recommended	5685 a	4554 c	5084 a
Intermittent	Excessive	5476 a	2631 b	3540 b
Average		5684	3410	4154

1 lb/ac = 1.1208 Kg/Ha

Yields followed by the same letter are not significantly different than other values in that column.

days prior to panicle differentiation. The delay in molinate application during 1974 and 1975 was a result of an effort to postpone the collection of molinate water samples until after completion of the propanil analysis when the gas chromatograph and extraction could be done without delay. The fertility aspects of the field experiments were sacrificed in order to maintain high quality analytical capabilities for the pesticides.

Effect of a Water Conservation and Pollution Prevention Technique

Releasing the floodwater from the rice field 10 days before crop maturity is a common water management practice which serves to dry the soil and thus facilitate harvesting. The desirable dry soil condition at harvest could be obtained by sparingly metering the irrigation water so that all the floodwater is evapotranspired at about 10 days prior to harvest. Since the evapotranspiration technique of obtaining a dry soil would conserve water and reduce the possibility of surface water pollution from irrigation return flow, the effect of this technique on rice yields was evaluated in 1975. Two of the intermittent plots were irrigated as usual while the other four received no further irrigation 16 days prior to the anticipated day that the floodwater is normally released to allow the soil to dry. The 16 days cut-off time was chosen assuming an evapotranspiration rate of 0.56 cm/day and 10 cm depth of floodwater. Water added to the plots by rainfall, which amounted to about 13 cm during the 16 day period, was released from the plots soon after the rains. The evapotranspiration technique of obtaining a dry soil at harvest did not reduce yields and, thus, could be used to conserve water and reduce the possibility of water pollution from irrigation return flow.

Substantial rainfall would prevent the evapotranspiration technique of obtaining a dry soil from working ideally, but the technique appears to be an effective guideline for conserving water and reducing the possibility of water pollution caused by irrigation return flow from rice fields.

MODEL

A Model of Irrigation Return Flow

The quality of irrigation return flow which is released from the paddy after a period of flooding, or that which leaches from the field below the root zone, is a result of water and salt balance. The water balance includes the quantity and frequency of irrigation, precipitation, the water lost by evaporation, transpiration, runoff losses, and the movement into or through the soil profile. The salt balance must include consideration of the initial salt concentrations in the soil profile, the distribution of root water and salt uptake, and the reaction exchanges and subsequent equilibrium concentrations in the soil solution and on the exchange sites. In addition, fertilizer applications and timing will influence the concentration of certain ions.

The large number of factors involved makes it difficult to keep track of the concentrations of ions in the system without the use of a computerized model. Several researchers have developed models to track the movement of ions in the soil system. The flooded rice paddy, however, presents a set of

circumstances which cannot be adequately handled by the available models. In addition, advances in formulation and solution techniques are available which should allow more precise and universally applicable solutions to certain parts of the system.

A model was developed which allows the consideration of all factors mentioned above. The water balance part of the model may be written as:

$$\Delta H = I + P - T - E - R - L$$

where ΔH = the change in depth of water in the paddy

I = irrigation

P = precipitation

T = transpiration

E = evaporation

R = runoff

L = leaching

In the model, parameters on the right are entered as variables on a daily basis, and the change in water depth is updated once a year. Flood water of the quality and amount specified may be added on any day. If so desired, once the initial flood is established, the program will automatically irrigate the paddy to a level of 10 cm when the water level drops to a level of 4 cm. Precipitation is assumed to be free of ions and to have a simple diluting effect on the ions in the floodwater. Evaporation from the water surface is assumed to have the reverse effect. The transpired water is assumed to be taken up by the roots within the soil profile. The uptake is simulated to occur over a 14-hour period, with the total daily uptake being divided into hourly values by assuming a sinusoidal distribution of uptake over the period. This helps to realistically simulate the possibility of diffusion of ions from the soil to the floodwater during periods of low or zero transpiration. The water that moves into the profile to supply the transpiring stream is assumed to carry along with it into the first layer of soil ions at the concentration found in the floodwater. These ions subsequently redistribute from one layer to the next according to the flux of water and the calculated concentrations in solution. Root distribution fractions may be updated periodically during a particular run in order to simulate root growth.

Uptake of each ion by the roots is assumed to be represented by:

$$Q_{iz} = K_i \cdot T_z$$

where Q_{iz} = the sink strength corresponding to ion i at depth z

K_i = a proportionality factor

T = the sink strength for water uptake by the roots at depth z

The values of K_i used in the program were selected to assume a charge balance for the ions taken up and to insure that the ion uptake over the entire season approximates the uptake rates reported in the literature for rice crops. The data utilized are shown in Table 64. A sensitivity analysis indicated that reasonable variations in the values of the K_i 's do not significantly influence the final concentrations in the irrigation return flow.

TABLE 64. CONCENTRATIONS OF IONS IN RICE FOLIAGE AND GRAIN AND VALUES OF K_i USED TO CALCULATE ION UPTAKE FROM THE SOIL*

Ion	Concentration	K_i
	%	$\frac{\text{g}}{\text{cm}^3}$
Ca	0.17	$8.10 \cdot 10^{-6}$
Mg	0.17	$8.10 \cdot 10^{-6}$
Na	0.30	$1.44 \cdot 10^{-5}$
K	2.00**	$9.60 \cdot 10^{-5}$
NH ₄	1.21**	$5.75 \cdot 10^{-5}$
Cl	.40	$1.92 \cdot 10^{-5}$
SO ₄	.24	$1.15 \cdot 10^{-5}$
NO ₃	4.58	$2.20 \cdot 10^{-4}$
HCO ₃	4.32	$2.07 \cdot 10^{-4}$

* The values were calculated assuming a water uptake of 25 cm/season and a total dry matter yield (roots, stems, leaves, and grain) of 12,000 kg/ha. Data from Westfall (personal communication), Yanagisawa and Takahashi (1959) and Ishizuka (1965).

** These values were adjusted to achieve charge balance.

The runoff is taken as a discrete event during which water of prevailing concentration in the paddy is released or overflows. Runoff may be scheduled daily in the case of continuous flow, may only occur on a few occasions such as after a heavy storm, or may be held to zero throughout a simulation. The percolation rate, L, is taken as the amount of water moving into the soil to supply the wetting front. The change in water content with time above the wetting front is taken to be zero.

Fertilizer applications are taken as discrete events that cause an increase in the concentration of the ions in the floodwater. For fertilizers of

low solubility, the release may be spread over several days. Throughout the calculations, it is assumed that mixing of the floodwater resulting from air flow, thermal gradient, and thermal diffusion is sufficient to render concentration gradients within the floodwater negligible.

Other parameters needed include the initial concentration of ions in the soil profile, the bulk density of the soil, and the cation exchange capacity. The program keeps account of the water depth and utilizes subprograms SOIL and EQUIL to calculate the flux of ions into or out of the soil surface as well as to calculate the distribution of ions with time in the profile. A detailed discussion of the development of these submodels will be considered next.

Development of the Program

Applications of the theory of simultaneous movement of water and solutes through porous media are numerous and diverse. They range from laboratory studies of chromatography to prediction of post-application redistribution of chemicals in fields and aquifers. Theories applicable to chromatographic column operations appeared more than 30 years ago (deVall, 1943), but only in the last 20 years have extensions and modifications been made to include the complex behavior associated with solute movement in soil. These extensions have corresponded to a large influx of information from laboratory and field studies that have isolated various phenomena operative in transport processes. These studies have verified that convective transport is the dominant mechanism of solute transfer, except in cases of near-zero flow velocities. Molecular diffusion and hydrodynamic dispersion have been identified as important modifiers of the solute space-time distribution resulting from convective transport alone (Biggar and Nielsen, 1967; Kirda et al., 1973; Sadler et al., 1965). Moreover, researchers have shown that a number of other factors may influence the rate and extent of solute movement depending on the medium and/or conditions under which the experiments were conducted. Among these additional factors are: cation exchange (Dutt and Tanji, 1962; Rible and Davis, 1955; Lai and Jurinak, 1972), anion exclusion (Dyer, 1965; Thomas and Swoboda, 1970; Smith, 1972), vertically nonuniform density and/or viscosity distributions (Biggar and Nielsen, 1967; Krupp and Elrich, 1969; James and Rubin, 1972), transient flow conditions (Bresler and Hanks, 1969; Kirda et al., 1973; Bresler, 1973), and zones of solution that are stagnant or slow moving with respect to the bulk solution (Coats and Smith, 1964; Skopp and Warrick, 1974).

In addition to laboratory and field experimentation, mathematical models have been developed to include the effects of one or more of the above-mentioned phenomena. Although earlier models were based on chromatographic plate concepts (Biggar et al., 1966), many of the more recent ones were based on solutions of convection-diffusion type equations (hereafter referred to as CDT equations) with associated boundary and initial conditions. With comparatively few exceptions, these solutions were developed to describe the transport of a single solute under steady-flow conditions. No thorough investigation has been made to determine the feasibility of extending finite-difference methods to the simultaneous solution of several CDT equations. The objectives of the development were, therefore:

1. To compare the performance of selected finite-difference schemes in solving CDT equations for conditions of: one solute, one-dimensional steady flow, without sources or sinks.
2. To develop a method for extending one of the selected schemes to simultaneous solution of two or more CDT equations.
3. To develop a subroutine, based on such an extension, that will simulate the convective-dispersive transport of selected ions in a soil system where local chemical equilibrium is assumed.

Solutions Available in the Literature

Analytical Solutions--

Analytical (exact) solutions of CDT equations are expressed in closed-form, infinite-series, or integrals and yield values of the dependent variable (concentration) directly, given values of the independent variables (distance and time). Parlange and Starr (1971) have provided a discussion of such solutions for the linear, one-dimensional CDT equation for a variety of boundary conditions. Reiniger and Bolt (1972) reviewed analytical solutions of problems involving absorption of two exchangeable cations. Shamir and Harleman (1967) presented a solution for the one-ion problem for layered media. Coats and Smith (1964) solved the one ion problem for a CDT equation which contained a capacitance term to account for dead-end pore volume. Skopp and Warrick (1974) treated a similar problem by ignoring longitudinal dispersion and including diffusion into a stagnant phase. Warrick et al. (1971) applied an analytical solution to an infiltration problem involving one solute. These solutions are all restricted in application to situations which approximately conform to certain boundary and initial conditions required for their derivation. In spite of this restriction, they are valuable tools when applicable because little computational effort is required for their evaluation. Moreover, they serve as checks on the performance of numerical solutions.

Numerical Solutions--

Where boundary and initial conditions are too complex or other complicating factors preclude an analytical approach, it is necessary to adopt a numerical procedure. Such procedures rely on estimates of a change in the spatial concentration profile over a time period: $t_1 \leq t \leq t_1 + \Delta t$, based on approximate knowledge of the profile at time, t_1 . Thus, given an initial concentration profile, numerical solutions are advanced in time over discrete time steps, Δt , to span the entire time interval of interest. The various procedures are distinguished, either by the numerical representation of the profile at t_1 (e.g. values of the dependent variables defined at discrete points in space as opposed to their definition by approximating polynomials) or by the means used to advance the solution from t_1 to $t_1 + \Delta t$ (e.g. by Taylor's approximation of the time derivative, predictor-corrector methods, etc.).

Finite-Difference Methods--

Finite-difference methods for the solution of partial differential equations are based on finite-difference (Taylor's) approximations to the partial derivatives which appear in these equations (Carnahan et al., 1969). For CDT equations (and other equations of the parabolic type), at a fixed time, t_1 ,

such an approximation is made at each point of a grid network that divides the space for which a solution is desired into discrete intervals, or rectangles, depending on the dimensionality of the transport. Thus, a system of algebraic equations results, including one approximating equation and one unknown for each interior grid point of the network. The knowns in these equations are the values of the concentration at each of the grid points at t_1 and boundary values of the concentration at t_1 and $t_1 + \Delta t$. The unknowns are values of the concentration at each interior grid point at $t_1 + \Delta t$. If the resulting system of approximating equations is such that each can be evaluated independently, the procedure is termed "explicit". If simultaneous solution of all of the equations is necessary, the procedure is an "implicit" term.

Finite-difference schemes are mutually distinguished on the basis of the particular approximations employed either for the space or time derivatives. For example, the explicit scheme (not to be confused with the more general use of the term above) utilizes second-order, central-difference approximations for the space derivatives and a first-order, forward difference approximation for the time derivative (Shamir and Harleman, 1967; Fried and Combarous, 1971). Although some use has been made of this scheme for solute transport problems in soils (Lai and Jurinak, 1972; Kirda et al., 1973), it has been criticized due to an apparent need for unreasonably small time and space increments to insure stability of the computational procedure (Shamir and Harleman, 1967; Fried and Combarous, 1971).

A second finite-difference approach that has been utilized for solving CDT equations is the Crank-Nicolson scheme, which is of second-order accuracy of approximation with respect to both space and time derivatives (Stone and Brian, 1963; Fried and Combarous, 1971). The higher-order accuracy with respect to the time derivative is achieved by use of Crank-Nicolson (centered-in-time) approximations for the space derivatives. Peaceman and Rachford (as reported by Stone and Brian, 1963) were apparently the first to use this approach to solving CDT equations. They found for large values of the velocity to dispersion coefficient ratio (V/D) that small grid spacings were required to prevent oscillations from developing in the simulated concentration profile.

Stone and Brian (1963) derived a finite-difference scheme on the basis of optimal propagation velocity and decay of harmonics present in a sharp concentration front. In its final form, the scheme they demonstrated utilizes Crank-Nicolson approximations for the space derivatives, and a weighted-average (over three spatial grid points) approximation for the time derivative. Their weighting factors are used in conjunction with cycling over successive time steps. They demonstrated that a scheme employing three time steps per cycle, with predetermined values of the weighting factor used in each time step, greatly reduced oscillations incurred by use of the Crank-Nicolson scheme for the case: $D = 0$. Shamir and Harleman (1967) later extended the Stone-Brian scheme to a special problem of higher dimension.

Chaudhari (1971) derived a finite-difference approximation which is approximately second-order in time for high V/D . Realizing the tendency for high order schemes to develop oscillations for high V/D and large grid spacings he derived the scheme so as to produce an explicit computational procedure and include a "brute-force" mechanism to prevent oscillations.

Bresler (1973) followed Chaudhari's example and derived an approximately second-order accurate scheme for treatment of solute transport phenomena under transient flow conditions. The computational procedure for his scheme is implicit and can be shown to reduce to the Crank-Nicolson approach for saturated steady-flow conditions in a homogeneous medium.

Other Numerical Methods--

Garder et al. (1964) pointed out the approximate hyperbolic nature of CDT equations for high values of V/D . Accordingly, they developed an approach based on characteristic curves of a convective-transport equation (i.e. an equation obtained by setting $D = 0$ in a CDT equation). Smajstrla et al. (1974) extended the use of this "method of characteristics" to unsaturated, transient-flow problems. A discussion of the basic computational procedure can be found in their paper or in the paper by Garder et al. (1964).

Price et al. (1968) applied techniques based on variational methods to the single solute problems and showed that the resulting schemes were of high order accuracy (>3) with respect to space derivatives.

Simultaneous Consideration of Several Solutes--

Comparitively few attempts have been made to describe the simultaneous movement of several solutes. In such cases, interactions among the solutes and between various solutes and the porous medium must be considered. Dutt et al. (1972b) demonstrated the use of simultaneous solution of chemical equilibrium equations in a program they developed for predicting gypsum and leaching requirements for sodium-affected soils. They assumed convective transport only but accounted for cation exchange, ion pairing, and solubility-precipitation reactions. Dutt et al. (1972a) utilized the same basic equilibrium scheme as part of a simulation model for prediction of moisture and fertilizer redistribution in field situations. They utilized the concept of "mixing cells" to simulate the effects of dispersion and diffusion. This concept is based on the artificial smearing of concentration fronts that occur when plates or segments of finite thickness are utilized in simulating convective transport.

Frissel and Reiniger (1974) used a similar approach in their model of simultaneous transport of Ca, Na, Mg, and K with provisions for cation exchange (all cations) and fixation of K. They gave a more quantitative description of the effect of plate thickness on the artificial mixing introduced. For their computational procedure, they utilized a computer simulation package, CSMP, which provides subroutines for numerical integration and solution of non-linear algebraic equations.

Lai and Jurinak (1972) utilized the explicit finite difference scheme to provide solutions of a CDT equation containing a generalized non-linear exchange isotherm. The resulting scheme is applicable for the displacement of one cation by another under restricted boundary and initial conditions. DeWit and van Keulen (1972) used CSMP to solve a system of DCT equations for one anion and two exchangeable cations.

An alternative approach to a problem involving the simultaneous solution of two or more CDT equations was taken by James and Rubin (1972). They used

a Galerkin method to solve three equations which included cation exchange relationships.

The Use of Finite-Difference Solutions to the One Dimensional Linear Convection-Diffusion Equation

The Basic Equation and Boundary Conditions--

In order to provide a starting point for the development of a more general ion-transport model, it is helpful to first consider finite-difference approximations that have been developed to obtain solutions of the problem characterized by the single linear equation:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial z^2} - V \cdot \frac{\partial C}{\partial z} \quad , \quad (4)$$

and associated boundary conditions. In Equation 4, $C(M/L^3)$ is solute concentration; $t(T)$ is time; $z(L)$ is distance; $V(L/T)$ is mean pore velocity (i.e. the solution flux density $q(L/T)$ divided by the volumetric moisture content $\theta(L^3/L^3)$); and $D(L^2/T)$ is the apparent diffusion coefficient of the solute. Although the physical meaning of Equation 4 has been discussed at length in the literature, e.g. Fried and Combarous (1971), a brief account of the derivation will help motivate the ensuing discussion.

In a homogeneous, inert, saturated, porous medium, the solute flux, J_{s_z} , in the z direction is assumed to obey:

$$J_{s_z} = -D_m \cdot \left(\frac{\partial C}{\partial z}\right) - D_h \cdot \left(\frac{\partial C}{\partial z}\right) + q \cdot C. \quad (5)$$

In Equation 5, $D_m(L^2/T)$ is the molecular diffusion coefficient of the solute for the porous medium and $D_h(L^2/T)$ is the hydrodynamic dispersion coefficient. The first and second terms on the R-H-S of Equation 5 represent the contributions of molecular diffusion and hydrodynamic dispersion, respectively, to the total flux. The term qC constitutes the solute flux due to convective transport. The equation of continuity (mass-balance) for one-dimensional flow can be written:

$$\frac{\partial(\theta C)}{\partial t} = - \frac{\partial J_{s_z}}{\partial z},$$

or

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z} [(D_m + D_h) \cdot \frac{\partial C}{\partial z}] - \frac{\partial(qC)}{\partial t}. \quad (6)$$

Realizing that for the prescribed conditions, θ , q , D_m , and D_h are independent of t and z , Equation 4 is obtained by dividing both sides of Equation 6 by θ and setting $D = (D_m + D_h)/D$. Alternatively, Equation 4 can be derived from statistical considerations (Fried and Combarous, 1971), as opposed to the mass balance approach taken here.

The boundary conditions most often associated with Equation 4 for a

column or profile of finite depth, L_c , are of the form:

$$C(z,0) = f(z), \quad 0 \leq z \leq L_c$$

$$C(0,t) = g(t), \quad t \geq 0$$

or

$$-D \cdot \left. \frac{\partial C}{\partial z} \right|_{z=0} + V \cdot C(0,t) = V \cdot Q(t), \quad t \geq 0$$

and

$$\left. \frac{\partial C}{\partial z} \right|_{z=L_c} = 0, \quad t \geq 0.$$

More specifically, the conditions:

$$C(z,0) = C_1, \quad 0 \leq z \leq L_c \quad (7a)$$

$$C(0,t) = C_o, \quad t > 0 \quad (7b)$$

or

$$-D \cdot \left. \frac{\partial C}{\partial z} \right|_{z=0} + V \cdot C(0,t) = V \cdot C_o, \quad t > 0 \quad (7c)$$

and

$$\left. \frac{\partial C}{\partial z} \right|_{z=L_c} = 0, \quad t > 0 \quad (7d)$$

have been convenient for comparison of numerical results with analytical solutions (Bresler, 1973; Shamir and Harleman, 1967; and Brenner, 1962). Equation (7a) represents an initially uniform distribution of the solute throughout the porous medium, while condition (7b) represents a constant concentration (infinite source or sink) condition at $z = 0$, and condition (7c) constitutes an alternative constant flux condition at $z = 0$. The zero-gradient condition (7d) at $z = L_c$ implies that flux across this boundary is due to convective transport alone. The use of (7d) in preference to a constant flux condition has been discussed by Brenner (1962) and Danckwerts (1953).

Numerical Difficulties--

As was indicated earlier, attempts to obtain approximations to solutions of CDT equations by numerical means have not always achieved satisfactory results. The foremost difficulty manifested by finite-difference solutions has been a failure to properly describe the spreading of sharp concentration fronts as they progress in time and space. In the absence of diffusion and dispersion (i.e. convective transport only), it is easy to show analytically that such fronts progress without smearing or spreading. To show the same thing with a finite-difference solution is more difficult. Stone and Brian

(1963) present graphs illustrating the oscillatory behavior of certain finite-difference solutions for the case, $D=0$. Although in most physically meaningful problems D is never absolutely zero, it can be appreciated that severe difficulties may be encountered when the ratio V/D is very large. These authors showed that this oscillatory behavior is related to poor propagation and decay rate of the harmonics present in the simulated concentration front.

Even if the solutions do not develop oscillations, they may be plagued by an artificial smearing which results from a numerically induced dispersion (Stone and Brian, 1963 and Garder et al., 1964). A classical example of numerical dispersion can be illustrated by a finite-difference approximation to the convective-transport equation:

$$\frac{\partial C}{\partial t} = -V \cdot \frac{\partial C}{\partial z} \quad (8)$$

The method of Courant, Isaccson and Reese (Stone and Brian, 1963) is based on an approximation to equation (8) of the form:

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = V \cdot \frac{C_{i-1}^j - C_i^j}{\Delta z} \quad (9)$$

where i and j are positive integers and C_i^j is the solute concentration having space and time coordinates $(i\Delta z, j\Delta t)$. To show that artificial dispersion is implicitly included in the approximation to $-V \frac{\partial C}{\partial z}$ in equation (9), a Taylor's approximation to $\frac{\partial C}{\partial z}$ can be written:

$$C_{i-1}^j = C_i^j - \Delta z \left(\frac{\partial C}{\partial z} \right)_i^j + \frac{\Delta z^2}{2} \cdot \left(\frac{\partial^2 C}{\partial z^2} \right)_i^j + O(\Delta z^3).$$

Solving for $\left(\frac{\partial C}{\partial z} \right)_i^j$ yields the first-order correct approximation:

$$\left(\frac{\partial C}{\partial z} \right)_i^j = \frac{C_i^j - C_{i-1}^j}{\Delta z} + O(\Delta z), \quad (10a)$$

and the second-order correct approximation:

$$\left(\frac{\partial C}{\partial z} \right)_i^j = \frac{C_i^j - C_{i-1}^j}{\Delta z} + \frac{\Delta z}{2} \cdot \left(\frac{\partial^2 C}{\partial z^2} \right)_i^j + O(\Delta z^2). \quad (10b)$$

Substituting equations (10a) and (10b) into equation (8) the result is:

$$\frac{\partial C}{\partial t} = V \cdot \frac{C_{i-1}^j - C_i^j}{\Delta z} + O(\Delta z), \quad (11a)$$

and

$$\frac{\partial C}{\partial t} = V \cdot \frac{C_{i-1}^j - C_i^j}{\Delta z} - V \cdot \frac{\Delta z}{2} \cdot \left(\frac{\partial^2 C}{\partial z^2} \right)_i + O(\Delta z^2). \quad (11b)$$

From these last two equations it can be seen that the use of equation (10a) to approximate $\left(\frac{\partial C}{\partial z} \right)_i^j$, as is the case in equation (9), has the effect of adding the numerical dispersion term $D_n \cdot \frac{\partial^2 C}{\partial z^2}$ where $D_n = V \frac{\Delta z}{2}$. The result is that the right-hand side of equation (9) provides a second-order correct approximation to the expression:

$$D_n \cdot \frac{\partial^2 C}{\partial z^2} - V \cdot \frac{\partial C}{\partial z}$$

but only a first-order correct approximation to the right-hand side of equation (8). Stone and Brian (1963) demonstrated the artificial smearing that results when equation (9) is used to approximate equation (8).

Selected Finite-Difference Approximations--

In order to gain experience with the numerical difficulties reported in the literature and to provide a basis for selection of a scheme to extend to the several-solute, non-linear case, five difference equations were studied and compared with respect to efficiency and accuracy. The schemes selected for the study are (a) the explicit scheme, (b) Chaudhari's scheme, (c) Bresler's scheme, (d) Stone and Brian's scheme, and (e) a second-order (in time) explicit scheme that has not appeared in the literature.

To facilitate discussion and comparison of the various difference equations, the following notations are introduced:

$$\Delta_t (C_i^j) = \frac{C_i^{j+1} - C_i^j}{\Delta t} = \left(\frac{\partial C}{\partial t} \right)_i^j + O(\Delta t), \quad (12)$$

$$\delta_z (C_i^j) = \frac{C_{i+1}^j - C_{i-1}^j}{2 \cdot \Delta z} = \left(\frac{\partial C}{\partial z} \right)_i^j + O(\Delta z^2), \quad (13)$$

$$\text{and} \quad \delta_z^2 (C_i^j) = \frac{C_{i+1}^j - 2 \cdot C_i^j + C_{i-1}^j}{\Delta z^2} = \left(\frac{\partial^2 C}{\partial z^2} \right)_i^j + O(\Delta z^2). \quad (14)$$

The explicit scheme--The basic approximating equation for the explicit scheme can be written:

$$\Delta_t(C_i^j) = D \cdot \delta_z^2(C_i^j) - V \cdot \delta_z(C_i^j). \quad (15)$$

The scheme derives its name from the fact that the concentrations C_i^{j+1} at each grid point $i \Delta z$ are defined explicitly in terms of the concentrations C_{i-1}^j , C_i^j , and C_{i+1}^j . The equation corresponding to each grid point can be evaluated independently and therefore does not require the simultaneous solution of the equations corresponding to all grid points. Two of the other schemes to be discussed are also "explicit" in this sense.

Kirda et al. (1973) used an approximation based on the explicit scheme for simulation of solute movement in soils under infiltration conditions. Their difference approximation reduces to the explicit scheme (15) under saturated, steady-flow conditions. Lai and Jurinak (1972) used a modified version of the explicit scheme to simulate the displacement of one cation species by another from a soil column. Their approximation is equivalent to the explicit scheme (15) when their separation factor, α_a^b , is unity.

The explicit scheme has been criticized by Shamir and Harleman (1967) and Fried and Combarnous (1971). These authors contend that small values of the grid spacing:

$$\Delta z \leq \frac{2D}{V}, \quad (16)$$

are necessary to insure stability of the numerical computations. The former authors derived equation (13) from the criteria:

$$\frac{D\Delta t}{\Delta z^2} \leq .5 \quad (17)$$

and

$$\frac{V\Delta t}{\Delta z} < 1. \quad (18)$$

The inequality (17) must be satisfied to prevent instability (Richtmeyer, 1957) and condition (18) provides an accuracy of the decay factor of order (Δt) . Fried and Combarnous (1971) showed that the off-diagonal elements of the coefficient matrix associated with the system of approximating equations (15) are negative if condition (16) is violated. They concluded from this that violation of condition (16) would cause the scheme to be unstable.

In spite of their criticism of the scheme none of these authors presented evidence which would support their claim. Of those who used the explicit scheme, Kirda et al. (1973) acknowledged the use of (16), but Lai and Jurinak (1972) made no mention of it.

Chaudhari's Scheme--Chaudhari (1971) developed a finite-difference approximation for simulation of multi-dimensional solute transport. The one-dimensional version of his approximating equation can be written:

$$\theta \cdot \Delta z \cdot (C_i^{j+1} - C_i^j) = \{ (\theta \cdot D - D^*)_{i-\frac{1}{2}} \cdot \left(\frac{C_{i-1}^j - C_i^j}{\Delta z} \right) + q_{i-\frac{1}{2}} \cdot C_{i-1}^j - (\theta \cdot D - D^*)_{i+\frac{1}{2}} \cdot \left(\frac{C_i^j - C_{i+1}^j}{\Delta z} \right) + q_{i+\frac{1}{2}} \cdot C_i^j \} \Delta t,$$

Where $D^* = q_{i-\frac{1}{2}} \cdot \frac{\Delta z}{2} \cdot \left(1 - \frac{v_i \Delta t}{\Delta z} \right)$. Chaudhari called the number D^* a numerical dispersion coefficient. This coefficient results from the use of a second-order correct approximation to the derivative $\frac{\partial(qC)}{\partial z}$ and an approximately second-order correct approximation to $\frac{\partial(\theta C)}{\partial t}$. Upon rearrangement Chaudhari's equation can be represented for saturated, steady-flow conditions as:

$$\Delta_t (C_i^j) = (D + D^{**}) \cdot \delta_z^2 (C_i^j) - v \cdot \delta_z (C_i^j), \quad (19)$$

$$\text{where } D^{**} = \frac{v^2 \Delta t}{2}.$$

Although Chaudhari did not indicate that his scheme manifested any particular relationship to the explicit scheme, the only difference between the explicit scheme (15) and Chaudhari scheme (19) is the coefficient of $\delta_z^2 (C_i^j)$. The number D^{**} in the explicit scheme (19) can be derived in a straightforward manner as follows.

Substituting equations (13) and (14) into equation (15) we have:

$$\left(\frac{\partial C}{\partial t} \right)_i^j = D \cdot \delta_z^2 (C_i^j) - v \cdot \delta_z (C_i^j) + O(\Delta z^2). \quad (20)$$

An alternative expression for $\left(\frac{\partial C}{\partial t} \right)_i^j$ can be obtained by a second-order correct Taylor's approximation:

$$\left(\frac{\partial C}{\partial t} \right)_i^j = \frac{C_i^{j+1} - C_i^j}{\Delta t} - \frac{\Delta t}{2} \cdot \left(\frac{\partial^2 C}{\partial t^2} \right)_i^j + O(\Delta t^2). \quad (21)$$

Substituting equation (21) into equation (20) and rearranging yields:

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = D \cdot \delta_z^2(C_i^j) - V \cdot \delta_z(C_i^j) - \frac{\Delta t}{2} \cdot \left(\frac{\partial^2 C}{\partial t^2}\right)_i^j + O(\Delta z^2) + O(\Delta t^2). \quad (22)$$

In order to estimate the value of $\left(\frac{\partial^2 C}{\partial t^2}\right)_i^j$, Chaudhari suggested using the following approximation, valid for $V \gg D$:

$$\left(\frac{\partial C}{\partial t}\right)_i^j \approx -V \cdot \left(\frac{\partial C}{\partial z}\right)_i^j. \quad (23)$$

Differentiating both sides of equation (23) with respect to t and interchanging the order of differentiation on the RHS yields:

$$\left(\frac{\partial^2 C}{\partial t^2}\right)_i^j = -V \frac{\partial}{\partial t} \left(\frac{\partial C}{\partial z}\right)_i^j,$$

and again making use of equation (23), we obtain the desired approximation:

$$\left(\frac{\partial^2 C}{\partial t^2}\right)_i^j \approx V^2 \left(\frac{\partial^2 C}{\partial z^2}\right)_i^j = V^2 \cdot \delta_z^2(C_i^j) + O(\Delta z^2). \quad (24)$$

Substituting equation (24) into equation (22) and combining terms yields:

$$\Delta_t(C_i^j) = \left(D + \frac{V^2 \Delta t}{2}\right) \cdot \delta_z^2(C_i^j) - V \cdot \delta_z(C_i^j) + O(\Delta z^2) + O(\Delta t^2),$$

which is equivalent to Chaudhari's solution (19) when terms of order greater than two are ignored. Note that elimination of all terms of order $O(\Delta t)$ or higher in equation (21) would result in equation (15), i.e. the approximating equation for the explicit scheme. The conclusion that may be drawn is that any improvement manifested by use of Chaudhari's scheme equation (19) over the explicit scheme equation (15) to approximate the CDT equation (4) is due solely to the accuracy of approximation of $\frac{\partial C}{\partial t}$.

Bresler's scheme--Bresler (1973) proposed the use of the following finite-difference approximation for simulation of solute transport under transient flow conditions:

$$\begin{aligned} \frac{\theta_i^{j+1} \cdot C_i^{j+1} - \theta_i^j \cdot C_i^j}{\Delta t} &= \frac{D_{i-\frac{1}{2}}^{j+\frac{1}{2}} - N_{i-\frac{1}{2}}^{j+\frac{1}{2}}}{2\Delta z^2} \cdot (C_{i-1}^{j+1} + C_{i-1}^j - C_i^{j+1} - C_i^j) \\ &\quad - \frac{D_{i+\frac{1}{2}}^{j+\frac{1}{2}} - N_{i+\frac{1}{2}}^{j+\frac{1}{2}}}{2\Delta z^2} \cdot (C_i^{j+1} + C_i^j - C_{i+1}^{j+1} - C_{i+1}^j) \\ &\quad - \frac{1}{2\Delta z} [q_{i+\frac{1}{2}}^{j+\frac{1}{2}} \cdot (C_i^{j+1} + C_i^j) - q_{i-\frac{1}{2}}^{j+\frac{1}{2}} \cdot (C_{i-1}^{j+1} + C_{i-1}^j)] . \end{aligned}$$

Where D' may be identified with $\theta \cdot D$ in previous discussion and:

$$N_{i+\frac{1}{2}}^{j+\frac{1}{2}} = \frac{\Delta z}{2} \cdot q_{i+\frac{1}{2}}^{j+\frac{1}{2}} - \frac{v_i^{j+\frac{1}{2}} \cdot v_{i+\frac{1}{2}}^{j+\frac{1}{2}} \cdot \Delta t \cdot (\theta_i^{j+1} - \theta_i^j)}{8} .$$

The quantity $N_{i-\frac{1}{2}}^{j+\frac{1}{2}}$ is a numerical dispersion coefficient derived in a manner similar to that used by Chaudhari (1971) to derive D^* . Without the numerical dispersion coefficient, the approximation is only first-order correct for both the time and space derivatives. For saturated steady-flow conditions, Bresler's difference equation reduces to:

$$\Delta_t (C_i^j) = D \cdot \delta_z^2 \left(\frac{C_i^{j+1} + C_i^j}{2} \right) - v \cdot \delta_z \left(\frac{C_i^{j+1} + C_i^j}{2} \right) . \quad (25)$$

The quantities $\delta_z^2 \left(\frac{C_i^{j+1} + C_i^j}{2} \right)$ and $\delta_z \left(\frac{C_i^{j+1} + C_i^j}{2} \right)$ are Crank-Nicolson, or centered-in-time approximation to the space derivatives $\left(\frac{\partial^2 C}{\partial z^2} \right)_i^j$ and $\left(\frac{\partial C}{\partial z} \right)_i^j$, respectively. Although Bresler's scheme (25) is second-order correct both in

time and space, its use has been criticized due to oscillations which develop in simulated concentration profiles near sharp concentration fronts for large V/D (Stone and Brian, 1963). It is interesting to note also that Chaudhari (1971) chose an explicit procedure in order to prevent oscillation by a "brute force" mechanism, whereby he transferred overshoot occurring in regions of oscillation into regions where the concentration varies within acceptable limits. Although Bresler followed Chaudhari's example in the derivation of his numerical dispersion coefficient, he did not mention the possibility of oscillations occurring. Nor did he acknowledge the earlier criticism of the use of Bresler's scheme (25) by Stone and Brian (1963).

Stone and Brian's scheme--Stone and Brian (1963) presented the following approximation to equation (4) as an alternative to equation (25):

$$(1-\eta) \cdot \Delta_t(C_i^j) + \frac{\eta}{2} \cdot \{\Delta_t(C_{i-1}^j) + \Delta_t(C_{i+1}^j)\} =$$

$$D \cdot \delta_z^2 \left(\frac{C_i^{j+1} + C_i^j}{2} \right) - V \cdot \delta_z \left(\frac{C_i^{j+1} + C_i^j}{2} \right), \quad (26)$$

where η cyclically takes on the values 0.1250, 0.4145 and 0.4605 during successive time steps. In other words, at $t=0$, η has the value 0.1250, at $t = \Delta t$, η is given the value 0.4145, etc. The basic equation they used, from which equation (26) can be derived, contains five weighting factors in addition to η . Equation (26) is the result of substituting their recommended values for the other weighting factors. We also note that η in equation (26) corresponds to θ in their equation (16). Their choice of $\delta_z^2 \left(\frac{C_i^j + C_i^{j+1}}{2} \right)$

to approximate $\frac{\partial^2 C}{\partial z^2}$ was based on the success of previous use of Crank-Nicolson approximations in solving diffusion equations. Choices of the weighting factors, as well as the cyclic use of z , were based on optimal propagation velocities and proper decay of harmonics present in sharp concentration fronts. Their theoretical deviation of η included the assumption, $D=0$.

The authors presented graphs showing the superiority of their method over the Crank-Nicolson approach, represented by Bresler's scheme equation (25), for $D = 0$. Shamir and Harleman (1967) made test runs with Stone and Brian's scheme for $V/D = 10$ and 100 but made no comparison with the Crank-Nicolson approach for these values of V/D .

Second order explicit scheme--In addition to the above approximations, which have been derived from equations appearing in the literature, an additional difference approximation was investigated. The approximation can

easily be derived, beginning with equation (22), and does not require the assumption (23). Equation (22) can be expressed in the form:

$$\frac{C_i^{j+1} - C_i^j}{\Delta t} = G_i^j + \frac{\Delta t}{2} \cdot \frac{\partial G_i^j}{\partial t} + O(\Delta z^2) + O(\Delta t^2), \quad (27)$$

where:

$$G_i^j = D \cdot \delta_z^2(C_i^j) - V \cdot \delta_z(C_i^j). \quad (28)$$

To obtain $\frac{\partial G_i^j}{\partial t}$ in equation (27), both sides of equation (28) can be differentiated with respect to t to yield:

$$\begin{aligned} \frac{\partial G_i^j}{\partial t} &= D \cdot \frac{\partial}{\partial t} \{ \delta_z^2(C_i^j) \} - V \cdot \frac{\partial}{\partial t} \{ \delta_z(C_i^j) \} = \\ &= \frac{D}{\Delta z^2} \cdot (G_{i-1}^j - 2 \cdot G_i^j + G_{i+1}^j) - \frac{V}{2\Delta z} \cdot (G_{i+1}^j - G_{i-1}^j). \end{aligned}$$

The desired approximation scheme is therefore:

$$\begin{aligned} \frac{C_i^{j+1} - C_i^j}{\Delta t} &= G_i^j + \frac{\Delta t}{2} \cdot \left\{ \frac{D}{\Delta z^2} \cdot (G_{i-1}^j - 2 \cdot G_i^j + G_{i+1}^j) - \frac{V}{2\Delta z} \cdot \right. \\ &\quad \left. (G_{i+1}^j - G_{i-1}^j) \right\}. \end{aligned} \quad (29)$$

Since G_i^j is a function of the concentrations at time t , C_{i-1}^j , C_i^j , and C_{i+1}^j ; the approximation scheme is explicit. It is formally second-order accurate in space and time by virtue of (27).

Since the scheme has not previously appeared in the literature, the essential steps in an efficient computational procedure are presented below. Equations (7a), (7b), and (7d) are the assumed boundary and initial conditions.

(1) Define the coefficients A, B, A', and B' as follows:

$$A = \frac{\Delta t}{\Delta z} \cdot \left(\frac{D}{\Delta z} + \frac{V}{2} \right) ,$$

$$B = \frac{\Delta t}{\Delta z} \cdot \left(\frac{-D}{\Delta z} + \frac{V}{2} \right) ,$$

$$A' = \frac{\Delta t}{2} \cdot A ,$$

and

$$B' = \frac{\Delta t}{2} \cdot B .$$

(2) Define the initial and surface boundary concentrations:

$$C_i = C_I, \text{ for } i = 2, \dots, M ,$$

$$C_1 = C_o ,$$

and

$$G_1 = 0 .$$

The following steps are carried out for each successive time step.

(3) Define:

$$F_2 = A \cdot C_1 + B \cdot C_2 ,$$

$$F_i = A \cdot C_{i-1} + B \cdot C_i ,$$

$$G_{i-1} = F_{i-1} - F_i ,$$

$$DF_{i-1} = A' \cdot G_{i-2} + B' \cdot G_{i-1} ,$$

$$i = 3, 4, \dots, M$$

and

$$DF_M = (A' + B') \cdot G_{M-1} .$$

(4) Update the concentrations for $i = 2, 3, \dots, M-1$:

$$C_i^{(new)} = C_i + G_i + DF_i + DF_{i+1}, \quad i = 2, 3, \dots, M-1$$

and

$$C_M^{(new)} = C_{M-1}^{(new)}.$$

In step (4), the condition $\left. \frac{\partial C}{\partial z} \right|_{z=L_c(sc)} = 0$, where $L_c = (M-3/2) \cdot \Delta z$, is approxi-

mated by the equality, $C_M^{(new)} = C_{M-1}^{(new)}$. Bresler (1972) discusses this approximation in more detail. The definition of DF_M in step (3) is a result of the equality of C_M and C_{M-1} for all times.

The second-order explicit scheme therefore requires four multiplications per interior grid point per time interval (steps 2 and 3). In comparison, the explicit scheme (15) and Chaudhari's scheme (19) require at least two multiplications per grid point per time interval (Carnahan et al., 1969). The Crank-Nicolson approach (25) and Stone and Brian's scheme can both be arranged for solution by inversion of a tri-diagonal matrix and probably require at least four or five multiplications per grid point per time interval, depending on the algorithm used to invert the associated matrix (Carnahan et al., 1969). The use of Bresler's scheme and Chaudhari's scheme as originally presented would require more computational effort due to the necessity of recalculating the coefficients of the concentrations for each time interval. Chaudhari (1971) suggested using a transfer-of-mass mechanism to prevent oscillations from appearing in the numerical solutions generated by his scheme. The use of this mechanism would also increase the computational effort somewhat.

Simulation Runs--

The characteristics of a numerical method which are probably the most important to a potential user are the amount of time and effort required for programming and the actual computer simulation time required to achieve a given degree of accuracy for a particular type of problem. If the numerical procedure is to be extended to a new type of problem, a judgment must also be made as to the probability of success or failure of the potential extension.

For the present study it was desired to determine whether one or more of the procedures investigated were superior in solving the CDT equation (4), with the boundary conditions (7a), (7b), and (7d) for a range of V/D found in soils. Based on the literature review, it would be expected that the explicit scheme would perform unsatisfactorily compared to some of the other schemes. However, the limitation on grid-spacing, which is uniquely associated with this scheme, is part of the reason for investigating the explicit scheme. The analysis carried out earlier showed that the only difference between the explicit scheme and Chaudhari's scheme (equation 19) is related to time step size and not to grid-spacing. The final test, of course, must be in terms of numerical results generated by use of the two schemes.

Bresler (1972) purported to have developed a finite-difference approximation which eliminates numerical dispersion. He presented graphs showing near-perfect agreement between results obtained by the use of his scheme and those obtained from an analytical solution presented by Brenner (1962), for saturated, steady-flow conditions. However, he did not give any indication of the time step sizes or grid-spacings necessary to achieve his results. Moreover, he failed to indicate the fact that his scheme reduces to the Crank-Nicolson approach (25) for these conditions.

Stone and Brian's scheme (26) apparently has more to offer for high values of V/D , at least from a theoretical point of view, than either the Crank-Nicolson approach or Chaudhari's scheme (equation 19). The reason is that Stone and Brian included weighting factors in their scheme which result in reduced oscillations in the numerical solutions for high V/D . However, comparisons of the performance of these schemes for low values of V/D have not been made. Since the derivations of both Stone and Brian's scheme and Chaudhari's scheme included the assumption, $D = 0$, it was desired to check their performance relative to that of the Crank-Nicolson approach for values of V/D of 10 or less.

The second-order explicit scheme has the same theoretical accuracy of approximation as the Crank-Nicolson approach, but has an explicit rather than an implicit computational procedure. Moreover, it is not based on approximation (23), and can readily be extended to non-linear systems. Tests were thus run to determine if its performance is similar to that of the Crank-Nicolson approach, as theory indicates.

Computer programs--The explicit scheme, Chaudhari's scheme, Stone and Brian's scheme, the Crank-Nicolson scheme, and the second-order explicit scheme were programmed in FORTRAN for the purpose of making computer simulation runs. The systems of equations corresponding to Stone and Brian's scheme and the Crank-Nicolson scheme (25) were arranged in tri-diagonal matrix form, and the algorithm outlined by Carnahan et al. (1969) was used to invert the tri-diagonal matrices. A transfer-of-mass mechanism, as suggested by Chaudhari (1971), was included in the programming of Chaudhari's scheme. The method outlined on page 231 was the basis for the program corresponding to the second-order explicit scheme. The boundary and initial conditions given in equation (7a), (7b), and (7d) were incorporated into the programs in a manner similar to that suggested when the second-order explicit scheme was presented on page 231.

Conditions and basis for comparison--In order to compare the performances of the finite-difference approximations, computer runs were made for various values of the quantities Δz , $r = V/D$, and $\beta = V \cdot \Delta t / \Delta z$. The velocity, V , was 0.01 cm min^{-1} for all runs, so that varying β was equivalent to varying the time step size Δt , provided Δz was held constant. However, it is more meaningful to express the relative magnitude of the time step size in terms of β because interpretation of results can be extended to a broader spectrum of conditions. Note that $\beta = 1$ is equivalent to the time interval required for the solvent to move a distance, Δz , at the velocity, V . It has already been suggested that the numerical results obtained from some of the schemes are

sensitive to the value of Δz used in conjunction with a particular value of r . Finally, since the computational effort required for a given scheme on a particular problem is related to time step size and grid spacing, conclusions can be drawn about the relative efficiency of the various schemes by considering the values of Δz and β in conjunction with the number of computations per grid point per time step required for each scheme.

The quality of the results obtained from the various schemes was determined by comparison with results from the analytical solution presented in Appendix J. Comparisons were made for $T \sim 0.5$, where $T = V \cdot t / L_c$. The column length, L_c , was either 10 cm or 20 cm for all of the runs.

Results of Comparisons--

The discussion of the performances of the finite-difference schemes is divided into two parts. The first part is confined to the explanation of the behavior of the explicit scheme, Figures 100 and 101. The second part consists of observations on the performances of the remaining schemes for values of $r = 2$, Figures 102 to 107, and $r = 32$, Figures 108-110.

The explicit scheme--In Figure 100, results obtained from the explicit scheme are plotted along with results obtained from the analytical solution (solid line), for $r = 8$. Three of the cases presented were obtained by using the approximation scheme (15), the representative equation for the explicit scheme. For the fourth case, the apparent diffusion coefficient was increased by the amount $D^{**} = 0.5 \cdot V^2 \cdot \Delta t$; so that equation (19) is the basis for the results for this case. Of the four cases, the worst performance is manifested for the conditions, $\Delta z = 0.2$ and $\beta = 0.75$. Since $\Delta z = 0.2 < 2 \cdot D/V = 0.25$, the inequality (16) is satisfied for this case. In addition, since $D \cdot \Delta t / \Delta z^2 = \left(\frac{D}{V}\right) \cdot \left(\frac{1}{\Delta z}\right) \cdot \left(\frac{V \cdot \Delta t}{\Delta z}\right) = \left(\frac{1}{8}\right) \cdot (5) \cdot (0.75) = \frac{15}{32} < 0.5$, the criterion (17) is also satisfied.

For the conditions $\Delta z = 0.2$ and $\beta = 0.25$, a vast improvement resulted from the reduction in time step size. For the two cases for which $\Delta z = 0.4$, the inequality (16) is violated. The results obtained for $\Delta z = 0.4$ and $\beta = 0.05$ are a significant improvement over the results for $\Delta z = 0.2$ and $\beta = 0.75$. This is undoubtedly due to the smaller time step size used in the former case, which is $\frac{1}{7.5}$ the size of the time step size used in the latter case.

The best results presented in Figure 100 correspond to use of the correction to the apparent diffusion coefficient by substituting $(D + D^{**})$ for D in the explicit scheme (15). The value of $\beta = 0.5$ represents an increase by a factor of 10 over the time step size used for the conditions, $\beta = 0.05$ and $\Delta z = 0.4$. Nevertheless, the results indicate an improved performance, which is due to the correction to the apparent diffusion coefficient.

In Figure 101 results are presented for the explicit scheme and the Crank-Nicolson scheme for $V/D = 32$ and $\Delta z = 0.2$. For these values of r and Δz , $\Delta z > 2 \cdot D/V = 0.0625$, so that the condition given in equation (16) is violated. The results from the explicit scheme exhibit severe oscillations for

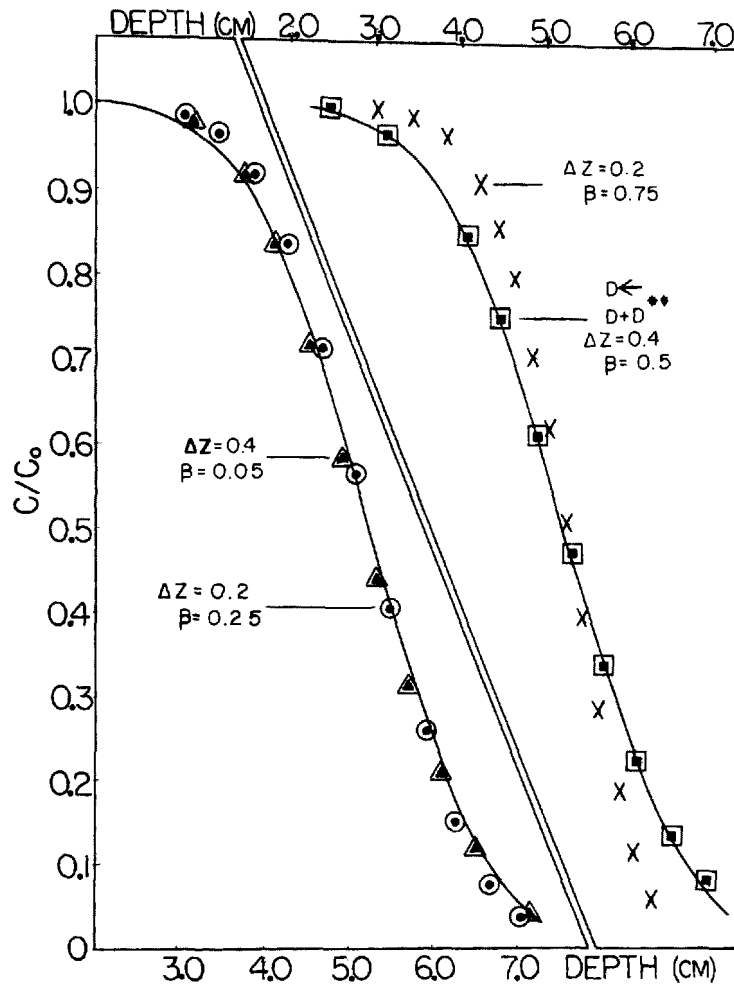


Figure 100. Predicted C/C_0 profiles using the explicit scheme with $r = 8$. The analytical solution is shown as the solid line on both sides of the figure. X is the solution with $\Delta z = 0.2$; $\beta = 0.75$; \odot is the solution with $\Delta z = 0.2$; $\beta = 0.25$; \triangle is the solution with $\Delta z = 0.4$; $\beta = 0.05$; and \square is the solution with $\Delta z = 0.4$; $\beta = 0.4$; and D replaced by $D + 0.5 \cdot V^2 \cdot \Delta t$.

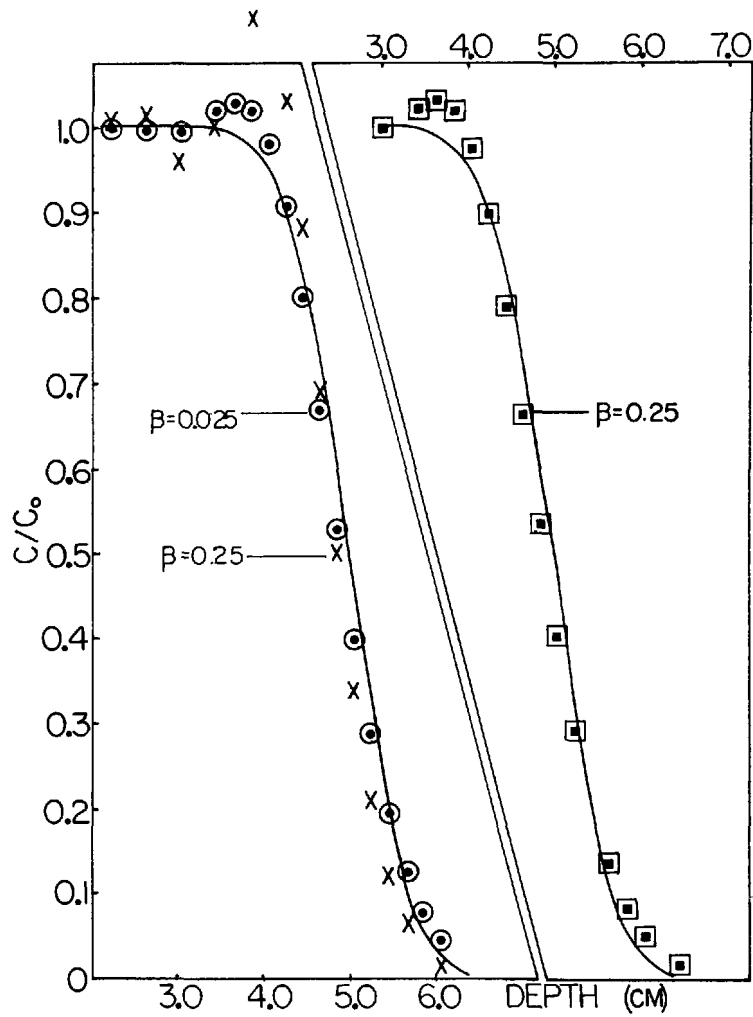


Figure 101. Predicted C/C_0 profiles with $r = 32$ and $\Delta z = 0.2$. The analytical solution is shown as the solid line on both sides of the figure where \blacksquare is the Crank-Nicolson scheme with $\beta = 0.25$; x is the explicit scheme with $\beta = 0.025$; and \odot is the explicit scheme with $\beta = 0.25$.

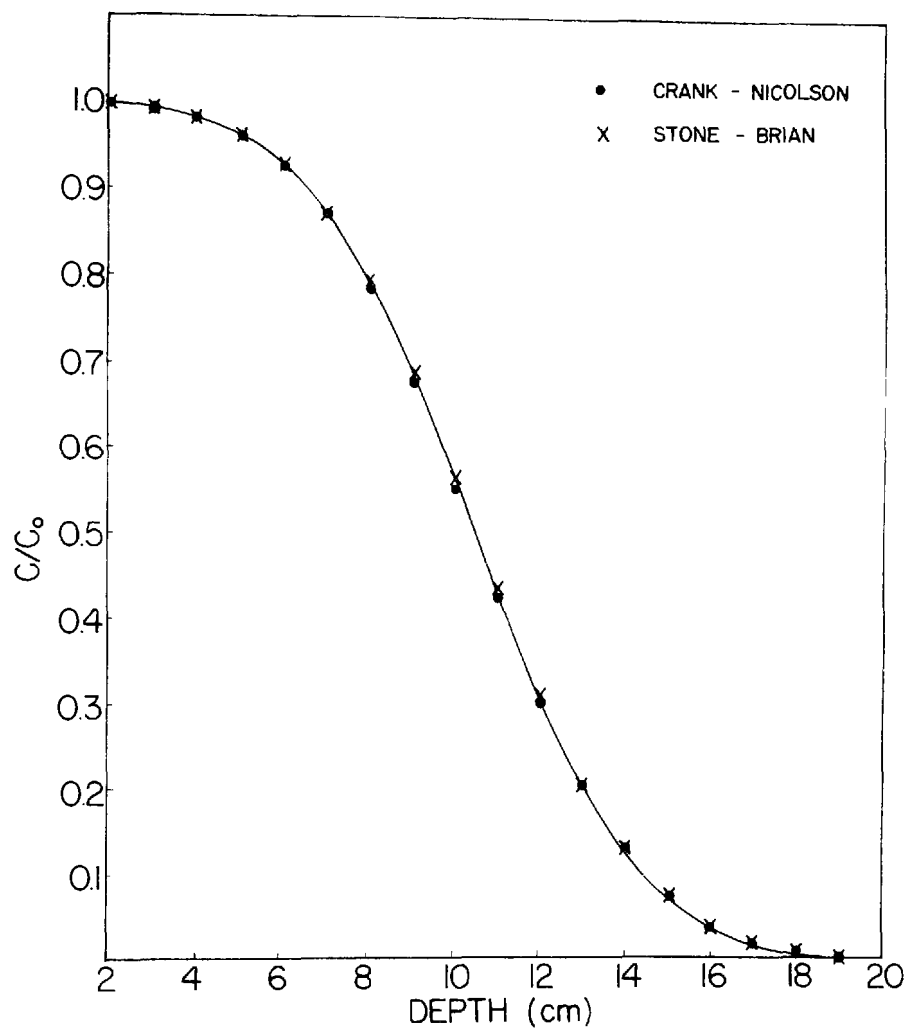


Figure 102. Predicted C/C_0 profiles with $r = 2$, $\Delta z = 0.5$, and $\beta = 0.5$. The analytical solution is shown as a solid line.

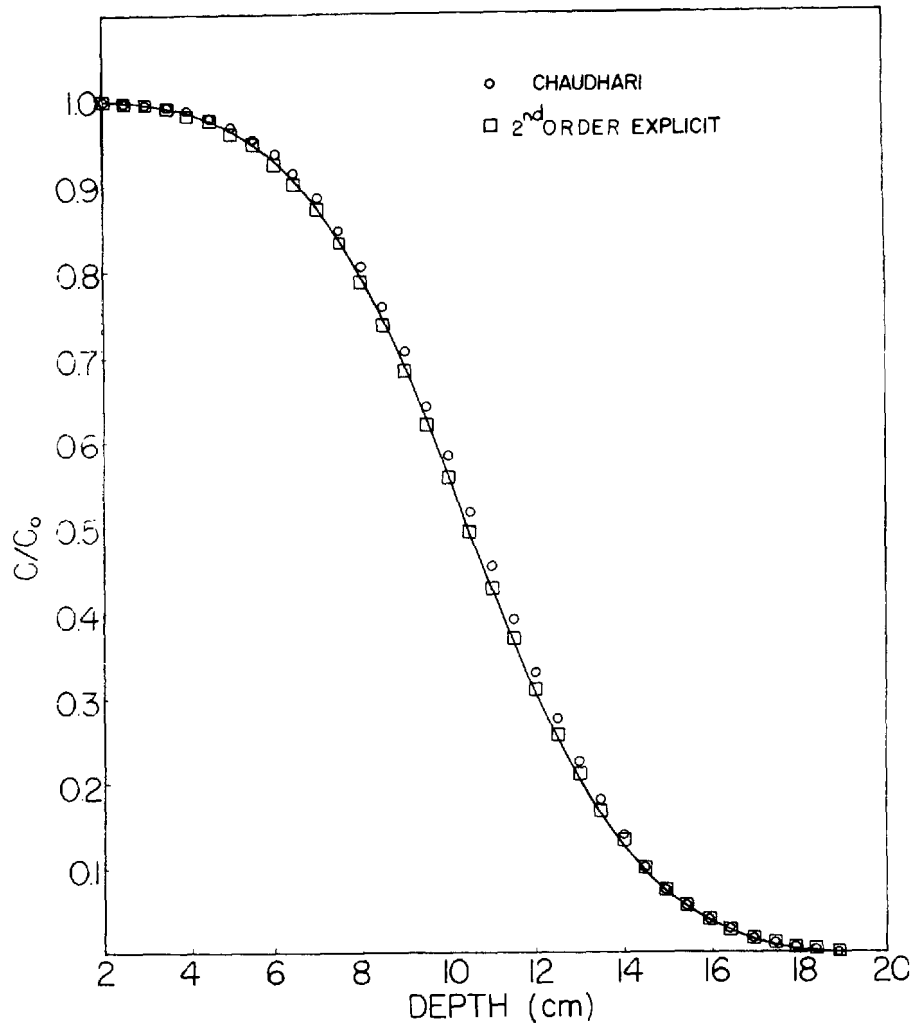


Figure 103. Predicted C/C_0 profiles with $r = 2$, $\Delta z = 0.5$ and $\beta = 0.4$. \circ is the Chaudhari scheme and \square is the explicit scheme. The analytical solution is shown as the solid line.

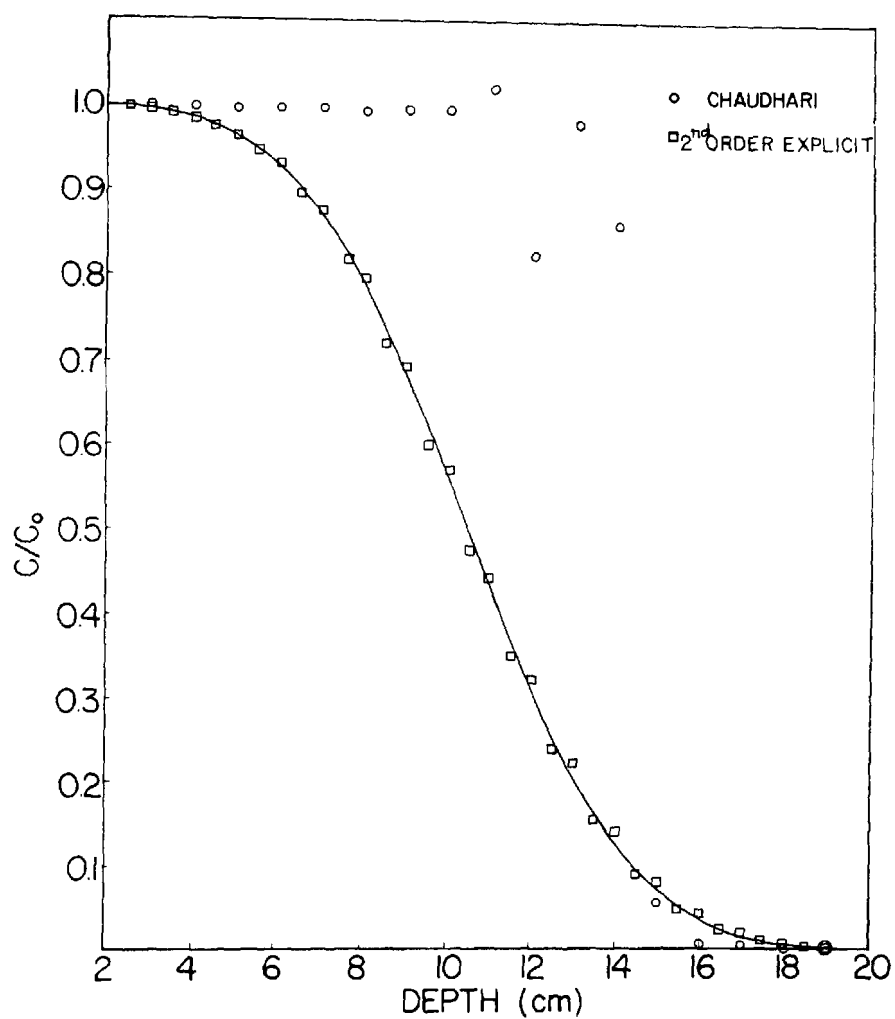


Figure 104. Predicted C/C_0 profiles with $r = 2$, $\Delta z = 0.4$, and $\beta = 0.5$. \circ is the Chaudhari scheme and \square is the explicit scheme. The analytical solution is shown as the solid line.

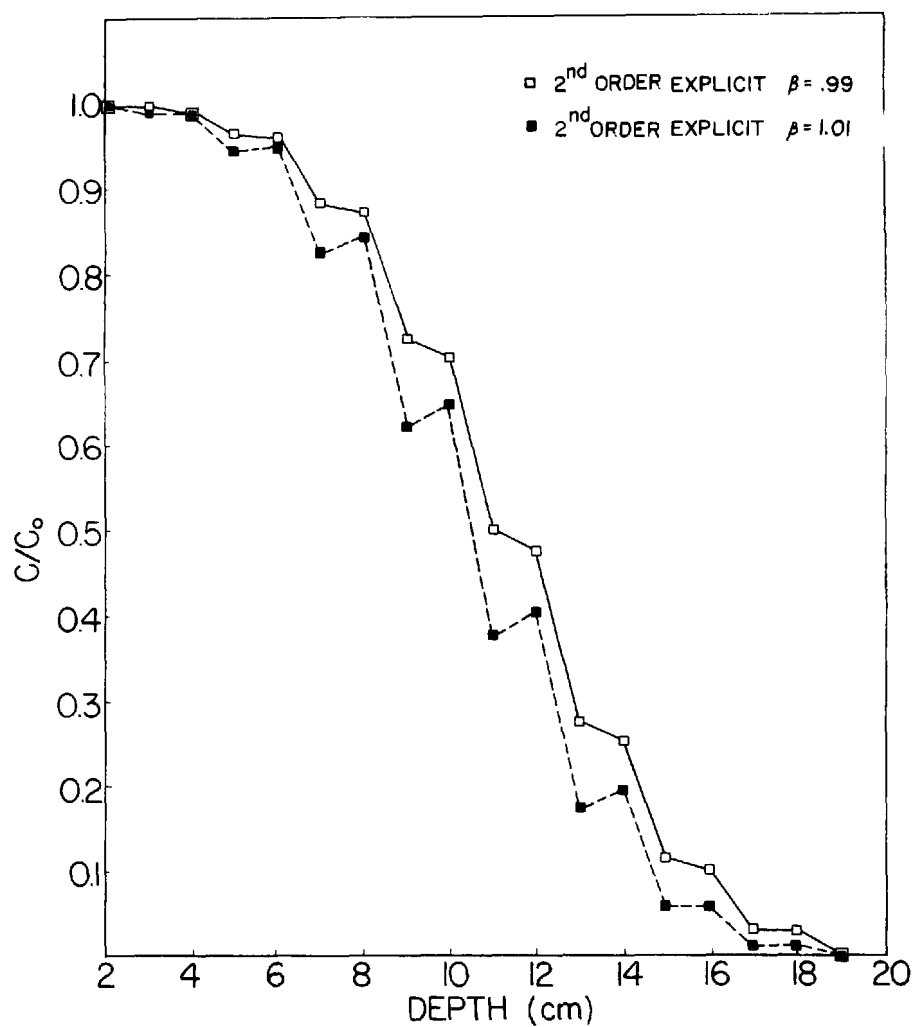


Figure 105. C/C_o profiles calculated using the second order explicit scheme where \square is $\beta = 0.46$ and \blacksquare is $\beta = 0.51$.

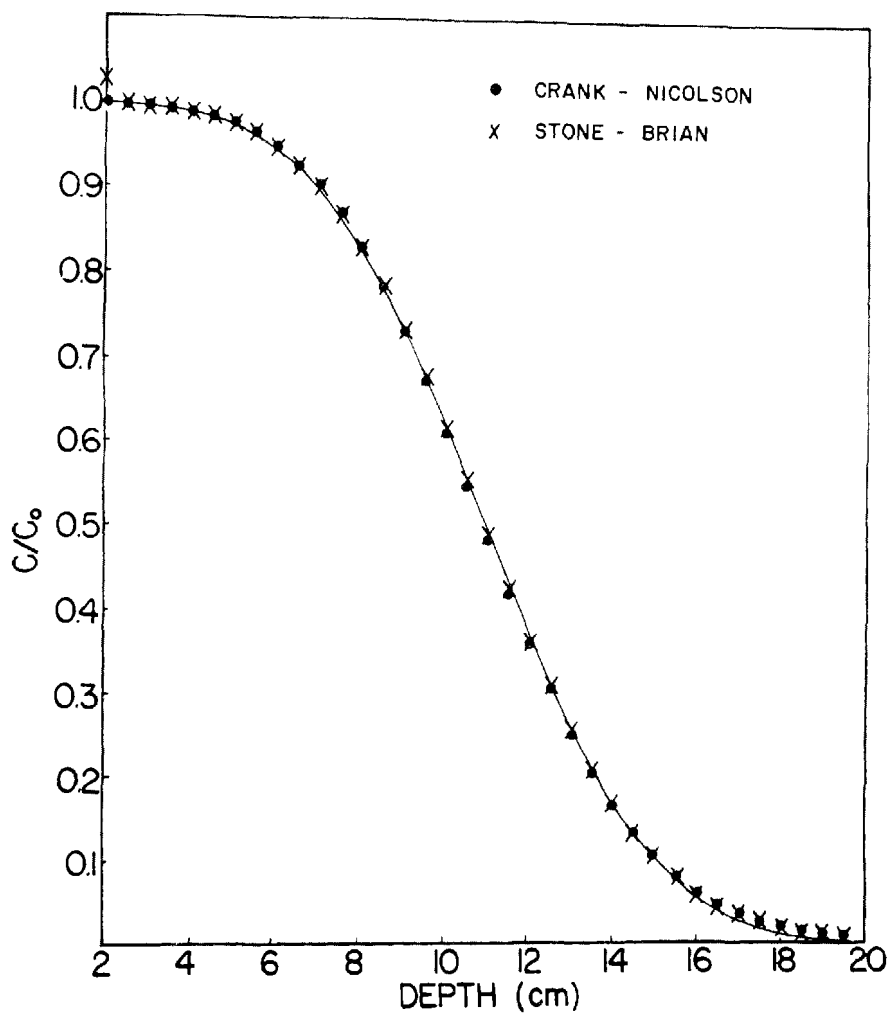


Figure 106. Predicted C/C_0 profiles with $r = 2$, $\Delta z = 0.5$ and $\beta = 1.75$. \circ is the Crank-Nicolson scheme and x is the Stone-Brian scheme. The analytical solution is shown as a solid line.

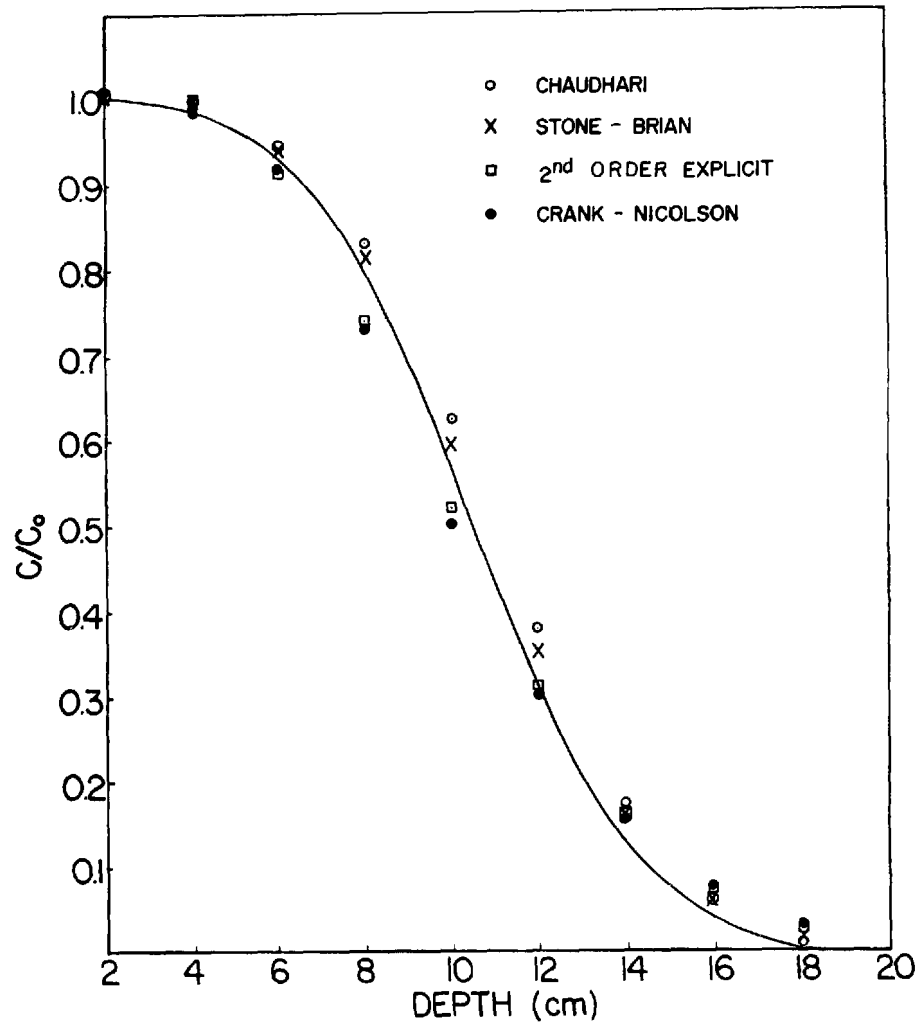


Figure 107. Predicted C/C_0 profiles with $r = 2$, $\Delta z = 2$ and $\beta = 0.5$. \circ is the Chaudhari scheme, \times is the Stone-Brian scheme, \square is the explicit scheme, and \bullet is the Crank-Nicolson scheme. The analytical solution is shown as the solid line.

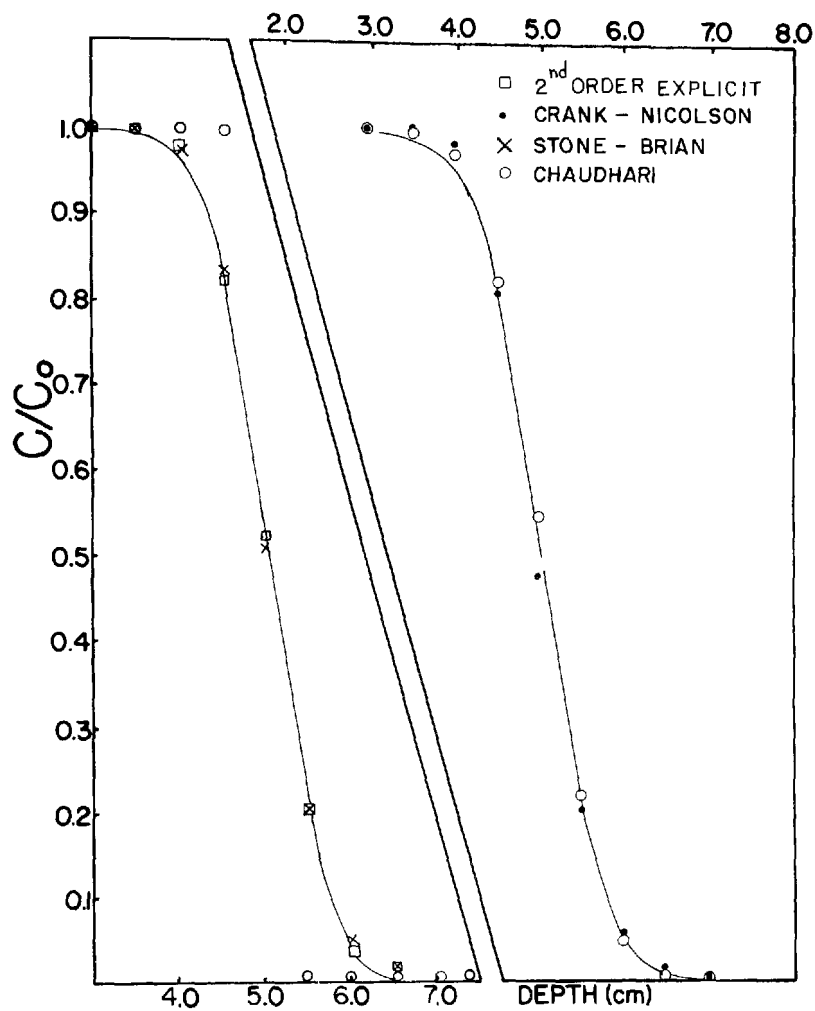


Figure 108. Predicted C/C_0 profiles with $r = 32$ and $\Delta z = 0.125$. The Stone and Brian scheme, Chaudhari scheme, and second order explicit scheme are shown on the left side for $\beta = 1$. On the right side the Chaudhari scheme is shown for $\beta = 0.5$ and the Crank-Nicolson scheme for $\beta = 1$. The analytical solution is shown as a solid line on the right side.

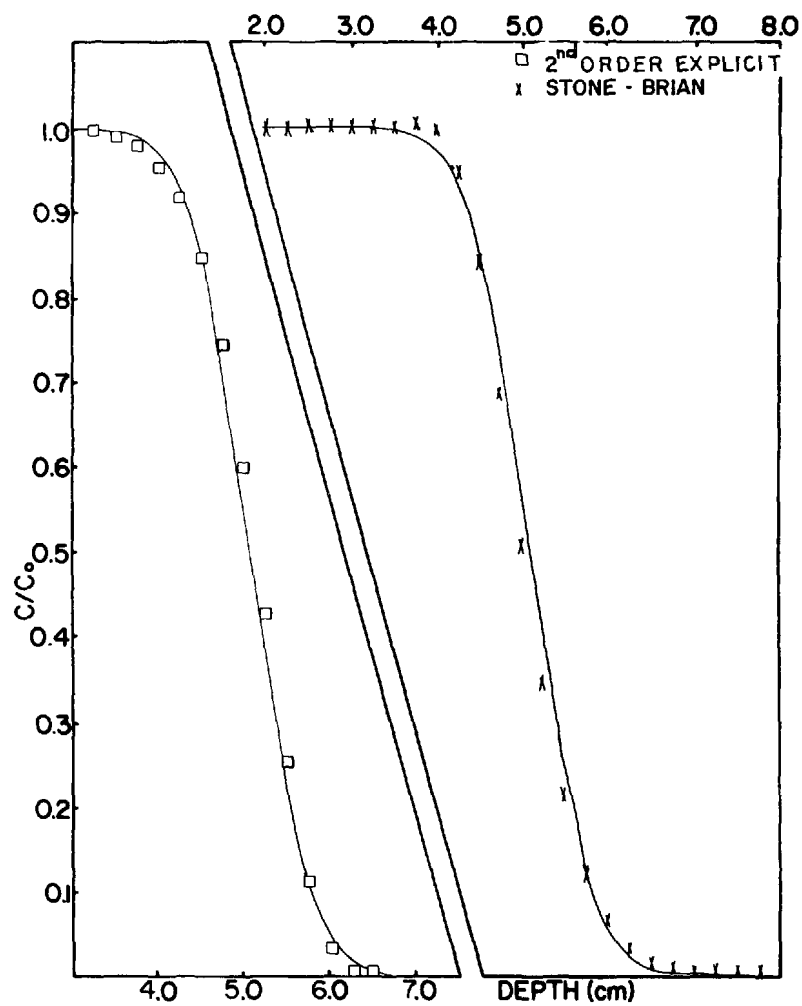


Figure 109. Predicted C/C_0 profiles with $r = 32$ and $\Delta z = 0.125$. The second order explicit scheme with $\beta = 1.5$ is shown on the left. The Stone and Brian scheme with $\beta = 1.75$ is shown on the right.

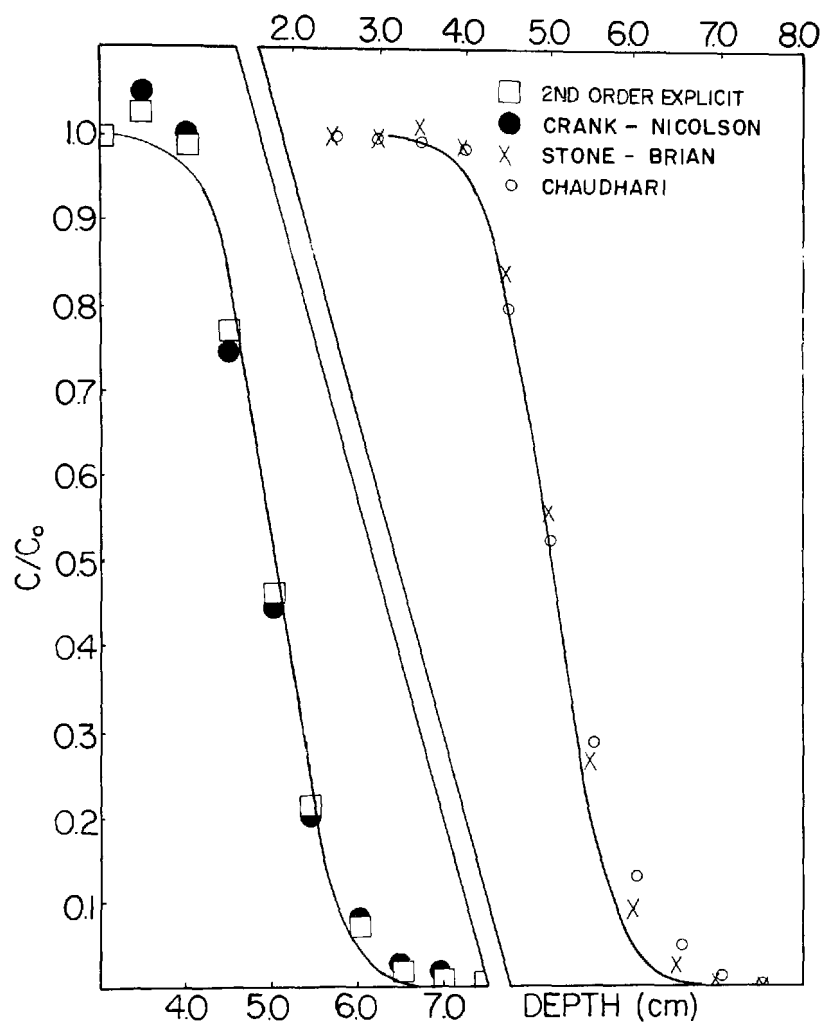


Figure 110. Predicted C/C_0 profiles with $r = 32$ and $\beta = 0.5$. The Crank-Nicolson scheme and the second order explicit scheme with $\Delta z = 0.25$ are shown on the left side. The solution is shown as a solid line. The Chaudhari scheme and Stone and Brian scheme with $\Delta z = 0.5$ are shown on the right. The analytical solution is shown as a solid line.

$\beta = 0.25$. On the other hand, the results for $\beta = 0.025$ are almost identical to those from the Crank-Nicolson scheme for $\beta = 0.25$. The oscillations should not be confused with instability, since the oscillations in all cases were found to be less pronounced as the solutions progressed in space and time. (For a discussion of this type of oscillation, see Shamir and Harleman, 1967. For a discussion of instability, see Carnahan et al., 1969).

The following conclusions can be drawn regarding the behavior and use of the explicit scheme. First of all, the criterion on grid-spacing (16) is misleading. The scheme is not necessarily unstable when (16) is violated, as has been suggested by Fried and Combarnous (1971) and Shamir and Harleman (1967). Two stable solutions were presented for cases where (16) was violated. Moreover, cases were presented showing that the quality of results was better when (16) was violated and a relatively small time step was used than when (16) was satisfied but a larger time step was used. The implication is that good results should not be expected from use of the explicit scheme just on the basis that (16) and (17) are satisfied.

Secondly, the explicit scheme manifests a performance which is much inferior to that of schemes utilizing second-order (equation 25) or approximately second-order (equation 19) accurate finite-difference approximations to the time derivative in the CDT equation (4). Cases were presented showing that results of better quality were obtained using Chaudhari's equation (19) than those obtained using the explicit scheme, although the time step size used with the explicit scheme was a factor of 10 smaller. These results are significant since no more computational effort is required for Chaudhari's scheme (19) than for the explicit (15) on a grid point per time step basis.

Finally, the inferiority of the explicit scheme is well-founded in theory, in as much as the difference in equation (15) and (19) is related to time step size and not to grid-spacing. The extreme sensitivity of the explicit scheme to time step size, which is indicated in Figures 100 and 101, substantiates this theoretical difference.

Performances of the other schemes--The results obtained from runs using the Crank-Nicolson and Stone and Brian schemes, for $r = 2$, $\Delta z = 0.5$, and $\beta = 0.5$, are shown in Figure 102. Results for the Chaudhari and second-order explicit schemes, for the same values of r and Δz and for $\beta = 0.4$ and 0.5 , respectively, are presented in Figures 103 and 104, respectively.

It is evident from Figure 102 that the Stone and Brian and Crank-Nicolson schemes yield close approximations to the analytical solution for $\beta = 0.5$. The second-order explicit scheme yields correspondingly good results for $\beta = 0.4$, but the results from Chaudhari's scheme exhibits more deviation from the analytical solution than those from the other schemes. For $\beta = 0.5$, results from the Chaudhari scheme exhibit severe oscillations in the frontal region, while those from the second-order explicit scheme manifest less pronounced oscillations about the analytical solution.

In order to understand the reason for this seemingly strange behavior of Chaudhari's scheme and the explicit scheme, it is helpful to reconsider the

relationship between the two. It was pointed out earlier that the only difference in the basic approximating equations for the two schemes is the value of the coefficient of $\delta_z^2 (C_1^j)$ appearing in both the explicit and Chaudhari's scheme 15 and 19. The inequality (17) which must be satisfied to insure stability of the explicit scheme, can be translated to the following inequality for Chaudhari's scheme:

$$\frac{(D + D^{**}) \cdot \Delta t}{\Delta z^2} \leq 0.5 ,$$

which can also be expressed in terms of r , β , and Δz :

$$\beta \cdot \left(\frac{1}{r \cdot \Delta z} + 0.5 \right) \leq 0.5 . \quad (30)$$

Since $\frac{1}{r \cdot \Delta z} > 0$, an immediate consequence of (30) is the strict inequality:

$$\beta < 1 .$$

The maximum value of β which satisfies (30), for $r = 2$ and $\Delta z = 0.5$, is $\beta = 0.41$. Therefore, the use of $\beta = 0.5$ with these values of r and Δz is a violation of (30). The transfer-of-mass mechanism included in the programming of Chaudhari's scheme curtails uncontrolled oscillations outside of the frontal region, even if (30) is violated. However, the approximation to the analytical solution in the frontal region degenerates as a result of the violation.

It might also be expected that the second-order explicit scheme should be restricted with respect to time step size as a result of the explicit computational procedure associated with the scheme. Empirical observations from a number of runs revealed that the oscillatory behavior illustrated in Figure 104 occurs when $D \cdot \Delta t / \Delta z^2 = \beta / (r \cdot \Delta z) \sim 0.5$. Further evidence of this phenomenon is presented in Figure 105, for $r = 2$, $\Delta z = 1$ and $\beta \sim 1$. One graph corresponds to $\beta = 0.99$ $\{\beta / (r \cdot \Delta z) = 0.495\}$, while the other graph corresponds to $\beta = 1.01$ $\{\beta / (r \cdot \Delta z) = 0.505\}$. The degeneration of the approximate numerical results with increasing $\beta / (r \cdot \Delta z)$, for $\beta / (r \cdot \Delta z) \sim 0.5$, was also observed for the values of r and Δz used for Figure 104. Due to small differences in the time step sizes, Δt , used to produce the two solutions in Figure 105, the results presented there do not correspond to exactly the same simulated time. However, observations were made for other simulated times and for the same values of r , Δz , and β . For $\beta / (r \cdot \Delta z) = 0.505$, the oscillations became more pronounced with increasing time, while for $\beta = 0.495$, the oscillations tended

to smooth out with increasing time. While these observations do not constitute "proof" of instability of the second-order explicit scheme for $\beta/(r \cdot \Delta z) > 0.5$, they are indicative of a certain sensitivity of the results to the magnitude of this ratio.

Results from the Crank-Nicolson and Stone and Brian schemes, for $\Delta z = 0.5$, $r = 2$ and $\beta = 1.75$, are presented in Figure 106. Very little adverse effect was caused by the increase in β from 0.5 to 1.75, for these two schemes, although, the results from the Stone and Brian scheme exhibited an overshoot of 0.3% at $z = 2$ for the larger value of β . An overshoot of 0.6% was observed for the Crank-Nicolson scheme for $\beta = 2$ (not shown).

The results for all four schemes, for $r = 2$, $\beta = 0.5$ and $\Delta z = 2$, are presented in Figure 107. The effect of increasing Δz can be observed by comparing Figure 107 with Figures 102 and 103. The deviations from the analytical solution are evident for the higher value of Δz . In addition, minor overshoots of 0.5% and 1.0% occur for the second-order explicit and Crank-Nicolson schemes, respectively. Since the time step size, Δt , was also increased by a factor of four in order to hold β constant, it might be thought that the poorer quality results in Figure 107 are due partially to the increase in time step size. However, runs made for $\Delta z = 2.0$ and $r = 2.0$ and for the same time step sizes used for Figures 102 and 103 resulted in no significant improvements for any of the schemes.

The results from the Stone and Brian, second-order explicit, and Chaudhari schemes, for, $r = 32$, $\Delta z = 0.125$, and $\beta = 1.0$ are presented on the left in Figure 108. The symbols on the right of Figure 108 correspond to the Chaudhari scheme, for $\beta = 0.5$, and the Crank-Nicolson scheme, for $\beta = 1.0$. The results from the Crank-Nicolson scheme exhibit an overshoot of 0.5% C_0 at $z = 3.5$. The response of the Chaudhari scheme, for $\beta = 1.0$, has the appearance of a step-function: $C/C_0 = 1.0$, for $0.0 \leq z \leq 5.0$, and $C/C_0 = 0.0$, for $z \geq 5.0$. This response is another manifestation of the violation of (30) for Chaudhari's scheme.

The effect of increasing β to 1.5, for the second-order explicit scheme, and to 1.75, for the Stone and Brian scheme, is shown in Figure 109. The quality of fit for the Stone and Brian scheme, for this value of β , is about the same as that of the Crank-Nicolson scheme for $\beta = 1.0$, both having overshoots of 0.5%. The results from the second-order explicit scheme, for $\beta = 1.5$, also show some decrease in quality from the corresponding results for $\beta = 1.0$, although no overshoot occurred for either value of β . Results from the second-order explicit scheme, for $\beta = 1.75$ (not shown), exhibited rather severe oscillations.

Finally, the results corresponding to the Crank-Nicolson and second-order explicit schemes, for $r = 32$, $\Delta z = 0.25$, and $\beta = 0.5$, are presented in Figure 110. Also shown there are results from the Stone and Brian and Chaudhari schemes, for $\Delta z = 0.50$. In this case, the quality of fit for the Stone and Brian scheme is better than for the second-order explicit and Crank-Nicolson schemes even though the grid spacing and time step size used for the former scheme are both twice as large as those used for the latter two

schemes. Although the results from the Chaudhari scheme show no overshoot, the deviation from the analytical solution in the frontal region is rather severe. Runs were also made with the Stone and Brian scheme for $r = 32$ and $\Delta z = 0.25$ (not shown). No overshoot was present for $\beta = 0.5$. For $\beta = 1.0$, the quality of results, including overshoot, was about the same as that for $\Delta z = 0.5$ and $\beta = 0.5$.

Assessing the relative efficiency and accuracy of the four finite-difference schemes, excluding the explicit scheme, is not as straightforward as the comparison of the performance of the explicit scheme with that of the others. However, at least some rather qualitative assessments can be made on the basis of the figures presented. To aid in this discussion, attention is first directed to an aspect of the finite-difference approximation schemes presented in equations (15), (19), (25), (26), and (29), which has not heretofore been pointed out. Each of these approximations can be expressed in the general form:

$$f(C_{i+1}^j, C_i^j, C_{i-1}^j, C_{i+1}^{j+1}, C_i^{j+1}, C_{i-1}^{j+1}, \beta, r \cdot \Delta z) = 0,$$

although the analytical expression for f varies somewhat from scheme to scheme. The fact that all of the schemes are similar in their general functional form is not as important from the present point of view as the fact that, for a particular scheme, different solutions resulting from the same values of β and $r \cdot \Delta z$ have something in common. The similarity between such solutions exists in terms of the grid point number, i , and time step number, j , rather than in terms of the total distance to a grid-point, $i \cdot \Delta z$, or the total time spanned from $t = 0$, $j \cdot \Delta t$. In other words, with a particular scheme, and for a grid-network with a sufficient number of grid points so that the lower boundary exerts negligible influence on the concentration C_i^j after j time steps, any two approximations to the solution of the CDT equation (4), with the conditions given in (7a), (7b) and (7d) produced from the same values of β and $r \cdot \Delta z$, will be identical after j time steps at all grid points, k , such that $k \leq i$. To illustrate what is meant, the results from the Stone and Brian scheme, with $r = 32$, $\Delta z = 0.125$, and $\beta = 0.5$, are compared in Table 65 with results using the same scheme with $\beta = 0.5$ but with $r = 2.0$ and $\Delta z = 2.0$. The results for the first 10 grid points and after 10 time steps are identical for the two pairs of r and Δz . By utilizing this translational quality of the schemes, it is possible to glean additional information from the results which are presented in Figures 102-110.

First of all, the Crank-Nicolson and Stone and Brian schemes appear to have some advantage over the second-order explicit and Chaudhari's schemes for low values of $r \cdot \Delta z$, due to a greater flexibility in the choice of β for the former two schemes. For $r \cdot \Delta z = 1$, and for $\beta = 1.75$, the results of these two schemes showed little decreases in quality from the corresponding results for $\beta = 0.5$. The maximum value of β for the Chaudhari scheme is 0.41 (for $r \cdot \Delta z = 1$), by virtue of equation (30), and that for the second-order explicit scheme appears to be approximately 0.5. The translational property discussed above indicates that the oscillatory behavior of the second-order explicit scheme illustrated in Figures 104 and 105 would occur for $\beta/r \cdot \Delta z \sim 0.5$ and

TABLE 65. C/CO VALUES FOR $r \cdot \Delta z = 4$, AFTER TEN TIME STEPS FROM TWO RUNS USING THE STONE AND BRIAN SCHEME.

		r=2	$\Delta z=2.0$	r=32	$\Delta z=0.125$
Grid Point	Z	C/Co		C/Co	Z
1	0.0	1.0000		1.0000	0.000
2	2.0	0.9996		0.9996	0.125
3	4.0	0.9895		0.9895	0.250
4	6.0	0.9404		0.9404	0.375
5	8.0	0.8110		0.8110	0.500
6	10.0	0.5953		0.5953	0.625
7	12.0	0.3519		0.3519	0.750
8	14.0	0.1614		0.1614	0.875
9	16.0	0.0569		0.0569	1.000
10	18.0	0.0158		0.0158	1.125

for $r \cdot \Delta z = 1.0$ and $r \cdot \Delta z = 2$, regardless of the value of r . However, the values of C/C_0 presented in these figures would be shifted to shorter simulated times and distances for higher values of r .

The results presented in Figures 107 and 110 indicate that the Stone and Brian and Chaudhari schemes resist overshoot for higher values of $r \cdot \Delta z$ (i.e. $r \cdot \Delta z = 4, 8$, and 16 , respectively, corresponding to Figures 107, 109 and 110, respectively) than do the Crank-Nicolson or second-order explicit schemes. It is interesting to note that the value of $r \cdot \Delta z$ which produced oscillations in the observed C/C_0 profiles for the Crank-Nicolson, Stone and Brian, and second-order explicit schemes was higher for the cases where $r = 32$ than for those where $r = 2$. Shamir and Harleman (1967) pointed out the tendency of overshoot in solutions produced by the Stone and Brian scheme to die out as the simulated concentration front progresses in space and time. This same tendency can be observed for the other two schemes from the present analysis. The results for $r = 2$ and $\Delta z = 2$ can be viewed as an early observation (i.e. after 10 time steps) from any run for which $\beta = 0.5$ and $r \cdot \Delta z = 4$. The results for $r = 32$ and $\Delta z = 0.125$ can be viewed as a later observation (i.e. after 80 time steps) from the same run, assuming the provision of a sufficient number of grid points. Overshoot would occur in the early observation for the Crank-Nicolson and second-order explicit schemes but would not be present for the later observation. Overshoot would be absent in both corresponding observations. Overshoot would be absent in both corresponding observations of results from the Stone and Brian scheme.

Chaudhari's scheme provides results which are free of overshoot for large values of $r \cdot \Delta z$. It is difficult to assess the relative merit of this characteristic from the present analysis since the deviation from the analytical solution in the frontal region was noticeably worse than that for the Stone and Brian scheme for $r = 2$, $\Delta z = 2$, and $\beta = 0.5$ and for $r = 32$, $\Delta z = 0.5$ and $\beta = 0.5$. The scheme is certainly a simple alternative to the explicit scheme, due to the similarity of the explicit scheme equation (15) and Chaudhari's scheme equation (19). The transfer of mass mechanism for preventing overshoot can apparently be used to best advantage when only qualitative results, free of overshoot, are required. In such cases large values of $r \cdot \Delta z$ can be used and the restriction on β due to (30) is not as severe as for smaller values of $r \cdot \Delta z$. However, in any case, β must be less than 1.

The Crank-Nicolson scheme appears to be somewhat more sensitive to overshoot for higher values of $r \cdot \Delta z$ ($r \cdot \Delta z = 4$) than either the second-order explicit or the Stone and Brian scheme. For $r = 2$, $\Delta z = 2$, and $\beta = 0.5$, the overshoot for the Crank-Nicolson scheme was slightly greater than for the second-order explicit scheme. While for $r = 32$ and $\Delta z = 0.125$, results for the former scheme exhibited overshoot for $\beta = 1.0$, whereas the results for the latter scheme showed no overshoot for $\beta = 1.5$. In resisting overshoot, the Stone and Brian scheme exhibited at least a factor of 2 advantage in the magnitude of $r \cdot \Delta z$, with $\beta = 0.5$, over both of the other schemes. However, increasing β to 1.0 or increasing $r \cdot \Delta z$ by an additional factor of 2, for $\beta = 0.5$, resulted in overshoot in the observed results for this scheme.

Summary--Five finite-difference schemes were investigated. Predicted values of C/C_0 produced by the various schemes were compared to results from the analytical solution presented in Appendix J. The explicit scheme, represented by equation (15), was found to be inferior to schemes possessing a second-order (or approximate second-order) accurate approximation to the time derivative in equation (4). Time steps required to produce an accuracy comparable to that obtained by use of Chaudhari's scheme equation (19) or of that using the Crank-Nicolson scheme were smaller by a factor of 10 for the explicit scheme. The scheme produced stable solutions even when condition (16) was violated.

It was pointed out that all of the schemes are functions of the two dimensionless quantities, $\beta = V \cdot \Delta t / \Delta z$ and $r \cdot \Delta z$, where $r = V/D$. It was demonstrated that this property allows observations on the qualitative aspects of numerical results from a particular scheme to be applied to other numerical results which are generated from the same values of these two quantities.

It was demonstrated that larger values of β (~ 1.75) could be used with the Stone and Brian and Crank-Nicolson schemes than with the Chaudhari or second-order explicit schemes ($\beta > 0.5$) for low values of $r \cdot \Delta z$ ($=1.0$). For higher values of $r \cdot \Delta z$, the Crank-Nicolson scheme was found to be more sensitive to increases in β than the second-order explicit scheme, and the Stone and Brian scheme was found to lose some of its advantage in this respect. However, the Stone and Brian and Chaudhari schemes both produced solutions which were free of overshoot for values of $r \cdot \Delta z$, a factor of 2 higher than those for which overshoot occurred for the other two schemes. The deviation from the analytical solution in the frontal region was found to be more pronounced for Chaudhari's scheme than for the Stone and Brian scheme at the higher values of $r \cdot \Delta z$.

Chemical Equilibrium Equations

Choice of a System--

Ions--In today's environment a large number of different chemicals are applied to soils of various textures and under a variety of climatic conditions. It would therefore be difficult to even discuss all of the chemical interactions that might be important, given the right situation. There are, however, certain cations and anions which are present in almost all soils. For example, the exchangeable bases: calcium, magnesium, sodium and potassium are included in many soil chemical analyses and in many instances occupy most of the effective cation exchange capacity of soils. An additional cation which is important in agricultural soils is ammonium, a constituent of certain nitrogen fertilizers, e.g. $(\text{NH}_4)_2\text{SO}_4$. The anion chloride is present in appreciable amounts in many irrigation waters and is also applied to soils as a companion anion in fertilizer applications of potassium. Sulfate is present in some irrigation waters and is applied in fertilizers as a nutrient additive. These same cations and anions are very often chosen for laboratory column studies for the reasons outlined above.

Chemical interactions--Clay particles or platelets are present to some extent in virtually all soils and play a major role in their chemistry and fertility. The clay particles carry a net negative charge which serves to

attract cations. The cations which neutralize this negative charge are in equilibrium with the cations which remain in solution. The process by which a soil system achieves equilibrium with respect to cations neutralizing the negative charge of the clay (adsorbed cations) and those in solution is cation exchange. Cation exchange is important both in the soil storage of cations and in the distribution of cations between the solution and adsorbed phases.

Another ion interaction which can be important when calcium and/or magnesium and sulfate are together in soil solutions is that of ion-pair formation (Dutt et al. 1972a). Ion pairs of calcium and sulfate or magnesium and sulfate are formed; the extent of ion pairing is determined by an equilibrium relationship between the paired and unpaired ions in solution.

Ions and interactions considered in the model--The ions chosen for inclusion in the model are: calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), sulfate ($\text{SO}_4^{=}$), chloride (Cl^-), and bicarbonate (HCO_3^-). The choice of bicarbonate instead of nitrate, which may be important for some applications, perhaps seems arbitrary. However, the decision to use HCO_3^- was partly based on an intended application of the model, for which this ion is important. Moreover, it will subsequently become clear that the monovalent anions, as well as the cations, can easily be replaced by other species for varied application of the model. The chemical interactions considered are those of cation exchange and ion-pairing.

Mathematical Description of Chemical Interaction: Types of Equations--

To describe the equilibrium phenomena discussed above, the basic equations presented by Dutt, et al. (1972b) for cation exchange, ion-pairing and ionic activities were chosen for the present work. However, the numerical approach to the solution of the system of equations differs from the approach taken by these authors. A brief account of the types of equations is given below.

Ionic activity--Dutt et al. (1972a,b), ignoring the effects of temperature and ionic radius, used the following equation to define the activity, (C_i), of ion i, whose molar concentration is C_i :

$$(C_i) = \gamma_i \cdot C_i \quad (31)$$

where

$$\gamma_i = \exp\{-1.17 \cdot Z_i^2 \cdot u / 1 + u\},$$

and

$$u = \sqrt{\frac{1}{2} \sum Z_j^2 \cdot C_j}.$$

The quantity u is the ionic strength, Z_j is the valence of ion j, and the sum is over all ions in solution. The coefficient γ_i is termed the activity

coefficient for ion i. It is clear from equation (31) that only two activity coefficients are mathematically distinguished for solutions containing only monovalent and divalent ions. These are:

$$\gamma_m = \gamma = \exp\{-1.17 \cdot \mu/(1 + \mu)\}$$

for monovalent ions, and:

$$\gamma_d = \gamma^4,$$

for divalent ions.

Cation exchange--The equations utilized for cation exchange are of two types, one which describes exchange between two cations of the same valence, and one which describes exchange between divalent and monovalent cations. The former can be written:

$$Y_1/Y_2 = E_{12} \cdot (C_1)/(C_2) = E_{12} \cdot C_1/C_2 \quad (32)$$

In equation (32) Y_1 and Y_2 represent the adsorbed phase concentrations of ions 1 and 2, respectively, and E_{12} is a constant exchange coefficient whose value is characterized by the soil and the particular cations 1 and 2.

For exchange between a divalent cation, ion 1, and a monovalent cation, ion 3, the following (Gapon) equation is used:

$$Y_1/Y_3 = E_{13}(C_1)^{1/2}/(C_3) = E_{13} \cdot \gamma \cdot C_1^{1/2}/C_3 \quad (33)$$

In (33) the units of Y_1 and Y_3 are arbitrary, but the value of E_{13} is dependent on choice of units for C_1 and C_3 . For subsequent discussion C_1 and C_3 will be assumed to have units (moles/liter) or (millimoles/cm³) and the exchange coefficient for divalent-monovalent exchange reactions will have units (moles/liter)^{1/2}. The dimensionality of the exchange coefficient in this case illustrates the empirical nature of the equation. Nevertheless, much success has been achieved with its use (Dutt et al., 1972b and Frissel and Reiniger, 1974).

Ion-pairing--An example of the type of equation used to describe ion-pair formation is:

$$K_{11} \cdot X_{11} = (C_1) \cdot (A_1)$$

where X_{11} is the molar concentration of the undissociated ion-pair species formed by interaction of divalent cation 1 with divalent anion 1, and K_{11} is the dimensionless dissociation constant for the ion-pair species. The quantity X_{11} may be identified with the molar concentration of undissociated calcium-sulfate (CaSO_4) which is in equilibrium with the dissociated ion concen-

trations C_1 , $\{Ca^{++}\}$ and A_1 , $\{SO_4^{--}\}$. Letting $D_{11} \approx \frac{1}{K_{11}}$ and using the definition of activities for divalent ions, the above equation can be written:

$$X_{11} = D_{11} \cdot \gamma^8 \cdot C_1 \cdot A_1 \quad (34)$$

Conservation of charge among adsorbed cations--The negative charge on the soil which is neutralized by adsorbed cations is assumed to be a fixed quantity at a given depth in the soil and is usually expressed as cation exchange capacity (CEC meq/100 gm soil). If Q_i (meq/100 gm) of cation i is adsorbed then:

$$\sum_i Q_i = CEC$$

If Y_i is the adsorbed quantity of ion i expressed in units of (moles/liter), based on the volumetric water content θ (cm^3 water/ cm^3 soil) and bulk density ρ_b (gm dry soil/ cm^3 soil), then assuming unit density for water, we have:

$$\sum_i \alpha_i \cdot Y_i = CEC$$

$$\alpha_i = 100 \cdot Z_i \cdot \theta / \rho_b$$

Total ion concentration--In a finite volume of moist soil, V (cm^3), at equilibrium, the total amount, T_i (mmoles), of ion i present is a fixed quantity, regardless of the amounts of the ion which are in various phases (adsorbed, solution, etc.). If T_i is divided by the volume of water V_w (cm^3) present in the finite volume of moist soil, another fixed quantity is the result:

$$C_{iT} = T_i / V_w$$

where C_{iT} is the total concentration (mmoles/ cm^3) of ion i at the specified moisture content V_w/V_s . Moreover, we have:

$$C_i + Y_i + \sum_j X_{ij} = C_{iT} \quad (35)$$

where C_i = (mmoles of ion i unpaired)/ V_w

Y_i = (mmoles of ion i adsorbed)/ V_w

X_{ij} = (mmoles of cation i paired with anion j)/ V_w .

These quantities can be expressed equivalently in units of either (moles/liter) or (mmoles/ cm^3).

TABLE 66. SYMBOLS USED FOR DIFFERENT PHASES OF THE IONS

Ion	Solution	Adsorbed	Ion Pairs	Total
Ca^{++}	C_1	Y_1	X_{11}	C_{1T}
Mg^{++}	C_2	Y_2	X_{21}	C_{2T}
Na^+	C_3	Y_3	---	C_{3T}
K^+	C_4	Y_4	---	C_{4T}
NH_4^+	C_5	Y_5	---	C_{5T}
$\text{SO}_4^{=}$	A_1	---	X_{11}, X_{21}	A_{1T}
Cl^-	A_2	---	---	A_{2T}
HCO_3^-	A_3	---	---	A_{3T}

TABLE 67. COMPLETE SYSTEM OF EQUILIBRIUM EQUATIONS.

Description		
Mass Balance	$C_1 + Y_1 + X_{11} = C_{1T}$	(36)
	$C_2 + Y_2 + X_{21} = C_{2T}$	(37)
	$C_3 + Y_3 = C_{3T}$	(38)
	$C_4 + Y_4 = C_{4T}$	(39)
	$C_5 + Y_5 = C_{5T}$	(40)
	$A_1 + X_{11} + X_{21} = A_{1T}$	(41)
	$A_2 = A_{2T}$	(42)
	$A_3 = A_{3T}$	(43)
	$Y_1 / Y_2 = E_{12} \cdot \frac{(C_1)}{(C_2)} = E_{12} \cdot C_1 / C_2$	(44)
	$Y_1 / Y_3 = E_{13} \cdot \frac{(C_1)}{(C_3)^{1/2}} = E_{13} \cdot C_1^{1/2} / C_3 \cdot \gamma$	(45)
Cation-Exchange	$Y_1 / Y_4 = E_{14} \cdot C_1^{1/2} / C_4 \cdot \gamma$	(46)
	$Y_1 / Y_5 = E_{15} \cdot C_1^{1/2} / C_5 \cdot \gamma$	(47)
Conservation of Charge (Adsorbed Cations)	$\sum_{i=1}^5 \alpha_i Y_i = \text{CEC}$	(48)
	where $\alpha_i = 100 \cdot Z_i \cdot \theta / \rho_b$	
Ion-Pairs	$X_{11} = \frac{1}{K_{11\text{CaSO}_4}} (C_1)(A_1) = D_{11} \cdot \gamma^8 \cdot C_1 \cdot A_1$	(49)
	$X_{21} = D_{21} \cdot \gamma^8 \cdot C_2 \cdot A_1$	(50)
Activity Coefficient	$\gamma = \exp(-1.17u/(1+u))$	(51)
	where $u = \sqrt{2(C_1 + C_2 + A_1) + .5(C_3 + C_4 + C_5 + A_2 + A_3)}$	

The ions included in the model are shown in Table 66 together with the symbols used to represent the various phases in which the ions occur. The complete system of equilibrium equations is discussed in Table 67.

Rearrangement of the System of Simultaneous Equations--

Theoretically, the system of equations (36) through (51) could be solved simultaneously, by numerical means, in its present form. However, if some of the dependent variables in the system can be obtained explicitly in terms of the remaining variables, the number of equations that must be solved simultaneously can be reduced by back-substitution. The advantages of a back-substitution approach for a system that must be solved by an iterative technique (e.g. a general non-linear system) are as follows:

- (1) Iterative techniques require an initial estimate for each unknown in the system of simultaneous equations to be solved. Each back-substitution reduces the possibility of a "bad" estimate. This in turn reduces the probability that a large number of iterations will be required for convergence.
- (2) If the system of equations constitutes a mathematical model of a physical system, such as the chemical equilibrium system, knowledge of the system may be used to reduce computational effort.

For example, any physically meaningful solution of the system of chemical equilibrium equations will be such that $0 \leq C_1 \leq C_{1T}$. In other words, only non-negative concentrations are meaningful and in no case can the solution concentration, C_1 , exceed the total concentration C_{1T} . By bounding the variables which are obtained by an iterative technique, the effort expended in obtaining a solution can be reduced. In addition, situations which might lead to an abortion of the solution procedure can be avoided in this manner. In practice, the bounding of the variables is more straightforward for a system of fewer unknowns.

To reduce the system of equations (36) through (51), all of the dependent variables were obtained as functions of C_1 and γ . These two variables occur frequently in the system, whereas the other variables occur in at most four of the equations. The back-substitution scheme is presented in Appendix K. The rearranged system of equations which results from the back-substitution process is presented in Table 68, along with the equations from (36) through (51) used to obtain each new equation. Each equation in the system (36) through (51) was used at least once to obtain the new system (52) through (67).

Inspection of Table 68 reveals the following:

(a) In all of the equations except (54) and (61) variables are either defined directly in terms of C_1 and γ or in terms of other variables which are dependent only on C_1 and γ . In other words, if the root values of C_1 and γ are available, then the entire system is essentially solved.

TABLE 68. REARRANGEMENT OF THE EQUILIBRIUM EQUATIONS

Equations from the Original System
(36) - (51) Used to Define a New
Equation

The New System

$$(41), (50), \quad A_1 = \sqrt{(-BBB + BBB^2 - 4 \cdot AAA \cdot CCC) / (2 \cdot AAA)}, \quad (52)$$

$$(37), (44), \quad AAA = \gamma^8 \cdot (1 + D_{11} \cdot C_1 \cdot \gamma^8) \cdot (D_{21} - D_{11}/E_{12})$$

$$(49), (36), \quad BBB = [1 + D_{11} \cdot D_1 \cdot \gamma^8] \cdot [1 + C_{1T} / (E_{12} \cdot C_1) - 1/E_{12}] + \gamma^8 \cdot [D_{21} \cdot C_{2T} + A_{1T} \cdot$$

$$\left(\frac{D_{11}}{E_{12}} - D_{21}\right)]$$

$$CCC = A_{1T} \cdot \left[\frac{1}{E_{12}} - \frac{C_{1T}}{(E_{12} \cdot C_1)} - 1\right]$$

$$(49), (36) \quad Y_1 = C_{1T} - C_1 \cdot (L + D_{11} \cdot \gamma^8 \cdot A_1) \quad (53)$$

$$(48), (50) \quad Y_1 \cdot (\alpha_1 + T_{C_2} + T_{C_3} + T_{C_4} + T_{C_5}) = CEC \quad (54)$$

$$(37), (44), (38), \quad T_{C_2} = \alpha_2 \cdot C_{2T} / [Y_1 + E_{12} \cdot (1 + D_{21} \cdot \gamma^8 \cdot A_1) \cdot C_1]$$

$$(45), (39), (46),$$

$$(40), (47) \quad T_{C_3} = \alpha_3 \cdot C_{3T} / [Y_1 + \gamma \cdot E_{13} \cdot C_1^{1/2}]$$

$$T_{C_4} = \alpha_4 \cdot C_{4T} / [Y_1 + \gamma \cdot E_{14} \cdot C_1^{1/2}]$$

$$T_{C_5} = \alpha_5 \cdot C_{5T} / [Y_1 + \gamma \cdot E_{15} \cdot C_1^{1/2}]$$

(continued)

TABLE 68. (Continued)

$$\begin{array}{l} (50), (37) \\ (44) \end{array} \quad C_2 = (E_{12}/\alpha_2) \cdot C_1 \cdot T_{C_2} \quad (55)$$

$$(38), (45) \quad C_3 = (E_{13}/\alpha_3) \cdot \gamma \cdot C_1^{\frac{1}{2}} \cdot T_{C_3} \quad (56)$$

$$(39), (46) \quad C_4 = (E_{14}/\alpha_4) \cdot \gamma \cdot C_1^{\frac{1}{2}} \cdot T_{C_4} \quad (57)$$

$$(40), (47) \quad C_5 = (E_{15}/\alpha_5) \cdot \gamma \cdot C_1^{\frac{1}{2}} \cdot T_{C_5} \quad (58)$$

$$(42) \quad A_2 = A_{2T} \quad (59)$$

$$(43) \quad A_3 = A_{3T} \quad (60)$$

$$(51) \quad \gamma = \text{EXP} [-1.17 \cdot \mu / (1 + \mu)] \quad (61)$$

$$\mu = \sqrt{2 \cdot (C_1 + C_2 + A_1)} + 0.5 \cdot (C_3 + C_4 + C_5 + A_2 + A_3)$$

$$(49) \quad X_{11} = D_{11} \cdot \gamma^8 \cdot C_1 \cdot A_1 \quad (62)$$

$$(50) \quad X_{21} = D_{21} \cdot \gamma^8 \cdot C_2 \cdot A_1 \quad (63)$$

$$(50), (37), (44) \quad Y_2 = (Y_1/\alpha_2) \cdot T_{C_2} \quad (64)$$

$$(38), (45) \quad Y_3 = (Y_1/\alpha_3) \cdot T_{C_3} \quad (65)$$

(Continued)

TABLE 68. (Continued)

(39), (46)	$Y_4 = (Y_1/\alpha_4) \cdot T_{C_4}$	(66)
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(40), (49)	$Y_5 = (Y_1/\alpha_5) \cdot T_{C_5}$	(67)
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(b) Equations (52) through (61) constitute a system of equations which is independent of the remaining equations.

(c) For a given, fixed value of γ , (52) through (54) can be solved independently of the remaining equations.

The observations (a), (b), and (c) which serves as guidelines for the general approach to the solution of the chemical equilibrium equations, will be considered next.

Iterative Solution of the Chemical Equilibrium Equations--

The complexity of the system (52) through (67) and the presence of a transcendental equation precludes any closed-form solution procedure and necessitates the use of an iterative procedure. A Newton-Raphson technique was chosen as the basis of the solution algorithm for the following reasons: (1) The criteria for convergence of the scheme are not severely limiting (Householder, 1953); (2) It converges with high order, i.e. with few iterations for good initial estimates of the unknowns; (3) The partial derivatives required for the Newton-Raphson approach can be used both to provide estimates of the unknowns for successive solution steps and to calculate quantities needed to solve the transport equations.

The Newton-Raphson scheme for solving a single equation or a system of simultaneous equations can be found in Householder (1953). However, a brief description of the procedure for obtaining an approximation to a root, X^* , of the equation:

$$f(X) = 0$$

will serve as an introduction to the procedure used to solve the system of equilibrium equations.

The Newton-Raphson procedure yields the root X^* as the limit of a sequence of approximations $X^{(i)}$ to X^* . Each approximation, $X^{(i)}$, is obtained in terms of the previous approximation, $X^{(i-1)}$, according to:

$$X^{(i)} = X^{(i-1)} + dX^{(i-1)},$$

where:

$$dX^{(i-1)} = -f(X^{(i-1)})/f'(X^{(i-1)}).$$

The first approximation, X^0 , is an initial estimate of X^* . The approximation, $X^{(i)}$, can be interpreted geometrically as the X-coordinate of the point where the tangent line to the graph of $(X, f(X))$ at the point, $(X^{(i-1)}, f(X^{(i-1)}))$, intersects the X-axis.

Since there are many equations in the chemical equilibrium system, the approach to solving that system is not quite as straightforward. It was

pointed out in the previous section that all of the equations in the system (52) through (67) except (54) and (61) define other variables in terms of C_1 and γ . By making appropriate substitutions into (54) and (61), two equations which contain only the unknowns C_1 and γ would result. Since this would constitute a system of two equations in two unknowns, that system could be resolved to obtain roots, C_1^{**} and γ^* , assuming a solution exists.

Moreover, if equation (54), after appropriate substitutions, could be solved for C_1 in terms of γ , then additional substitutions could be made to reduce (61) to an equation in the single variable γ . This can be done since equations (52) through (54) constitute an independent system for a given value of γ (see observation (3) of 5.d). The solution procedure can be described as follows. Initial estimates, C_1^{00} and γ^0 , are made for C_1^{00} and γ^0 from equations (52) and (53). These values are then substituted into (54) to yield an expression of the form:

$$F_3^{00} = Y_1(C_1^{00}, \gamma^0) \cdot \{\alpha_2 + T_{C_2}(C_1^{00}, \gamma^0) + T_{C_3}(C_1^{00}, \gamma^0) + T_{C_4}(C_1^{00}, \gamma^0) + T_{C_5}(C_1^{00}, \gamma^0)\} - \text{CEC}.$$

From Table 67 it can be seen that if $F_3^{00} = 0$, then the equations (52) through (54) are all satisfied. If $F_3^{00} \neq 0$, a new estimate of C_1 , C_1^{10} , is made according to:

$$C_1^{10} = C_1^{00} + dC_1^{00} \quad (68)$$

where:

$$dC_1^{00} = -F_3^{00} / (\partial F_3 / \partial C_1) \gamma^{00}.$$

The superscripts indicate evaluation in terms of C_1^{00} and γ^0 . The subscript, γ , indicates that γ is held constant for the differentiation of F_3 with respect to C_1 . This process is continued until $F_3^{j0} \approx 0$ for some j . The value of C_1^{j0} is taken as the desired approximation to the root $C_1^{*0} = C_1(\gamma^0)$. The accuracy of the approximation is controlled by an appropriate convergence criterion.

Assuming the error of approximation is negligible, we have at this point values $A_1^{*0} = A_1(C_1^{*0}, \gamma^0)$, $Y_1^{*0} = Y_1(C_1^{*0}, \gamma^0)$, and $C_1^{*0} = C_1(\gamma^0)$. The quantities C_2^0 , C_3^0 , C_4^0 , and C_5^0 are then evaluated from equations (54) through (58) and substituted along with A_{2T} , A_{3T} , C_1^{*0} , and A_1^{*0} into (61) to yield an expression of the form:

$$F_4^0 - \gamma^0 - \text{EXP}\{-1.17 \cdot U^0 / (1+U^0)\},$$

where $U^0 = [2 \cdot (C_1^{*0} + C_2^0 + A_1^{*0}) + 0.5 \cdot (C_3^0 + C_4^0 + C_5^0 + A_{2T} + A_{3T})]^{1/2}$

Again, it is apparent that if $F_4^0 = 0$, then the entire system of equations (55) through (67) is satisfied. If $F_4^0 \neq 0$, a new estimate of γ , γ^1 , is made according to:

$$\gamma^1 = \gamma^0 + d\gamma^0, \quad (69)$$

where:

$$d\gamma^0 = -F_4^0 / (\partial F_4 / \partial \gamma)^0.$$

A new estimate of C_1 is provided according to:

$$C_1^{*1} = C_1^{*0} + (\partial C_1 / \partial \gamma)^0 \cdot d\gamma^0, \quad (70)$$

where

$$(\partial C_1 / \partial \gamma)^0 = (\partial F_3 / \partial \gamma)^0_{C_1} / (\partial F_3 / \partial C_1)^0_{\gamma}.$$

The entire process is repeated until $F_4^i \approx 0$ for some i . The meaning and use of the notation will be further clarified below, but for the present, the procedure can be seen to consist of two Newton-Raphson algorithms, one nested within the other. The inside algorithm provides C_1 in terms of a current value of γ , while convergence in the outside iteration loop amounts to solving the entire system of equations.

The step-wise procedure followed to obtain a solution of the equilibrium equations is listed below. For the sake of brevity, the superscripts i , j , etc. are dropped.

(1) Provide initial estimates of C_1 and γ .

(2) Evaluate A_1 from (52). Note that solving for A_1 is equivalent to satisfying the equation:

$$F_1 = 0,$$

where $F_1 = AAA \cdot A_1^2 + BBB \cdot A_1 + CCC$.

(3) Calculate $(\partial A_1 / \partial C_1)_{\gamma}$ according to:

$$(\partial A_1 / \partial C_1)_{\gamma} = -(\partial F_1 / \partial C_1)_{A_1, \gamma} / (\partial F_1 / \partial A_1)_{C_1, \gamma}$$

In order to illustrate the use of notation, this step is carried out in more detail. Differentiating equation (52), we have:

$$\left(\frac{\partial AAA}{\partial C_1}\right)_{A_1} = \gamma^8 \cdot D_{11} \cdot \gamma^8 (D_{21} - D_{11}/E_{12}) ,$$

$$\begin{aligned} \left(\frac{\partial BBB}{\partial C_1}\right)_{A_1, \gamma} &= (1 + D_{11} \cdot C_1 \cdot \gamma^8) \cdot \{-C_{1T}/(E_{12} \cdot C_1^2)\} \\ &+ D_{11} \cdot \gamma^8 \cdot \{1 + C_{1T}/(E_{12} \cdot C_1) - D_{11}/E_{12}\} \end{aligned}$$

and

$$\left(\frac{\partial CCC}{\partial C_1}\right)_{A_1, \gamma} = A_{1T} \cdot C_{1T}/(E_{12} \cdot C_1^2) .$$

Note that $\left(\frac{\partial AAA}{\partial A_1}\right)_{C_1, \gamma} = \left(\frac{\partial BBB}{\partial A_1}\right)_{C_1, \gamma} = \left(\frac{\partial CCC}{\partial A_1}\right)_{C_1, \gamma} = 0$.

Finally, we have:

$$\left(\frac{\partial F_1}{\partial C_1}\right)_{A_1, \gamma} = A_1^2 \cdot \left(\frac{\partial AAA}{\partial C_1}\right)_{A_1, \gamma} + A_1 \cdot \left(\frac{\partial BBB}{\partial C_1}\right)_{A_1, \gamma} + \left(\frac{\partial CCC}{\partial C_1}\right)_{A_1, \gamma} ,$$

and:

$$\left(\frac{\partial F_1}{\partial A_1}\right)_{C_1, \gamma} = 2 \cdot AAA \cdot A_1 + BBB .$$

Since $F_1 = 0$ from the previous step, we have:

$$\left(\frac{\partial F_1}{\partial C_1}\right)_{\gamma} = \left(\frac{\partial F_1}{\partial C_1}\right)_{A_1, \gamma} + \left(\frac{\partial F_1}{\partial A_1}\right)_{C_1, \gamma} \cdot \left(\frac{\partial A_1}{\partial C_1}\right)_{\gamma} = 0 ,$$

or:

$$\left(\frac{\partial A_1}{\partial C_1}\right)_{\gamma} = - \left(\frac{\partial F_1}{\partial C_1}\right)_{A_1, \gamma} / \left(\frac{\partial F_1}{\partial A_1}\right)_{C_1, \gamma} .$$

(4) Evaluate Y_1 in terms of A_1 , C_1 , and γ from (53).

(5) Calculate $\left(\frac{\partial Y_1}{\partial C_1}\right)_{\gamma}$ according to:

$$\left(\frac{\partial Y_1}{\partial C_1}\right)_{\gamma} = \left(\frac{\partial Y_1}{\partial C_1}\right)_{A_1, \gamma} + \left(\frac{\partial Y_1}{\partial A_1}\right)_{C_1, \gamma} \cdot \left(\frac{\partial A_1}{\partial C_1}\right)_{\gamma} .$$

(6) Evaluate T_{C_2} , T_{C_3} , T_{C_4} , and T_{C_5} from equation (54).

(7) Obtain the derivatives $(\frac{\partial T_{C_2}}{\partial C_1})_\gamma$, $(\frac{\partial T_{C_3}}{\partial C_1})_\gamma$, $(\frac{\partial T_{C_4}}{\partial C_1})_\gamma$, and $(\frac{\partial T_{C_5}}{\partial C_1})_\gamma$.

For example, $(\frac{\partial T_{C_2}}{\partial C_1})_\gamma$ is calculated as:

$$(\frac{\partial T_{C_2}}{\partial C_1})_\gamma = (\frac{\partial T_{C_2}}{\partial C_1})_{A_1, Y_1, \gamma} + (\frac{\partial T_{C_2}}{\partial A_1})_{C_1, Y_1, \gamma} \cdot (\frac{\partial A_1}{\partial C_1})_\gamma + (\frac{\partial T_{C_2}}{\partial Y_1})_{C_1, A_1, \gamma} \cdot (\frac{\partial Y_1}{\partial C_1})_\gamma .$$

(8) Evaluate the function, F_3 .

(9) Calculate the derivative $(\frac{\partial F_3}{\partial C_1})_\gamma$, according to:

$$(\frac{\partial F_3}{\partial C_1})_\gamma = (\frac{\partial Y_1}{\partial C_1})_\gamma \cdot (T_{C_2} + T_{C_3} + T_{C_4} + T_{C_5} + \alpha_1) + Y_1 \cdot \{ (\frac{\partial T_{C_2}}{\partial C_1})_\gamma + (\frac{\partial T_{C_3}}{\partial C_1})_\gamma + (\frac{\partial T_{C_4}}{\partial C_1})_\gamma + (\frac{\partial T_{C_5}}{\partial C_1})_\gamma \} .$$

(10) Evaluate dC_1 as in equation (68).

(11) Calculate the term:

$$T = Y_1 \cdot \{ |T_{C_2}| + |T_{C_3}| + |T_{C_4}| + |T_{C_5}| + \alpha_1 \} + CEC .$$

If $|dC_1|/T$ is sufficiently small, proceed to step (12). Otherwise, make a new estimate for C_1 as in equation (68) and return to step (2).

(12) Calculate $\frac{\partial C_1}{\partial \gamma}$. Since at this point $F_3 = 0$, we have:

$$\frac{\partial F_3}{\partial \gamma} = (\frac{\partial F_3}{\partial C_1}) \cdot (\frac{\partial C_1}{\partial \gamma}) + (\frac{\partial F_3}{\partial \gamma})_{C_1} = 0 ,$$

and therefore:

$$\frac{\partial C_1}{\partial \gamma} = -(\frac{\partial F_3}{\partial \gamma})_{C_1} / (\frac{\partial F_3}{\partial C_1}) .$$

(13) Using the chain rule, obtain $\frac{\partial A_1}{\partial \gamma}$ according to:

$$\frac{\partial A_1}{\partial \gamma} = \left(\frac{\partial A_1}{\partial \gamma}\right)_{C_1} + \left(\frac{\partial A_1}{\partial C_1}\right)_{\gamma} \cdot \left(\frac{\partial C_1}{\partial \gamma}\right) .$$

(14) In a similar fashion, calculate the derivatives $\frac{\partial Y_1}{\partial \gamma}$, $\frac{\partial T_{C_2}}{\partial \gamma}$, $\frac{\partial T_{C_3}}{\partial \gamma}$,

$$\frac{\partial T_{C_4}}{\partial \gamma}, \text{ and } \frac{\partial T_{C_5}}{\partial \gamma} .$$

(15) Evaluate C_2 , C_3 , C_4 , and C_5 from equations (55) through (58).

(16) Calculate $\frac{\partial C_2}{\partial \gamma}$, $\frac{\partial C_3}{\partial \gamma}$, $\frac{\partial C_4}{\partial \gamma}$, and $\frac{\partial C_5}{\partial \gamma}$.

(17) Evaluate the function F_4 .

(18) Calculate $\frac{\partial F_4}{\partial \gamma}$.

(19) Calculate $d\gamma$ as in equation (69), and check for convergence.

(20) If $|d\gamma|$ is too large, obtain new estimates for γ and C_1 as in equations (68) and (70).

Initial Estimates for C_1 and γ --

It was previously indicated that all of the variables in equations (51) through (67), which correspond to solution or adsorbed phase concentrations, can be evaluated in terms of C_1 and γ for given values of the total concentrations, cation exchange capacity, water content, bulk density, and the exchange and dissociation constants. It was further indicated that initial estimates, C_1^{00} and γ^0 , are required for the iterative solution technique presented in the previous section. Certain guidelines, which were followed for the selection of these initial estimates, are given below. Two cases are presented:

The first case corresponds to a "rough guess" estimate for C_1^{00} and γ^0 . Since a physically meaningful solution of the system, (51) through (67), is such that:

$$0 \leq C_1 \leq C_{1T} ,$$

the initial estimate, C_1^{00} , should satisfy:

$$0 \leq C_1^{00} \leq C_{1T} ,$$

It can be seen from equation (61) that γ always satisfies the dual inequality.

$$\exp(-1.17) = 0.310 < \gamma \leq 1.0 .$$

Consequently, an initial estimate, γ^0 , should also satisfy this inequality.

In the second case it is assumed that the system (51) through (67) has already been solved in terms of $C_{1T}, C_{2T}, \dots, C_{5T}, A_{1T}, A_{2T}, A_{3T}$, and θ . Another solution of the system is desired in terms of $C_{1T} + \Delta C_{1T}, C_{2T} + \Delta C_{2T}, \dots, C_{5T} + \Delta C_{5T}, A_{1T} + \Delta A_{1T}, A_{2T} + \Delta A_{2T}, A_{3T} + \Delta A_{3T}$, and $\theta + \Delta\theta$ where $\Delta C_{1T}, \Delta C_{2T}$, etc., are small changes of the total concentrations and water content from their original values. If:

$$C_1^{(old)} = C_1(C_{1T}, C_{2T}, \dots, C_{5T}, A_{1T}, A_{2T}, A_{3T}, \theta) ,$$

and

$$\gamma^{(old)} = \gamma(C_{1T}, C_{2T}, \dots, C_{5T}, A_{1T}, A_{2T}, A_{3T}, \theta) ,$$

are the values of C_1 and γ which satisfy the system (51) through (67) for the original values of the total concentrations and water content, and:

$$C_1^{(new)} = C_1(C_{1T} + \Delta C_{1T}, C_{2T} + \Delta C_{2T}, \dots, \theta + \Delta\theta)$$

and

$$\gamma^{(new)} = \gamma(C_{1T} + \Delta C_{1T}, C_{2T} + \Delta C_{2T}, \dots, \theta + \Delta\theta)$$

are the corresponding quantities for the final values, then Taylor's approximations yield:

$$\begin{aligned} \Delta C_1 = C_1^{(new)} - C_1^{(old)} &\approx \sum_{j=1}^5 \left(\frac{\partial C_1}{\partial C_{jT}} \right)^{(old)} \cdot \Delta C_{jT} + \sum_{j=1}^3 \left(\frac{\partial C_1}{\partial A_{jT}} \right)^{(old)} \\ &\quad \cdot \Delta A_{jT} + \left(\frac{\partial C_1}{\partial \theta} \right)^{(old)} \cdot \Delta \theta \end{aligned} \quad (71)$$

and

$$\Delta \gamma = \gamma^{(new)} - \gamma^{(old)} \approx \sum_{j=1}^5 \left(\frac{\partial \gamma}{\partial C_{jT}} \right)^{(old)} \cdot \Delta C_{jT} + \sum_{j=1}^3 \left(\frac{\partial \gamma}{\partial A_{jT}} \right)^{(old)}$$

$$\cdot \Delta A_{jT} + \left(\frac{\partial \gamma}{\partial \theta}\right)^{(old)} \cdot \Delta \theta . \quad (72)$$

Therefore, for small changes, ΔC_{iT} , etc., good initial estimates for $C_1^{(new)}$ and $\gamma^{(new)}$ are:

$$C_1^0 = C_1^{(old)} + \Delta C_1,$$

and

$$\gamma^0 = \gamma^{(old)} + \Delta \gamma$$

Initial estimates of this type are particularly useful when the total concentrations and/or water content are time-dependent with rates of change slow enough so that equilibrium between the various ion phases can be assumed. A particular application is given at a later point in the discussion. The step-wise procedure which was followed to obtain the derivatives of C_1 and γ with respect to C_{jT} , for $j = 1, 2, \dots, 5$, is as follows:

(1) Calculate $\left(\frac{\partial F_1}{\partial C_{jT}}\right)_{A_1, C_1, \gamma}$. Note: The notation used here is similar to that used in the previous section. The only difference is that the total concentrations and water content are now considered to be independent variables in the system. However, the symbols for total concentrations $C_{2T}, C_{3T}, C_{4T}, C_{5T}, A_{1T}, A_{2T}, A_{3T}$ and for the water content, θ , are omitted from the list of subscripts. One or more of the symbols y_1, A_1, C_1 , and γ are included in a subscript when the indicated differentiation is to be carried out holding the listed variables constant. By using the definition of F_1 from above and the definitions of AAA, BBB, and CCC from equation (52) we have:

$$\left(\frac{\partial F_1}{\partial C_{1T}}\right)_{A_1, C_1, \gamma} = \frac{1}{E_{12} \cdot C_1} \cdot \{A_1 (1 + D_{11} \cdot \gamma^8 \cdot C_1) - A_{1T}\} .$$

(2) Calculate $\left(\frac{\partial A_1}{\partial C_{jT}}\right)_{C_1, \gamma}$. Using the fact that $F_1 = 0$ for values of A_1 which satisfy equation (52), we have:

$$0 = \left(\frac{\partial F_1}{\partial C_{jT}}\right)_{C_1, \gamma} = \left(\frac{\partial F_1}{\partial C_{jT}}\right)_{A_1, C_1, \gamma} + \left(\frac{\partial F_1}{\partial A_1}\right)_{C_1, \gamma} \cdot \left(\frac{\partial A_1}{\partial C_{jT}}\right)_{C_1} .$$

Rearranging the above equation yields:

$$\left(\frac{\partial A_1}{\partial C_{jT}}\right)_{C_1, \gamma} = -\left(\frac{\partial F_1}{\partial C_{jT}}\right)_{A_1, C_1, \gamma} / \left(\frac{\partial F_1}{\partial A_1}\right)_{C_1, \gamma} .$$

The quantity $\left(\frac{\partial F_1}{\partial A_1}\right)_{C_1, \gamma}$ is calculated during the iterative solution procedure for equations (51) through (67). If this value is stored during the iterative solution process it need not be recalculated to evaluate $\left(\frac{\partial A_1}{\partial C_{jT}}\right)_{C_1, \gamma}$. This is also true of all derivatives with respect to A_1 , Y_1 , C_1 and γ which appear below.

(3) Calculate $\left(\frac{\partial Y_1}{\partial C_{jT}}\right)_{A_1, C_1, \gamma}$.

(4) Evaluate $\left(\frac{\partial Y_1}{\partial C_{jT}}\right)_{C_1, \gamma}$ according to:

$$\left(\frac{\partial Y_1}{\partial C_{jT}}\right)_{C_1, \gamma} = \left(\frac{\partial Y_1}{\partial C_{jT}}\right)_{A_1, C_1, \gamma} + \left(\frac{\partial Y_1}{\partial A_1}\right)_{C_1, \gamma} \cdot \left(\frac{\partial A_1}{\partial C_{jT}}\right)_{C_1, \gamma} .$$

(5) Calculate $\left(\frac{\partial T_{C2}}{\partial C_{jT}}\right)_{A_1, Y_1, C_1, \gamma}$, $\left(\frac{\partial T_{C3}}{\partial C_{jT}}\right)_{A_1, Y_1, C_1, \gamma}$,

$$\left(\frac{\partial T_{C4}}{\partial C_{jT}}\right)_{A_1, Y_1, C_1, \gamma}, \quad \left(\frac{\partial T_{C5}}{\partial C_{jT}}\right)_{A_1, Y_1, C_1, \gamma} .$$

(6) Calculate $\left(\frac{\partial T_{C2}}{\partial C_{jT}}\right)_{C_1, \gamma}$, $\left(\frac{\partial T_{C3}}{\partial C_{jT}}\right)_{C_1, \gamma}$, $\left(\frac{\partial T_{C4}}{\partial C_{jT}}\right)_{C_1, \gamma}$, and $\left(\frac{\partial T_{C5}}{\partial C_{jT}}\right)_{C_1, \gamma}$.

For example, the expression for $\left(\frac{\partial T_{C2}}{\partial C_{jT}}\right)_{C_1, \gamma}$ is:

$$\left(\frac{\partial T_{C2}}{\partial C_{jT}}\right)_{C_1, \gamma} = \left(\frac{\partial T_{C2}}{\partial A_1}\right)_{Y_1, C_1, \gamma} \cdot \left(\frac{\partial A_1}{\partial C_{jT}}\right)_{C_1, \gamma} + \left(\frac{\partial T_{C2}}{\partial Y_1}\right)_{A_1, C_1, \gamma} \cdot \left(\frac{\partial Y_1}{\partial C_{jT}}\right)_{C_1, \gamma} .$$

(7) Calculate $\left(\frac{\partial F_3}{\partial C_{jT}}\right)_{C_1, \gamma}$ according to:

$$\begin{aligned} \left(\frac{\partial F_3}{\partial C_{jT}}\right)_{C_1, \gamma} = & Y_1 \cdot \left\{ \left(\frac{\partial T_{C2}}{\partial C_{jT}}\right)_{C_1, \gamma} + \left(\frac{\partial T_{C3}}{\partial C_{jT}}\right)_{C_1, \gamma} + \left(\frac{\partial T_{C4}}{\partial C_{jT}}\right)_{C_1, \gamma} + \left(\frac{\partial T_{C5}}{\partial C_{jT}}\right)_{C_1, \gamma} \right\} \\ & + \left(\frac{\partial Y_1}{\partial C_{jT}}\right)_{C_1, \gamma} \cdot \{ \alpha_1 + T_{C2} + T_{C3} + T_{C4} + T_{C5} \} . \end{aligned}$$

(8) Calculate $\left(\frac{\partial C_1}{\partial C_{jT}}\right)_{\gamma}$, using the expression:

$$\left(\frac{\partial C_1}{\partial C_{jT}}\right)_{\gamma} = - \left(\frac{\partial F_3}{\partial C_{jT}}\right)_{C_1, \gamma} / \left(\frac{\partial F_3}{\partial C_1}\right)_{\gamma} .$$

(9) Using the quantities $\left(\frac{\partial A_1}{\partial C_1}\right)_{\gamma}$, $\left(\frac{\partial Y_1}{\partial C_1}\right)_{\gamma}$, $\left(\frac{\partial T_{C2}}{\partial C_1}\right)_{\gamma}$, $\left(\frac{\partial T_{C3}}{\partial C_1}\right)_{\gamma}$, $\left(\frac{\partial T_{C4}}{\partial C_1}\right)_{\gamma}$

and $\left(\frac{\partial T_{C5}}{\partial C_1}\right)_{\gamma}$ from the iterative solution procedure calculate

$$\left(\frac{\partial A_1}{\partial C_{jT}}\right)_{\gamma}, \left(\frac{\partial Y_1}{\partial C_{jT}}\right)_{\gamma}, \left(\frac{\partial T_{C2}}{\partial C_{jT}}\right)_{\gamma}, \left(\frac{\partial T_{C3}}{\partial C_{jT}}\right)_{\gamma}, \left(\frac{\partial T_{C4}}{\partial C_{jT}}\right)_{\gamma}, \text{ and } \left(\frac{\partial T_{C5}}{\partial C_{jT}}\right)_{\gamma} .$$

For example:

$$\left(\frac{\partial A_1}{\partial C_{jT}}\right)_{\gamma} = \left(\frac{\partial A_1}{\partial C_{jT}}\right)_{\gamma, C_1} + \left(\frac{\partial A_1}{\partial C_1}\right)_{\gamma} \cdot \left(\frac{\partial C_1}{\partial C_{jT}}\right)_{\gamma} .$$

(10) Calculate $(\frac{\partial C_2}{\partial C_{jT}})_\gamma$, $(\frac{\partial C_3}{\partial C_{jT}})_\gamma$, $(\frac{\partial C_4}{\partial C_{jT}})_\gamma$, and $(\frac{\partial C_5}{\partial C_{jT}})_\gamma$. For example,

from equation (55) we have:

$$C_2 = (\frac{E_{12}}{\alpha_2}) \cdot C_1 \cdot T_{C2}.$$

Differentiating with respect to C_{jT} yields:

$$(\frac{\partial C_2}{\partial C_{jT}})_\gamma = (\frac{E_{12}}{\alpha_2}) \cdot \{C_1 \cdot (\frac{\partial T_{C2}}{\partial C_{jT}})_\gamma + T_{C2} \cdot (\frac{\partial C_1}{\partial C_{jT}})_\gamma\}.$$

(11) Evaluate $(\frac{\partial A_2}{\partial C_{jT}})_\gamma$ and $(\frac{\partial A_3}{\partial C_{jT}})_\gamma$. By virtue of equations (59) and (60) we have:

$$(\frac{\partial A_2}{\partial C_{jT}})_\gamma = 0$$

and

$$(\frac{\partial A_3}{\partial C_{jT}})_\gamma = 0.$$

Moreover, $(\frac{\partial A_2}{\partial A_{3T}})_\gamma = 0$, for $j \neq 2$, $(\frac{\partial A_3}{\partial A_{jT}})_\gamma = 0$, for $j \neq 3$, $(\frac{\partial A_2}{\partial A_{2T}})_\gamma = 1$ and

$$(\frac{\partial A_3}{\partial A_{3T}})_\gamma = 1.$$

(12) Calculate $(\frac{\partial u}{\partial C_{jT}})$ according to:

$$(\frac{\partial u}{\partial C_{jT}}) = \frac{1}{2 \cdot u} \cdot \{2.0 [(\frac{\partial C_1}{\partial C_{jT}})_\gamma + (\frac{\partial C_2}{\partial C_{jT}})_\gamma + (\frac{\partial A_1}{\partial C_{jT}})_\gamma] + 0.5 \cdot [(\frac{\partial C_3}{\partial C_{jT}})_\gamma$$

$$+ \left(\frac{\partial C_4}{\partial C_{jT}} \right)_{\gamma} + \left(\frac{\partial C_5}{\partial C_{jT}} \right)_{\gamma} + \left(\frac{\partial A_2}{\partial C_{jT}} \right)_{\gamma} + \left(\frac{\partial A_3}{\partial C_{jT}} \right)_{\gamma}] \} .$$

(13) Calculate $\left(\frac{\partial F_4}{\partial C_{jT}} \right)_{\gamma}$ using the expression:

$$\left(\frac{\partial F_4}{\partial C_{jT}} \right)_{\gamma} = \left\{ \frac{-1.17}{(1+u)^2} \right\} \cdot \gamma \cdot \left(\frac{\partial u}{\partial C_{jT}} \right)_{\gamma} .$$

(14) Calculate $\frac{\partial \gamma}{\partial C_{jT}}$ according to:

$$\frac{\partial \gamma}{\partial C_{jT}} = - \left(\frac{\partial F_4}{\partial C_{jT}} \right) / \left(\frac{\partial F_4}{\partial \gamma} \right) .$$

(15) Calculate $\frac{\partial C_1}{\partial C_{jT}}$ by applying the chain rule:

$$\frac{\partial C_1}{\partial C_{jT}} = \left(\frac{\partial C_1}{\partial C_{jT}} \right)_{\gamma} + \left(\frac{\partial C_1}{\partial \gamma} \right) \cdot \left(\frac{\partial \gamma}{\partial C_{jT}} \right) .$$

For some values of j , not all of the calculations indicated above are required. For example, from equation (52), it can be seen that A_1 is not explicitly dependent on C_{3T} . Therefore, $\left(\frac{\partial A_1}{\partial C_{3T}} \right)_{C_1, \gamma} = 0$ so subsequent calculations involving $\left(\frac{\partial A_1}{\partial C_{3T}} \right)_{C_1, \gamma}$ as a multiplicative factor are not required and were not included in the operational form of the procedure. The above outline shows the general sequence which was followed to obtain derivatives of C_1 and γ with respect to total anion concentrations as well as with respect to total cation concentrations.

It will subsequently be shown that all derivatives of the form $\frac{\partial C_i}{\partial C_{jT}}$,

$\frac{\partial C_i}{\partial A_{jT}}$, $\frac{\partial A_i}{\partial C_{jT}}$, and $\frac{\partial A_i}{\partial A_{jT}}$ are required for another purpose. These can all be

obtained from quantities which result from the above procedure by straightforward application of the chain rule. For example:

$$\frac{\partial A_1}{\partial C_{jT}} = \left(\frac{\partial A_1}{\partial C_{jT}} \right)_{\gamma} + \left(\frac{\partial A_1}{\partial \gamma} \right) \cdot \frac{\partial \gamma}{\partial C_{jT}} .$$

Derivatives of the form $\frac{\partial C_i}{\partial \theta}$ and $\frac{\partial A_i}{\partial \theta}$ were obtained using the same general procedure.

The nested Newton-Raphson procedure for solving the system of chemical equilibrium equations was programmed in FORTRAN entitled SUBROUTINE EQUIL. A listing of the program is given in Appendix L and the FORTRAN names of quantities discussed in this section are given in Appendix M. A number of tests were made to insure that the calculations and programming had been performed correctly. Among the tests performed were:

(1) a test to indicate that the method used indeed provided solutions to the original system of equations (36) through (51),

(2) finite-difference approximations to the partial derivatives to indicate that the partial derivatives were calculated and programmed correctly, and

(3) counts of the number of iterations required for convergence for different values of the parameters in the equations. The results of the tests indicated under (2) are discussed in Appendix N.

A final note is that Frissel and Reiniger (1974) indicated that the Newton-Raphson scheme, as embodied in the simulation program, CSMP, failed to converge for a system of equations of the Gapon type when the percentage of adsorbed divalent cations was less than 50. No such difficulties have been encountered with the present approach. There are two requirements that certainly must be met for convergence with the scheme presented here. They are:

$$(1) C_{1T} > 0 .$$

and

$$(2) \sum_{i=1}^5 \alpha_i \cdot C_{iT} \geq \text{CEC} .$$

If $C_{1T} = 0$, the function F_3 cannot be defined. If condition (2) is not met, there are insufficient cations to satisfy the cation exchange capacity requirement and equation (54) cannot be satisfied.

Ion Transport Equations

The one-dimensional convection-diffusion equation (4) was derived earlier from mass-balance considerations for steady-flow conditions in a homogeneous, inert, saturated porous medium. Five cations and three anions have been selected for study. They were presented along with a system of related chemical equilibrium equations (36) through (51). In the present section a mass balance approach is used to derive a system of finite-difference equations which can be used in conjunction with appropriate boundary and initial conditions to characterize the concentrations of these eight ions as functions of depth and time in a soil profile. The second-order explicit scheme already presented will be extended to the multi-ion case for this purpose.

The second-order explicit scheme was previously shown to possess the important advantage of a second-order accurate approximation to the time derivative, $\frac{\partial C}{\partial t}$, which appears in equation (4). It will be shown subsequently that the second-order accuracy is retained when an extension of the scheme is made to a non-linear, multi-ion system. Extensions of the Crank-Nicolson scheme to non-linear systems have been made but require iteration across time steps (Carnahan, et al. 1969). Apparently, no extension of the Stone and Brian scheme has been made to multi-ion systems, although the original investigators indicated some use of the scheme for non-linear, single ion systems (Stone and Brian, 1963).

Physical Considerations--

The developments considered so far assumed that the primary mechanisms of transport of an ion are convection, diffusion, and hydrodynamic dispersion. Accordingly, a convective component of flux was defined as the product of the volumetric moisture flux, q , and the ion concentration, C . In addition, there was a diffusive flux component: $-D_a \cdot \frac{\partial C}{\partial z}$, where D_a was defined as the sum of the molecular diffusion coefficient, D_m , and the hydrodynamic dispersion coefficient, D_h . Because of the assumptions of homogeneity, saturation, and steady-flow, it was possible to treat the moisture flux, the water content, and the apparent diffusion coefficient as constant parameters. The non-interacting, inert nature of the system led to a linear partial differential equation for its characterization.

For the present case the assumptions of homogeneity, saturation and steady-flow are relaxed for greater generalization. Thus q and θ are allowed to vary with depth and time. Unlike the inert medium considered previously, the medium considered in this chapter is assumed to interact chemically with the ions in solution, so that two distinct ion phases, the adsorbed phase and solution phase, are included (indirectly) in the analysis. Of these two phases, only the solution phase is assumed to be mobile, so the primary mechanisms of transport are again convection, diffusion, and dispersion. The apparent diffusion coefficients are different for different ions due to differences in the molecular diffusion coefficients. Also, since the apparent diffusion coefficients are dependent on the moisture content, they are treated as time- and depth-dependent parameters. The admission of different diffusion coefficients for different ions could lead to artificially

large charge separations occurring in the system if the force which discourages such separations is ignored. Therefore, an additional component of flux is included in the analysis to simulate the effects of electric potential gradients on the total flux.

The Ion-flux Equations--

There were ten solution-phase concentrations discussed in the development of the chemical equilibrium equation. Different symbols were used for cations and anions due to fundamental differences in the mathematical treatment of these ions and their equilibrium relationships. For discussion of the transport processes and subsequent programming, it is expedient to standardize the symbolism to be used in this development. The correspondence between the symbols used previously and those to be used in the present development are shown in Table 69.

For ions 3, 4, . . . , 7 (Column 3 of Table 69), which have only one solution phase component, the equation which describes the convective component of flux, J_{Ci}^C , is similar to the corresponding equation (5):

$$J_{Ci}^C = q \cdot C_i, \quad i = 3, 4, \dots, 7. \quad (73)$$

However, the additional solution components X_{11} and X_{21} are associated with ions 1, 2, and 8. Thus the appropriate convective fluxes for these ions are given by the equations:

$$J_{C1}^C = q \cdot (C_1 + X_{11}), \quad (74)$$

$$J_{C2}^C = q \cdot (C_2 + X_{21}), \quad (75)$$

and

$$J_{C8}^C = q \cdot (C_8 + X_{11} + X_{21}). \quad (76)$$

The quantities in parentheses in equations (74), (75), and (76) are the total solution concentrations of ions 1, 2, and 8, respectively. Thus, as the soil solution moves, it transports not only the unpaired ions in solution, but also the ion pairs whose concentrations are X_{11} and X_{21} , for CaSO_4^0 and MgSO_4^0 , respectively.

The equations of diffusive flux for ions 3, 4, . . . , 7 are:

$$J_{Ci}^D = -D_{Ci} \cdot \frac{\partial C_i}{\partial Z}, \quad (77)$$

where D_{Ci} is the sum of the molecular diffusion coefficient for ion i and the hydrodynamic dispersion coefficient for the soil system. The equation used here to define D_{Ci} is based on a concept tested by Kirda et al. (1973) in a study of chloride transport under infiltration conditions. The defining equation can be written:

TABLE 69. CORRESPONDENCE BETWEEN SYMBOLS

Previous Use	Ion	Present Use
C_1	Ca^{++}	C_1
C_2	Mg^{++}	C_2
C_3	Na^+	C_3
C_4	K^+	C_4
C_5	NH_4^+	C_5
A_2	Cl^-	C_6
A_3	HCO_3^-	C_7
A_1	$SO_4^{=}$	C_8
X_{11}	$Ca\ SO_4^0$	X_{11}
X_{21}	$Mg\ SO_4^0$	X_{21}

$$D_{Ci} = 0.6 \cdot \theta \cdot D_{mi} + \theta \cdot \lambda \cdot |v|^\zeta \quad (78)$$

where D_{mi} is the molecular diffusion coefficient of ion i in free solution, λ and ζ are parameters of the system, and $v = q/\theta$ is the mean pore velocity as a function of depth and time. The 0.6 is a tortuosity factor. For ions 1, 2, and 8, the contributions of X_{11} and X_{21} to the diffusive fluxes are included in the following equations:

$$J_{C1}^D = -D_{C1} \cdot \frac{\partial C_1}{\partial Z} - D_{X11} \cdot \frac{\partial X_{11}}{\partial Z}, \quad (79)$$

$$J_{C2}^D = -D_{C2} \cdot \frac{\partial C_2}{\partial Z} - D_{X21} \cdot \frac{\partial X_{21}}{\partial Z},$$

and

$$J_{C8}^D = -D_{C8} \cdot \frac{\partial C_8}{\partial Z} - D_{X11} \cdot \frac{\partial X_{11}}{\partial Z} - D_{X21} \cdot \frac{\partial X_{21}}{\partial Z}. \quad (80)$$

The influence of electric potential on the simultaneous flux of ions having different diffusion coefficients has been discussed by deWit and van Keulen (1972). According to their analysis, the flux of ion i due to an electric potential gradient can be defined in terms of weighted average of concentration gradients. The equation used to describe this component of flux is:

$$J_{Ci}^E = D_{Ci} \cdot v_i \cdot \xi \cdot C_i, \quad i = 1, 2, \dots, 8, \quad (81)$$

where

$$\xi = \left\{ \sum_{j=1}^8 v_j \cdot D_{Cj} \cdot \frac{\partial C_j}{\partial Z} \right\} / \left\{ \sum_{j=1}^8 v_j^2 \cdot D_{Cj} \cdot C_j \right\}.$$

Equations (73) through (81) describe the components of instantaneous flux for ions 1 through 8 as functions of depth, time, concentrations, and concentration gradients. It must be remembered that the depth and time dependencies are due to depth- and time-dependent parameters occurring in the equations. The total flux of the ions can therefore be represented by the equation:

$$J_{Ci}^T = J_{Ci}^C + J_{Ci}^D + J_{Ci}^E, \quad i = 1, 2, \dots, 8. \quad (82)$$

The Finite-difference Equations--

The problem for present consideration is similar in the following respects to the initial-boundary value problem considered earlier. In both cases it is desired to obtain predictions of concentration values in the

interior of a one-dimensional soil column or profile as a function of depth in the column and time elapsed from some starting time. This is to be accomplished with a knowledge of the concentration distribution(s) within the column at the starting time and a knowledge of the concentration(s) and/or fluxes at the boundaries of the column. The fundamental mathematical tools available for solution of the problem are the equations describing ion flux and a mathematical description of mass conservation.

Figure 111 illustrates the setting in which the ion transport equations are to be derived. A schematic design of a one-dimensional soil profile of depth L_c is presented and is divided into compartments of thickness Δz , except for the surface compartment which has thickness $\Delta z/2$. The symbols, C_{iT}^t , represent the total concentration of ion i at a depth $Z = (k-1) \cdot \Delta z$ and time t .

The mass density $\rho_i(Z,t)$ (moles/cm³ soil) of ion i at any time t and depth Z in the profile can be represented by:

$$\rho_i(Z,t) = C_{iT}(Z,t) \cdot \theta(Z,t) ,$$

where $C_{iT}(Z,t)$ and $\theta(Z,t)$ are the continuous total concentration and water content distributions, respectively, in the column. Therefore the total mass M_{iT}^t of ion i in the k^{th} compartment at time t is given by:

$$M_{iT}^t = A \cdot \Delta z \cdot (\overline{\theta C_{iT}}) ,$$

where A is the cross-sectional area of the column and:

$$\overline{\theta C_{iT}} = \frac{1}{A \cdot \Delta z} \cdot \int_{Z=(K-3/2)\Delta z}^{Z=(k-1/2)\Delta z} \theta(Z,t) \cdot C_{iT}(Z,t) \, dz$$

is the average density for the k^{th} compartment. Assuming that $\theta \cdot C_{iT}$ varies smoothly as a function of Z , and that Δz is sufficiently small, then to a close approximation:

$$M_{iT}^t \approx A \cdot \Delta z \cdot \theta_k^t \cdot C_{iT_k}^t .$$

Differentiating the above equation with respect to t yields the approximate instantaneous mass rate of change for the compartment at time t :

$$\left(\frac{\partial M_{iT}}{\partial t}\right)^t \approx A \cdot \Delta z \cdot \frac{(\theta_k \cdot C_{iT})^t}{\theta_t} .$$

The net flux of ion i into the k^{th} compartment at time t is:

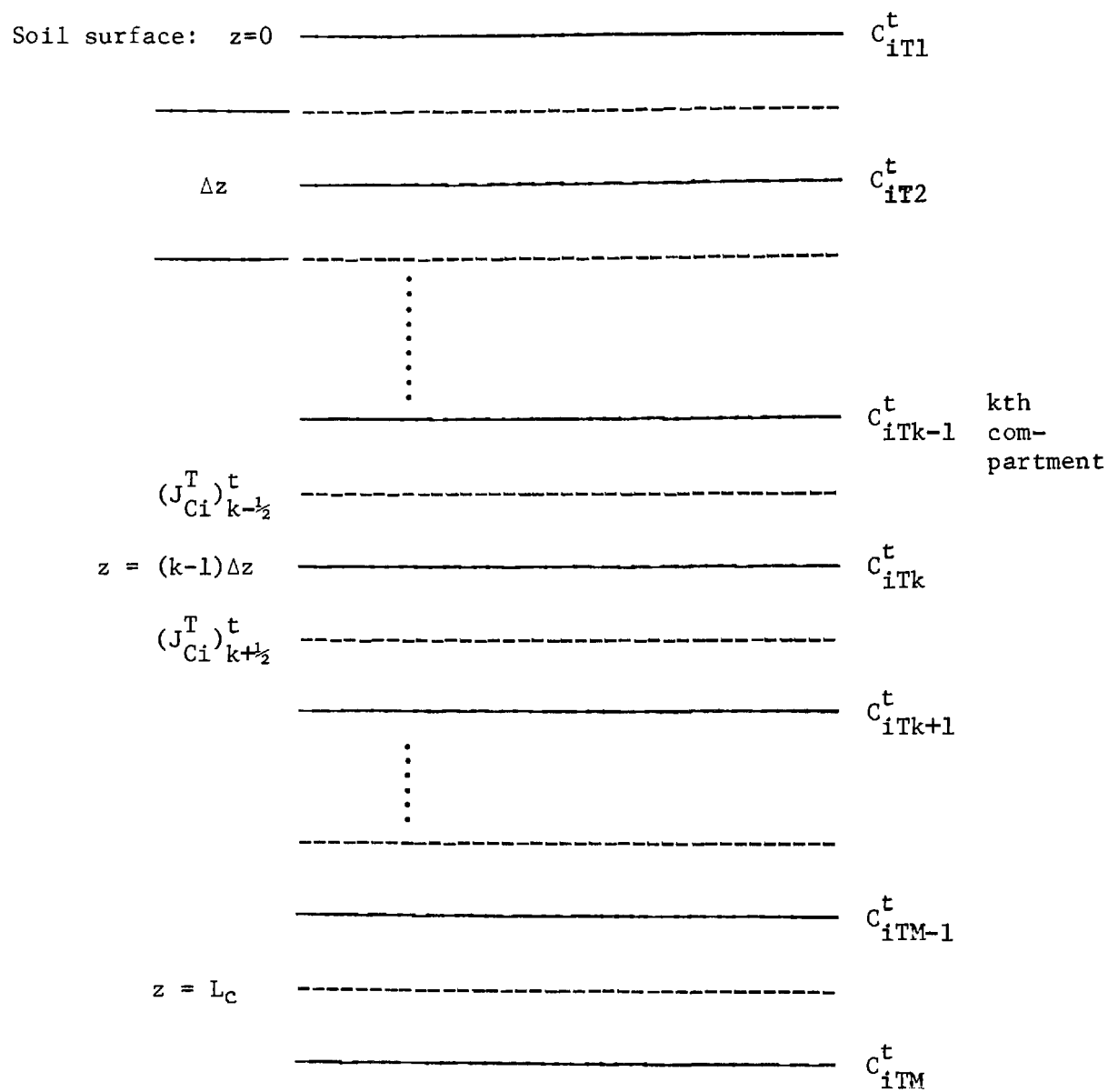


Figure 111. Schematic diagram of the finite difference grid.

$$(J_{Ci}^T)^t_{k-1/2} - (J_{Ci}^T)^t_{k+1/2},$$

where $(J_{Ci}^T)^t_{k-1/2}$ and $(J_{Ci}^T)^t_{k+1/2}$ represent the flux of ion i at the top and bottom of the compartment, respectively, as indicated in Figure 111. Since the rate of change of mass of ion i in the compartment at time t is equal to the net flux of ion i into the compartment multiplied by the compartment cross-sectioned area, we have:

$$A \cdot \Delta z \cdot \frac{(\theta_k \cdot C_{itk})^t}{\partial t} = A \cdot [(J_{Ci}^T)^t_{k-1/2} - (J_{Ci}^T)^t_{k+1/2}],$$

in the absence of sinks and sources. The above equation can be expressed in the equivalent form:

$$\left(\frac{\partial C_{itk}}{\partial t}\right)^t = G_{ik}^t, \quad (83a)$$

where:

$$G_{ik}^t = \frac{1}{\theta_k^t \cdot \Delta z} \cdot [(J_{Ci}^T)^t_{k-1/2} - (J_{Ci}^T)^t_{k+1/2}] - \frac{C_{iTk}^t}{\theta_k^t} \cdot \left(\frac{\partial \theta_k}{\partial t}\right)^t. \quad (83b)$$

As is indicated by equations (73) through (82), a precise evaluation of the total fluxes $(J_{Ci}^T)^t_{k-1/2}$ and $(J_{Ci}^T)^t_{k+1/2}$ would require knowledge of the concentrations, C_i , and of the partial derivatives, $\partial C_i / \partial z$, at time t and at the upper and lower boundaries of compartment k . For practical reasons it is desirable to approximate these quantities in terms of the concentrations, C_{ik}^t at the midpoints of the compartments. The following equations provide the desired approximations:

$$(J_{Ci}^T)^t_{k-1/2} = -D_{Ci \ k-1/2}^t \cdot \frac{C_{ik}^t - C_{ik-1}^t}{\Delta z} + q_{k-1/2}^t \cdot C_{i \ k-1/2}^t + D_{Ci \ k-1/2}^t \cdot V_i \cdot \xi_{k-1/2}^t$$

$$C_{i \ k-1/2}^t, \ i = 3, 4, \dots, 7, \quad (84)$$

$$(J_{C1}^T)^t_{k-1/2} = D_{C1 \ k-1/2}^t \cdot \frac{C_{1k}^t - C_{1 \ k-1}^t}{\Delta z} + q_{k-1/2}^t \cdot (C_{1 \ k-1/2}^t + X_{11 \ k-1/2}^t) -$$

$$D_{X11\ k-\frac{1}{2}}^t \cdot \frac{X_{11\ k}^t - X_{11\ k-1}^t}{\Delta z} + D_{C1k-\frac{1}{2}}^t \cdot v_1 \cdot \xi_{k-\frac{1}{2}}^t \cdot C_{1\ k-\frac{1}{2}}^t, \quad (85)$$

$$(J_{C_2\ k-\frac{1}{2}}^T = -D_{C2\ k-\frac{1}{2}}^t \cdot \frac{C_{2k}^t - C_{2k-1}^t}{\Delta z} + q_{k-\frac{1}{2}}^t \cdot (C_{2\ k-\frac{1}{2}}^t + X_{21\ k-\frac{1}{2}}^t) -$$

$$D_{X_{21}\ k-\frac{1}{2}}^t \cdot \frac{X_{21\ k}^t - X_{21\ k-1}^t}{\Delta z} + D_{C_2\ k-\frac{1}{2}}^t - v_2 \cdot \xi_{k-\frac{1}{2}}^t \cdot C_{2\ k-\frac{1}{2}}^t \quad (86)$$

and

$$(J_{C8\ k-\frac{1}{2}}^T = -D_{C8\ k-\frac{1}{2}}^t \cdot \frac{C_{8\ k}^t - C_{8\ k-1}^t}{\Delta z} + q_{k-\frac{1}{2}}^t \cdot (C_{8\ k-\frac{1}{2}}^t + X_{11\ k-\frac{1}{2}}^t + X_{21\ k-\frac{1}{2}}^t) \\ - D_{X11\ k-\frac{1}{2}}^t \cdot \frac{X_{11\ k}^t - X_{11\ k-1}^t}{\Delta z} - D_{X21\ k-\frac{1}{2}}^t \cdot \frac{X_{21\ k}^t - X_{21\ k-1}^t}{\Delta z} \\ + D_{C8\ k-\frac{1}{2}}^t \cdot v_8 \cdot \xi_{k-\frac{1}{2}}^t \cdot C_{8\ k-\frac{1}{2}}^t. \quad (87)$$

The terms on the right-hand sides of (84) - (87) which are subscripted with $k-\frac{1}{2}$ are evaluated as follows:

$$C_{ik-\frac{1}{2}}^t = \frac{C_{ik}^t + C_{ik-1}^t}{2} \quad (88)$$

$$\xi_{k-\frac{1}{2}}^t = \left[\sum_{j=1}^8 v_j \cdot D_{Cjk-\frac{1}{2}}^t \cdot (C_{jk}^t - C_{jk-1}^t) / \Delta z \right] / \left[\sum_{j=1}^8 v_j^2 \cdot D_{ckj-\frac{1}{2}}^t \cdot C_{jk-\frac{1}{2}}^t \right],$$

$$X_{11k-\frac{1}{2}}^t = D_{11} \cdot (\gamma_{k-\frac{1}{2}}^t)^8 \cdot C_{1k-\frac{1}{2}}^t \cdot C_{8k-\frac{1}{2}}^t,$$

$$\text{where } \gamma_{k-\frac{1}{2}}^t = \exp [-1.17 \cdot \mu_{k-\frac{1}{2}}^t / (1 + \mu_{k-\frac{1}{2}}^t)] \text{ and } \mu_{k-\frac{1}{2}}^t = \frac{1}{2} \sum_{j=1}^8 v_j^2 \cdot C_{jk-\frac{1}{2}}^t,$$

$$\text{and } X_{21k-\frac{1}{2}}^t = D_{21} \cdot (\gamma_{k-\frac{1}{2}}^t)^8 \cdot C_{2k-\frac{1}{2}}^t \cdot C_{8k-\frac{1}{2}}^t .$$

Finally, we have:

$$D_{Cik-\frac{1}{2}} = \left[\left(\frac{\theta_{k-1}^t + \theta_{k+1}^t}{2} \right) \cdot 0.6 \cdot D_{mi} + \lambda \right] \cdot \left[2 \cdot q_{k-\frac{1}{2}}^t / (\theta_{k-1}^t + \theta_k^t) \right]^{\zeta} \quad (89)$$

(5-20)

Equations (84) - (87) are spatial approximations where second-order Taylor's approximations have been utilized for partial derivatives of the form $\left(\frac{\partial C_{ik}}{\partial Z} \right)^t$

and for the concentrations $C_{ik-\frac{1}{2}}^t$. The equations defining $(J_{Ci}^T)_{k-\frac{1}{2}}^t$, which would correspond to (84) - (88) for $(J_{Ci}^T)_{k-\frac{1}{2}}^t$, need not be written down since they can be obtained by replacing k with $k+1$ in (84) - (88).

At this point, sufficient information has been provided to enable a rough approximation of the total concentrations at time $t + \Delta t$ using values of the total concentrations at time t . The sequence of operations that would be required to accomplish the approximation is: (1) Use the previously presented Newton-Raphson procedure to evaluate the solution concentrations C_{ik}^t in terms of C_{iTk}^t and θ_k^t for $i = 1, 2, \dots, 8$, and $k = 1, 2, \dots, M$.

(2) Use the resulting values of C_{ik}^t to evaluate the total fluxes at the compartment boundaries, $(J_{Ci}^T)_{k-\frac{1}{2}}^t$, for $k = 2, 3, \dots, M$. (3) Substitute the total fluxes into equation (83) to evaluate G_{iK}^t . (4) Substitute

$(C_{iTk}^{t+\Delta t} - C_{iTk}^t) / \Delta t$ for $(\partial C_{iTk} / \partial t)^t$ in equation (83a) and solve the resulting equation for $C_{iTk}^{t+\Delta t}$. However, as is the case for the explicit scheme, approximating $(\partial C_{iTk} / \partial t)^t$ with $(C_{iTk}^{t+\Delta t} - C_{iTk}^t) / \Delta t$ is only first-order correct. In order to achieve the desirable second-order accuracy demonstrated previously for the single-variable, linear equation, the derivative must be carried one step further. A Taylor's approximation to the time derivative, $\left(\frac{\partial C_{iTk}}{\partial t} \right)^t$ which appears on the left-hand side of equation (83), can be written:

$$\left(\frac{\partial C_{iTk}}{\partial t} \right)^t = \frac{C_{iTk}^{t+\Delta t} - C_{iTk}^t}{\Delta t} - \frac{\Delta t}{2} \cdot \left(\frac{\partial^2 C_{iTk}}{\partial t^2} \right)^t + O(\Delta t^2) .$$

Letting t_0 denote the time at the beginning of a time step, $t_0 \leq t \leq t_0 + \Delta t$, and substituting $G_{iK}^{t_0}$ for $(\partial C_{iTk} / \partial t)^{t_0}$ from equation (83a), we have to a close approximation:

$$C_{iTk}^{t_0+\Delta t/2} = C_{iTk}^{t_0} + \Delta t \cdot \left[G_{iK}^{t_0} + \frac{\Delta t}{2} \cdot \left(\frac{\partial G_{iK}}{\partial t} \right)^{t_0} \right] . \quad (90)$$

The term in brackets in equation (90) is an approximation to the value of G_{ik}^t for $t = t_0 + \Delta t/2$, i. e.:

$$G_{ik}^{t_0+\Delta t/2} \approx G_{ik}^{t_0} + \frac{\Delta t}{2} \cdot \left(\frac{\partial G_{ik}}{\partial t}\right)^{t_0}. \quad (91)$$

Two approaches may be taken to evaluate $G_{ik}^{t_0+\Delta t/2}$: (1) Evaluate $(\partial G_{ik}/\partial t)^{t_0}$ and $G_{ik}^{t_0}$ and substitute directly into the above expression or (2) Define an auxiliary function, G_{ik}^t , such that $G_{ik}^{t_0+\Delta t/2} = G_{ik}^{t_0+\Delta t/2}$ and use the auxiliary function to approximate $G_{ik}^{t_0+\Delta t/2}$. The second alternative may appear unwarranted, but the reasons for suggesting such an approach will subsequently be discussed. Attention is not directed toward obtaining an expression for $(\partial G_{ik}/\partial t)^{t_0}$, to be used in the first approach.

From equations (83b) through (89), it can be seen that G_{ik} is dependent on the following time-dependent variables: C_{iTk} ; C_{jk} , C_{jk-1} , and C_{jk+1} , for $j = 1, 2, \dots, 8$; θ_k , θ_{k-1} , θ_{k+1} ; $q_{k-1/2}$; and $q_{k+1/2}$; and $\partial \theta_k / \partial t$. However, there is a hidden dependence of G_{ik} on θ_k , θ_{k-1} , and θ_{k+1} due to the dependence of the solution concentrations on θ in the chemical equilibrium equations (51) through (67). Consideration of the above time-dependencies results in the following expression for $\left(\frac{\partial G_{ik}}{\partial t}\right)^{t_0}$:

$$\begin{aligned} \left(\frac{\partial G_{ik}}{\partial t}\right)^{t_0} = & \left(\frac{\partial G_{ik}}{\partial C_{iTk}}\right)^{t_0} \cdot \left(\frac{\partial C_{iTk}}{\partial t}\right)^{t_0} + \sum_{l=k-1}^{k+1} \left(\frac{\partial G_{ik}}{\partial C_{il}}\right)^{t_0} \cdot \left(\frac{\partial C_{il}}{\partial t}\right)^{t_0} + \\ & \left(\frac{\partial G_{ik}}{\partial q_{k-1/2}}\right)^{t_0} \cdot \left(\frac{\partial q_{k-1/2}}{\partial t}\right)^{t_0} + \left(\frac{\partial G_{ik}}{\partial q_{k+1/2}}\right)^{t_0} \cdot \left(\frac{\partial q_{k+1/2}}{\partial t}\right)^{t_0} + \left(\frac{\partial G_{ik}}{\partial (\partial \theta_k / \partial t)}\right)^{t_0} \cdot \\ & \left(\frac{\partial^2 \theta_k}{\partial t^2}\right)^{t_0} + \sum_{l=k-1}^{k+1} \sum_{j=1}^8 \left(\frac{\partial G_{ik}}{\partial C_{jl}}\right)^{t_0} \cdot \left\{ \sum_{n=1}^8 \left(\frac{\partial C_{jl}}{\partial C_{nTl}}\right)^{t_0} \cdot \left(\frac{\partial C_{nTl}}{\partial t}\right)^{t_0} + \left(\frac{\partial C_{jl}}{\partial \theta_l}\right)^{t_0} \cdot \right. \\ & \left. \left(\frac{\partial \theta_l}{\partial t}\right)^{t_0} \right\}. \quad (92) \end{aligned}$$

In equation (92) all derivatives of the general form, $\partial G_{ik} / \partial ()$, can be readily obtained by applying conventional rules for differentiation to the

defining equations for G_{ik}^t and the total fluxes, $(J_{Ci}^T)_{k-1/2}^{t_0}$ and $(J_{Ci}^T)_{k+1/2}^{t_0}$. If it is assumed that the solution concentrations are in equilibrium with the total concentration at time t , as is the case here, the derivatives of the form $(\partial C_{j1}/\partial C_{nT1})^{t_0}$ can be obtained in the manner outlined in Section 5. The derivatives $(\partial C_{nT1}/\partial t)^{t_0}$ can be evaluated from equation (83a) in terms of $G_{ik}^{t_0}$, and the time-rate of change of water content $(\partial \theta_1/\partial t)^{t_0}$ could normally be obtained from any numerical solution of the one-dimensional moisture-flow equation used to supply the water contents θ_k^t . The derivatives $(\partial q_{k-1/2}/\partial t)^{t_0}$ and $(\partial^2 \theta_k/\partial t^2)^{t_0}$, however, may not, in general, be available and would have to be calculated or estimated at the expense of additional effort. This difficulty can be avoided by defining an auxiliary function \hat{G}_{ik}^t which is identical to G_{ik}^t except that \hat{G}_{ik}^t is defined in terms of the values of the water contents at the middle of a time step. \hat{G}_{ik}^t may be represented as follows:

$$\hat{G}_{ik}^t = G_{ik}(C_{iT_k}^t, C_{j_k}^t, C_{j_{k-1}}^t, C_{k+1}^t, \theta_{k-1}^{t_0+\Delta t/2},$$

$$\theta_{k+1}^{t_0+\Delta t/2}, \theta_{k+1}^{t_0+\Delta t/2}, q_{k-1/2}^{t_0+\Delta t/2}, q_{k+1/2}^{t_0+\Delta t/2}, (\partial \theta_k/\partial t)^{t_0+\Delta t/2}),$$

for $j = 1, 2, \dots, 8$ and for $t_0 \leq t \leq t_0 + \Delta t$. The argument list is used to indicate that \hat{G}_{ik}^t is defined by equation (83b) except that θ_k^t and $(\partial \theta_k/\partial t)^t$ in equation (83b) are replaced by $\theta_k^{t_0+\Delta t/2}$ and $(\partial \theta_k/\partial t)^{t_0+\Delta t/2}$ and that the coefficients $D_{C_{ik-1/2}}^t$ which appear in equations (84) through (89) are replaced by $D_{C_{ik-1/2}}^{t_0+\Delta t/2}$. With this in mind it can be seen that over the time step $t_0 \leq t \leq t_0 + \Delta t$, \hat{G}_{ik}^t is time-dependent only by way of its dependency on the concentrations $C_{iT_k}^t$ and $C_{j_k}^t$, for $j = 1, 2, \dots, 8$. Moreover, \hat{G}_{ik}^t agrees with G_{ik}^t when $t = t_0 + \Delta t/2$, i.e. $\hat{G}_{ik}^{t_0+\Delta t/2} = G_{ik}^{t_0+\Delta t/2}$. Since an approximation to \hat{G}_{ik}^t is required only for $t = t_0 + \Delta t/2$, a Taylor's approximation to $\hat{G}_{ik}^{t_0+\Delta t/2}$ can be used effectively to approximate $G_{ik}^{t_0+\Delta t/2}$, as follows:

$$G_{ik}^{t_0+\Delta t/2} = \hat{G}_{ik}^{t_0+\Delta t/2} = \hat{G}_{ik}^{t_0} + \frac{\Delta t}{2} \cdot \left\{ \left(\frac{\partial \hat{G}_{ik}}{\partial C_{iT_k}} \right)^{t_0} \right.$$

$$\begin{aligned}
& + \sum_{l=k-1}^{k+1} \sum_{j=1}^8 \left(\frac{\partial \hat{G}_{ik}}{\partial C_{jl}} \right)^{t_0} \cdot \left(\sum_{n=1}^8 \left(\frac{\partial C_{jl}}{\partial C_{nTl}} \right)^{t_0} \cdot \left(\frac{\partial C_{nTl}}{\partial t} \right)^{t_0} \right. \\
& \quad \left. + \left(\frac{\partial C_{jl}}{\partial \theta_1} \right)^{t_0} \cdot \left(\frac{\partial \theta_1}{\partial t} \right)^{t_0} \right) \} + O(\Delta t^2). \tag{93}
\end{aligned}$$

Due to the treatment of θ_k , $q_{k-\frac{1}{2}}$, $q_{k+\frac{1}{2}}$, and $\partial \theta_k / \partial t$ as constants over the time step, the derivatives $\partial q_{k-\frac{1}{2}} / \partial t$, $\partial q_{k+\frac{1}{2}} / \partial t$, and $\partial^2 \theta_k / \partial t^2$ do not appear in the above equation. However, an additional problem arises due to the appearance of $(\partial C_{nTl} / \partial t)^{t_0} = G_{nl}^{t_0}$ in addition to $\hat{G}_{ik}^{t_0}$. Strict substitution of $G_{nl}^{t_0}$ for $(\partial C_{nTl} / \partial t)^{t_0}$ would require the evaluation of both \hat{G}_{nl} and G_{nl} for all n and l . This difficulty is avoided by substituting $\hat{G}_{nl}^{t_0}$ for $(\frac{\partial C_{nTl}}{\partial t})^{t_0}$ rather than $G_{nl}^{t_0}$.

The argument for doing this is that, due to the equality of $\hat{G}_{nl}^{t_0+\Delta t/2}$ with $G_{nl}^{t_0+\Delta t/2}$ and the differentiability of both functions, an upper bound for the absolute value of the error which arises from this substitution is (neglecting terms of order greater than 1 in a Taylor's expansion of the two functions) proportional to Δt . Using the term $(\partial \hat{G}_{ik} / \partial C_{iTl})^{t_0} \cdot (\partial C_{iTl} / \partial t)^{t_0}$ to illustrate the effect of the substitution on the approximation to $\hat{G}_{ik}^{t_0+\Delta t/2}$, we have:

$$\begin{aligned}
G_{ik}^{t_0+\Delta t/2} &= \hat{G}_{ik}^{t_0} + \frac{\Delta t}{2} \cdot \left\{ \left(\frac{\partial \hat{G}_{ik}}{\partial C_{iTl}} \right)^{t_0} \cdot (G_{ik}^{t_0}) + \text{other terms} \right\} \\
&+ O(\Delta t^2) = \hat{G}_{ik}^{t_0} + \frac{\Delta t}{2} \cdot \left\{ \left(\frac{\partial \hat{G}_{ik}}{\partial C_{iTl}} \right)^{t_0} \cdot (\hat{G}_{ik}^{t_0} + O(\Delta t) + \text{other} \right. \\
&\quad \left. \text{terms} \right\} + O(\Delta t^2) = \hat{G}_{ik}^{t_0} + \frac{\Delta t}{2} \cdot \left\{ \left(\frac{\partial \hat{G}_{ik}}{\partial C_{iTl}} \right)^{t_0} \cdot \hat{G}_{ik}^{t_0} + \text{other} \right. \\
&\quad \left. \text{terms} \right\} + O(\Delta t^2),
\end{aligned}$$

so that the order of accuracy of the approximation to $\hat{G}_{ik}^{t_0+\Delta t/2}$ is not impaired by substituting $\hat{G}_{ik}^{t_0}$ and $\hat{G}_{nl}^{t_0}$ for $(\partial C_{iTl} / \partial t)^{t_0}$ and $(\partial C_{nTl} / \partial t)^{t_0}$, respectively, in equation (93).

The water content and flux terms which are required to evaluate $G_{ik}^{t_o}$ and $G_{ik}^{t_o+\Delta t/2}$ are $\theta_{k-1}^{t_o+\Delta t/2}$, $\theta_k^{t_o+\Delta t/2}$, $\theta_{k+1}^{t_o+\Delta t/2}$, $(\partial\theta_k/\partial t)^{t_o}$, $q_{k-1}^{t_o+\Delta t/2}$, and $q_{k+1/2}^{t_o+\Delta t/2}$. These quantities are readily available from many numerical solutions of the moisture flow equation or may be easily approximated from other quantities that would be available from such solutions.

Finally, the equation used to obtain $C_{iT_k}^{t_o+\Delta t}$, can be written:

$$C_{iT_k}^{t_o+\Delta t} = C_{iT_k}^{t_o} + \Delta t \cdot G_{ik}^{t+\Delta t/2}, \quad (94)$$

where:

$$\begin{aligned} G_{ik}^{t+\Delta t/2} = & G_{ik}^{t_o} + \frac{\Delta t}{2} \cdot \left\{ \left(\frac{\partial G_{ik}}{\partial C_{iT_k}} \right)^{t_o} \cdot G_{ik}^{t_o} \right. \\ & + \sum_{i=k-1}^{k+1} \sum_{j=1}^8 \left(\frac{\partial G_{ik}}{\partial C_{j1}} \right)^{t_o} \cdot \left(\sum_{n=1}^8 \left(\frac{\partial C_{j1}}{\partial C_{nT1}} \right)^{t_o} \cdot G_{n1}^{t_o} \right. \\ & \left. \left. + \left(\frac{\partial C_{j1}}{\partial \theta_1} \right)^{t_o} \cdot \left(\frac{\partial \theta_1}{\partial t} \right)^{t_o} \right\} \right\}. \quad (95) \end{aligned}$$

We note that, for $\theta_k = \text{constant}$, $\frac{\partial \theta_k}{\partial t} = \frac{\partial q_{k-1/2}}{\partial t} = \frac{\partial q_{k+1/2}}{\partial t} = \frac{\partial^2 \theta_k}{\partial t^2} = 0$ and $G_{ik}^{t_o} = G_{ik}^{t_o}$ so the use of equations (94) and (95) are equivalent to using equations (90) through (92) for steady-flow conditions.

For purposes of computation, equation (95) can be represented in the alternative, but equivalent, form:

$$\begin{aligned} G_{ik}^{t+\Delta t/2} = & G_{ik}^{t_o} + \frac{\Delta t}{2} \cdot \sum_{l=k-1}^{k+1} \left\{ \sum_{j=1}^8 \left(\frac{\partial G_{ik}}{\partial C_{jT1}} \right)^{t_o} \cdot \right. \\ & \left. G_{j1}^{t_o} + \left(\frac{\partial G_{ik}}{\partial \theta_1} \right)^{t_o} \cdot \left(\frac{\partial \theta_1}{\partial t} \right)^{t_o} \right\}. \quad (96) \end{aligned}$$

The following equations are used to approximate constant concentration boundary conditions at $Z = 0$ ($k = 1$):

$$C_{i1}^{t_o+\Delta t} = C_{i1}^{t_o}$$

and

$$G_{i1}^{t_0} = 0,$$

for $t_0 \geq 0$ and $i = 1, 2, \dots, 8$. To approximate a zero-gradient condition $(\partial \bar{C}_i / \partial Z)|_{Z=L_c} = 0$ at the lower boundary, the following equations are used:

$$C_{iM}^{t_0+\Delta t} = C_{iM-1}^{t_0+\Delta t}$$

and

$$G_{iM}^{t_0} = G_{iM-1}^{t_0},$$

for $t_0 \geq 0$ $i = 1, 2, \dots, 8$.

Calculation Procedure--

Given below is a brief outline of the calculation procedure for advancing the total concentrations, C_{iT_k} , in time.

- (1) Set $t = 0$.
- (2) Supply values of the total concentrations $C_{iT_k}^t$, for $i = 1, 2, \dots, 8$ and $k = 2, 3, \dots, M-1$ and of the solution concentrations C_{i1}^t , X_{111}^t , X_{211}^t , for $i = 1, 2, \dots, 8$.
- (3) Supply values of $\theta_k^{t+\Delta t/2}$, $q_{k-1/2}^{t+\Delta t/2}$, and $(\partial \theta_k / \partial t)^t$ for $k = 2, 3, \dots, M$.
- (4) Calculate the coefficients $D_{Cik-1/2}^{t+\Delta t/2}$ according to equation (89). Similarly, calculate $D_{X11k-1/2}^{t+\Delta t/2}$, $D_{X21-1/2}^{t+\Delta t/2}$.
- (5) For $k = 2, 3, \dots, M-1$, calculate C_{ik}^t , X_{11k}^t , and X_{21k}^t in terms of $C_{iT_k}^t$ and θ_k^t according to the procedure outlined previously. Also, calculate all derivatives of the form $(\partial C_{ik} / \partial C_{jTk})^t$ and $(\partial C_{ik} / \partial \theta_k)^t$ as described previously.
- (6) Calculate the quantities $(J_{Ci}^{T'})_{k-1/2}^t$ for $k = 2, 3, \dots, M$ according to equations (84) through (89) except that $D_{Cik-1/2}^t$, $D_{X11k-1/2}^t$, $D_{X21k-1/2}^t$, and $q_{k-1/2}^t$ in those equations are replaced by $D_{Cik-1/2}^{t+\Delta t/2}$, $D_{X11k-1/2}^{t+\Delta t/2}$, $D_{X21-1/2}^{t+\Delta t/2}$, and $q_{k-1/2}^{t+\Delta t/2}$, respectively. Also calculate the

following derivatives:

$$\partial\{(J_{Ci}^{T'})_{k-1/2}\}^t/\partial C_{jTk}, \quad \partial\{(J_{Ci}^{T'})_{k-1/2}\}^t/\partial C_{jTk},$$

$$\partial\{(J_{Ci}^{T'})_{k-1/2}\}^t/\partial \theta_k \quad \text{and} \quad \partial\{(J_{Ci}^{T'})_{k-1/2}\}^t/\partial \theta_{k-1}$$

for $k = 2, 3, \dots, M$; $i = 1, 2, \dots, 8$; and $j = 1, 2, \dots, 8$.

- (7) For $k = 2, 3, \dots, M-1$, calculate G_{ik}^t and the derivatives of G_{ik}^t with respect to C_{jTk} , C_{jTk-1} , C_{jTk+1} , θ_k , θ_{k-1} , and θ_{k+1} .

For example:

$$G_{ik}^t = \frac{1}{\theta_k^{t+\Delta t/2} \cdot \Delta Z} \cdot \{(J_{Ci}^{T'})_{k-1/2}^t - (J_{Ci}^{T'})_{k+1/2}^t\} - \frac{C_{iTk}^t}{\theta_k^{t+\Delta t/2}} \cdot \left(\frac{\partial \theta_k}{\partial t}\right)^{t+\Delta t/2}$$

and,

$$\left(\frac{\partial G_{ik}^t}{\partial C_{jTk-1}}\right)^t = \frac{1}{\theta_k^{t+\Delta t/2} \cdot \Delta Z} \cdot \frac{\partial\{(J_{Ci}^{T'})_{k-1/2}\}^t}{\partial C_{jTk-1}}$$

- (8) For $k = 2, 3, \dots, M-1$ and $i = 1, 2, \dots, 8$, calculate $G_{ik}^{t+\Delta t/2}$ according to equation (95) and update the total concentrations:

$$C_{iTk}^{t+\Delta t} = C_{iTk}^t + \Delta t \cdot G_{ik}^{t+\Delta t/2}.$$

- (9) Set $t = t + \Delta t$.
- (10) For steady-flow conditions, repeat steps (5) through (9) until t reaches a desired maximum value. For transient flow conditions repeat steps (3) through (9) until t reaches a desired maximum value.

The above sequence of calculation was programmed in FØRTRAN. The resulting program, exclusive of the calculations of solution concentrations and derivatives of solution content ratios [step 5], is entitled SUBROUTINE SOIL.

A listing of the program can be found in Appendix L.

Testing of the Model

Introduction--

A computer model was constructed to simulate the simultaneous transport, by combined convection and diffusion processes, of five cations and three anions in a soil-water system. Instantaneous, local, chemical equilibrium among the various ions, and between the ions and the soil matrix, was assumed for the development of the model. The specific equilibrium phenomena considered were those of cation exchange and ion pairing. The effects of solution ionic activity on chemical equilibrium were also considered. The mathematical equations used to describe the equilibrium are similar to those presented by Dutt, et al. (1972b). No consideration was given to interactions between anions and the soil matrix or to solubility-precipitation reactions. The method used to solve the system of chemical equilibrium equations was discussed previously.

The primary mechanisms of ion transport which were considered in the development of the model are those of convection, molecular diffusion, and hydrodynamic dispersion. To counter-balance the effects of different molecular diffusion coefficients at low flow velocities, an additional (emf-induced) component of flux was included in the development. The equation which was used to describe this component of flux is similar to that used by deWit and van Keulen (1972). The mathematical equation used to describe the effects of diffusion and dispersion as a function of moisture content and mean pore velocity is based on an approach taken by Kirda, et al. (1973). No consideration was given to the effects that non-uniform solution density would have on the transport process. In order to predict the total concentrations of the eight ions as functions of time and depth in a soil profile, finite-difference equations were developed from considerations of total flux mass-balance. It was previously shown that calculational procedure used to solve these equations requires evaluation of partial derivatives of solution concentrations with respect to total concentrations but does not require iteration across time steps since the procedure is explicit.

Structurally, the computer model consists of two subroutines, SOIL and EQUIL, and a prompting program. The prompting program serves as a vehicle for reading in system parameters, initiating the execution of SUBROUTINE SOIL, and printing out calculated information at specified times. SUBROUTINE SOIL provides estimates of the total concentrations of the eight ions at each point of a finite-difference grid at time $t + \Delta t$ based on values of the solution concentrations and partial derivatives of solution concentrations with respect to total concentrations at time t . The calculation of solution concentrations and partial derivatives, as functions of the total concentrations, is carried out in SUBROUTINE EQUIL.

In previous discussion the variables which denote solution and adsorbed phase concentrations were identified with eight specific ions: Ca^{++} , Mg^{++} , Na^+ , K^+ , NH_4^+ , $\text{SO}_4^{=}$, Cl^- , and HCO_3^- . However, the model takes on a more

general character if the mechanisms which distinguish the roles of these ions are identified. The monovalent anions, Cl^- and HCO_3^- , are assumed to interact chemically with the remaining ions only through their influence on the activity coefficient γ . This can be seen from equations (31), (43), and (51). The monovalent cations Na^+ , K^+ , and NH_4^+ are distinguished from the divalent cation, Mg^{++} , by their valences, by the type of cation exchange equation used to describe their interaction with Ca^{++} (see equations (44), (45), (46), and (47)), and by their lack of interaction with SO_4^{--} . The monovalent cations are mutually distinguished only by the values of the exchange coefficients E_{13} , E_{14} , and E_{15} . The divalent cations are mutually distinguished by the values of the inverse dissociation constants, D_{11} and D_{21} , and by the value of the exchange coefficient E_{12} .

In the transport part of the model the ions are mutually distinguished by their valences and diffusion coefficients. The ions Ca^{++} , Mg^{++} , and SO_4^{--} are distinguished from the others due to assumed transport of ion pairs containing these three ions, as can be observed from equations (85) through (87).

The above observations were taken into account in the programming of the computer model. The ion valences, exchange coefficients, inverse dissociation constants, and molecular diffusion coefficients are included in the list of input parameters for the computer model which appears in Appendix M. The total numbers of divalent cations, monovalent cations and monovalent anions for a given run, as well as an indicator as to the presence or absence of the divalent anion, SO_4^{--} , are also included in the list. The model can be used with reasonable efficiency for simulations of the simultaneous transport of as few as two cations and no anions. For runs using fewer than five cations or three anions, extraneous calculations that would normally be performed in SUBROUTINE SOIL, with zero values for concentrations of ions not considered, are entirely skipped. The calculations of unnecessary partial derivatives in SUBROUTINE EQUIL are also avoided in these cases. Only the Newton-Raphson procedures for obtaining C_1 and γ in SUBROUTINE EQUIL are carried out with zero values of the total concentrations of ions which are considered absent for a particular run.

The assumption of a unit ionic activity coefficient is sometimes made when soil solution concentrations are low. Provisions were made in the program so that this assumption can be used if so desired. In such cases, only one pass is made through the outside (γ) loop of the Newton-Raphson procedure for calculating solution concentrations in SUBROUTINE EQUIL.

The use of the model for cases where fewer than eight ions are considered, or where unit activity coefficients are assumed, is further discussed in Appendix M. A complete list of required input for the model can also be found there.

In order to avoid unnecessary repetitive calculations of solution concentrations, flux terms and partial derivatives of solution concentrations as functions of the total concentrations, provisions were made in the computer program to skip these calculations at grid points where the predicted change in all total concentrations over a time step is less than some predetermined

value. Shamir and Harleman (1967) suggested the use of a similar device in conjunction with the Stone and Brian scheme. The approach used for the present model is outlined in Appendix M.

Simulation Runs Involving Two or Three Cations--

Effects chosen for observation--From the preceding discussion it is evident that there are a large number of system parameters whose combined influence on simulations produced by the model could be tested. For the present it was decided to examine the effects of varying some of the parameters in cases where only two or three cations and from zero to two anions were considered simultaneously in an assumed homogeneous soil column under steadyflow conditions. Specific parameters and effects chosen for observation are: (a) soil cation exchange capacity, CEC, (b) soil moisture content, θ , (c) the mean-pore velocity to apparent diffusion coefficient ratio, r , (d) the cation exchange coefficients, E_{12} and E_{13} , (e) the effect of the solution activity coefficient, γ , through its influence on the cation exchange relationship equation (56), and (f) the magnitude of the total cation concentration of the soil solution.

Solution concentration pulses--Solution concentration pulses were used as the means of manifesting the influence of these parameters and effects on simulated results. The following example illustrates the type of pulse which was used for this purpose. A homogeneous soil column, having bulk density, ρ_b , moisture content, θ , and cation exchange capacity, CEC, is assumed to initially contain adsorbed cations of only one species, cation 1. Thus there are CEC meq/100g or $Q_D = \rho_b \cdot \text{CEC} / (200 \cdot \theta)$ moles/liter of cation 1 occupying the cation exchange complex of the soil. In addition there are C_{1I} moles/liter of cation 1 uniformly distributed in the soil solution. It is further assumed that there are $A_{2I} = 2 \cdot C_{1I}$ moles/liter of monovalent anion 2 in the initial soil solution. At time $t=0$, a slug of solution of different ionic constituency is introduced into the column at the soil surface and is allowed to begin to displace the original soil solution at a constant velocity, $V=q/\theta$. The depth of the slug, in cm H_2O , is $V \cdot t_p$, where t_p is the time that the slug solution is assumed to be in contact with the soil surface. The slug solution is to be void of cation 1 and is assumed, instead, to contain C_{2S} moles/liter of divalent cation 2 and C_{3S} moles/liter of monovalent cation 3. In addition there are either $A_{2S} = 2 \cdot C_{2S} + C_{3S}$ moles/liters of monovalent anion 2 or $A_{3S} = 2 \cdot C_{2S} + C_{3S}$ moles/liter of anion 3 present in this solution. At time t_p , the slug is followed by a solution of the same ionic constituency as the original soil solution and the displacement process is continued at the velocity, v .

The geometric shape of the concentration profiles of cation 2 and 3 within the soil column for times greater than t_p will depend on a number of factors, including the magnitude of t_p , the relative preference of the cation exchange complex for cations 1, 2 and 3, and the original concentrations of the respective cations in their respective solutions. However, provided $v \cdot t_p < L_c$, the graphs of C_2 and C_3 versus depth in the column will have a pulse-shape. The simulation of such pulses offers a rather stringent test of the performance of the model due to the existence of concentration fronts at the leading and trailing edges of the pulses. In addition, the effects of

varying parameters can be observed on the height, spread and symmetry of a pulse at a given time of observation.

Simulated tests--For each simulation run made, a column length, L_c , of approximately 20 cm was used. The exact column length can be computed from the grid spacing, Δz , and the number of grid points, M , which were used for a particular run, according to: $L_c = (M-3/2) \cdot \Delta z$. See Figure 111. For most of the runs, the value of M used was 80.

The velocity, V , was established at 0.01 cm/min for all of the runs by adjusting the uniform volumetric moisture flux, q , so that $V = q/\theta = 0.01$. The pulse time, t_p , was 300 minutes and results corresponding to simulated times of 400 and 1600 minutes were observed for each run.

Particular values of the velocity to apparent diffusion coefficient ratio, r , were established by using $D_{mi} = 0$, for cations 1, 2, and 3 and anions 2 and 3, $\delta = 1.0$ and $\lambda = r$ in equation (78). For each run, the time step size, Δt , was chosen to establish a desired value for the quantity, $\beta = V \cdot \Delta t / \Delta z$.

The values of C_{1I} , A_{2I} , A_{3I} , C_{2S} , C_{3S} , A_{2S} , E_{12} , E_{13} , θ , CEC, r , Δz and β which were used for the runs, for which results are presented, are shown in Table 70 along with the run numbers R-1 through R-23. The runs for which the effects of solution activity were considered are indicated by a C under the column headed γ . Those runs for which a 1.0 occurs in this column were made with $\gamma = 1.0$ for all depths and all times.

Results and Discussion--

The calculated values of the solution concentration corresponding to cations 2 and 3 and anion 3 were normalized and plotted as C_2/C_{2S} , C_3/C_{3S} , and A_3/A_{3S} versus depth in the soil column. The resulting graphs are shown in Figures 112 through 131. In each of these figures, C/C_0 represents C_2/C_{2S} , C_3/C_{3S} , or A_3/A_{3S} , depending on which ions were included for the run corresponding to that figure. Figure 112 corresponds to runs R-1 through R-3, Figure 113 corresponds to R-4 and R-5 and Figures 114 through 131, respectively, correspond to runs R-6 through R-23.

Comparison of results from two-cation problems with an independent numerical solution--For runs R-1 through R-8, which were made with only cations 1 and 2 or cations 1 and 3 present, the calculated values were compared with results obtained from the numerical solution which is presented in Appendix J. The approach to solving a two-cation problem with this alternate method is fundamentally different from the approach which was outlined in Section 6 for solving multi-ion problems, because a finite-difference approximation to only one (as opposed to two) partial differential equation is required. All results from the independent numerical solution were obtained using a grid-spacing of 0.2 cm and a time-step size of 10 minutes ($\beta = 0.5$).

Runs R-1 through R-5 (Figures 112 and 113) were made with $\theta = 0.5$, CEC = 10.0, $\gamma = 1.0$, $r = 10.0$, $E_{12} = E_{13} = 1.0$, and $C_{1I} = 0.13$. Runs R-1, R-2, and R-3

TABLE 70. VALUES OF THE INPUT PARAMETERS USED IN THE TEST RUNS

Run	C _{1I}	C _{2s}	C _{3s}	A _{2I}	A _{2s}	A _{3I}	A _{3s}	E ₁₂	E ₁₃	θ	CEC	γ	r	Δz	β
R1	0.130	0.0	0.260	0.0	0.0	0.0	0.0	1.0	1.0	0.50	10.0	1.0	10.0	1.0	0.1
R2	"	"	"	"	"	"	"	"	"	"	"	"	"	0.5	"
R3	"	"	"	"	"	"	"	"	"	"	"	"	"	"	0.2
R4	"	0.130	0.0	"	"	"	"	"	"	"	"	"	"	1.0	0.1
R5	"	"	"	"	"	"	"	"	"	"	"	"	"	0.5	0.2
R6	0.050	0.050	"	"	"	"	"	"	"	"	"	"	"	0.25	0.5
R7	"	0.0	0.100	"	"	"	"	"	"	"	"	"	"	"	"
R8	0.025	"	0.050	"	"	"	"	"	"	"	"	"	"	"	"
R9	"	0.025	0.0	"	"	"	"	"	"	"	"	"	"	"	"
R10	0.050	0.050	0.100	"	"	"	"	"	"	"	"	"	"	"	"
R11	"	0.025	0.050	"	"	"	"	"	"	"	"	"	"	"	"
R12	"	0.050	0.100	"	"	"	"	"	"	"	20.0	"	"	"	"
R13	"	"	"	"	"	"	"	"	"	0.25	10.0	"	"	"	"
R14	0.100	0.050	0.100	"	"	"	"	"	"	0.50	"	"	"	"	"
R15	"	"	"	0.200	"	"	0.20	"	"	"	"	C	"	"	"
R16	0.050	0.025	0.050	0.100	"	"	0.100	"	"	"	"	"	"	"	"
R17	0.100	0.050	0.100	0.200	"	"	0.200	"	"	"	"	"	5.0	"	"
R18	0.050	0.025	0.050	0.0	"	"	0.0	"	"	"	"	1.0	"	"	"
R19	"	"	"	"	"	"	"	"	"	"	"	"	20.0	"	"
R20	0.100	0.050	0.100	"	"	"	"	0.5	"	"	"	"	10.0	"	"
R21	"	"	"	"	"	"	"	2.0	"	"	"	"	"	"	"
R22	"	"	"	"	"	"	"	0.0	0.5	"	"	"	"	"	"
R23	"	"	"	"	"	"	"	"	2.0	"	"	"	"	"	"

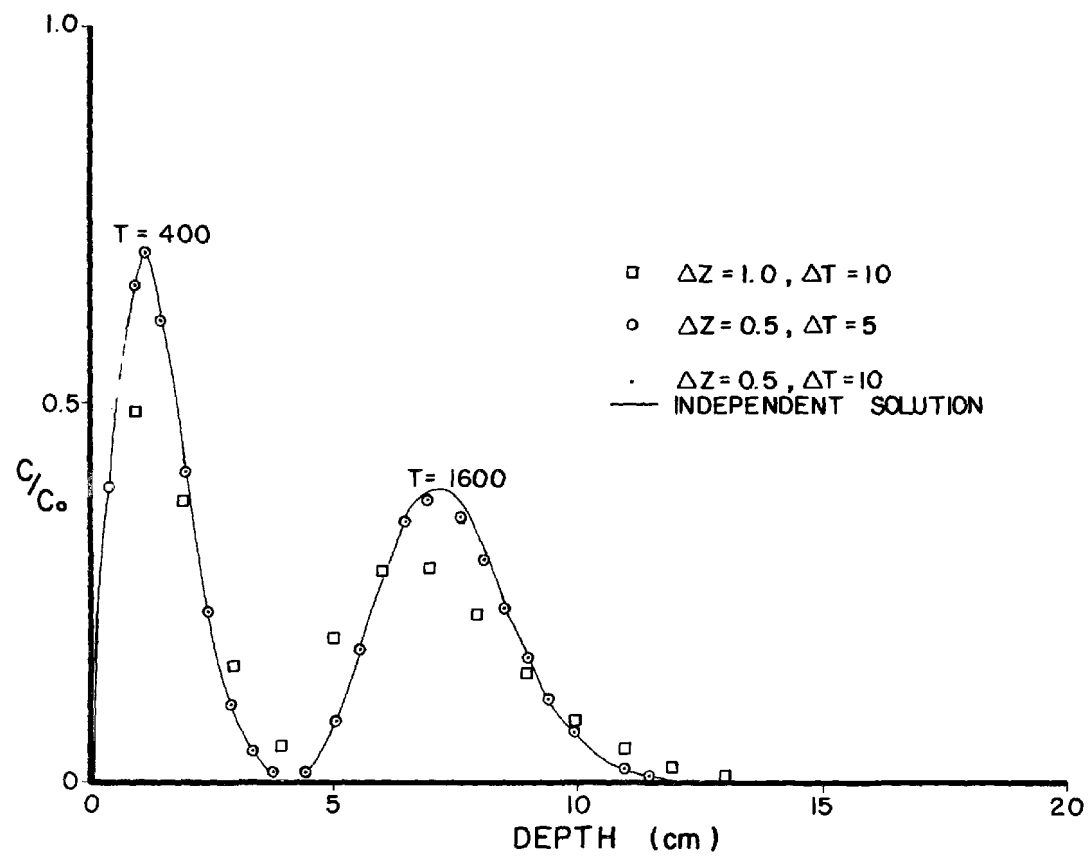


Figure 112. Simulated concentration pulses for cation 2 for conditions of runs R-1, R-2 and R-3.

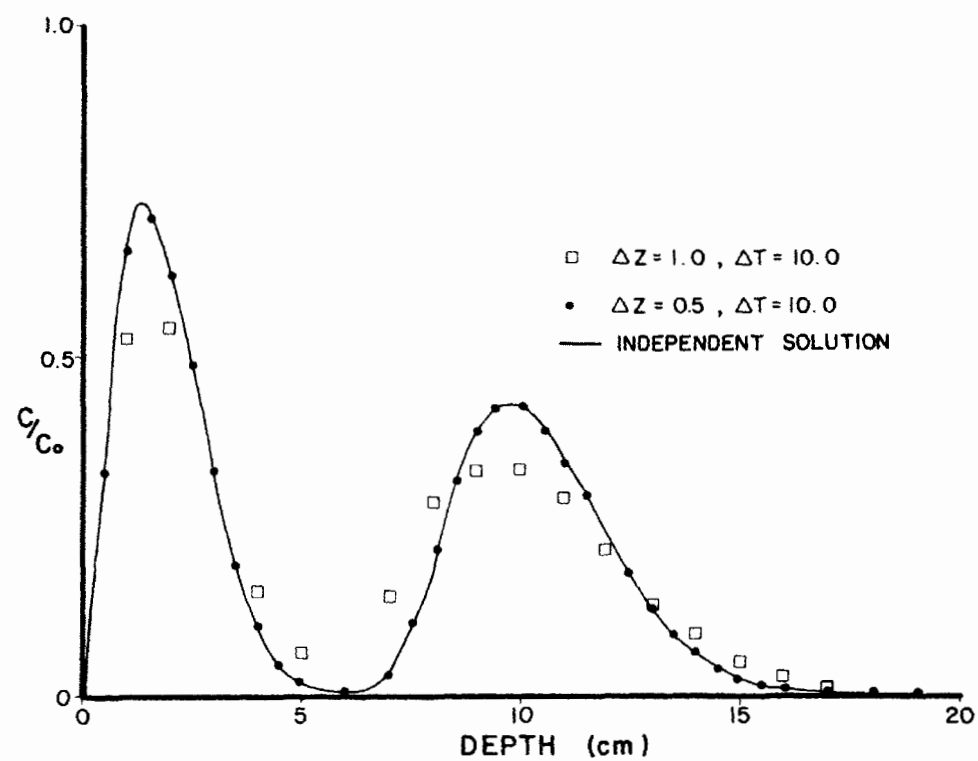


Figure 113. Simulated concentration pulses for cation 3 for conditions of runs R-4 and R-5.

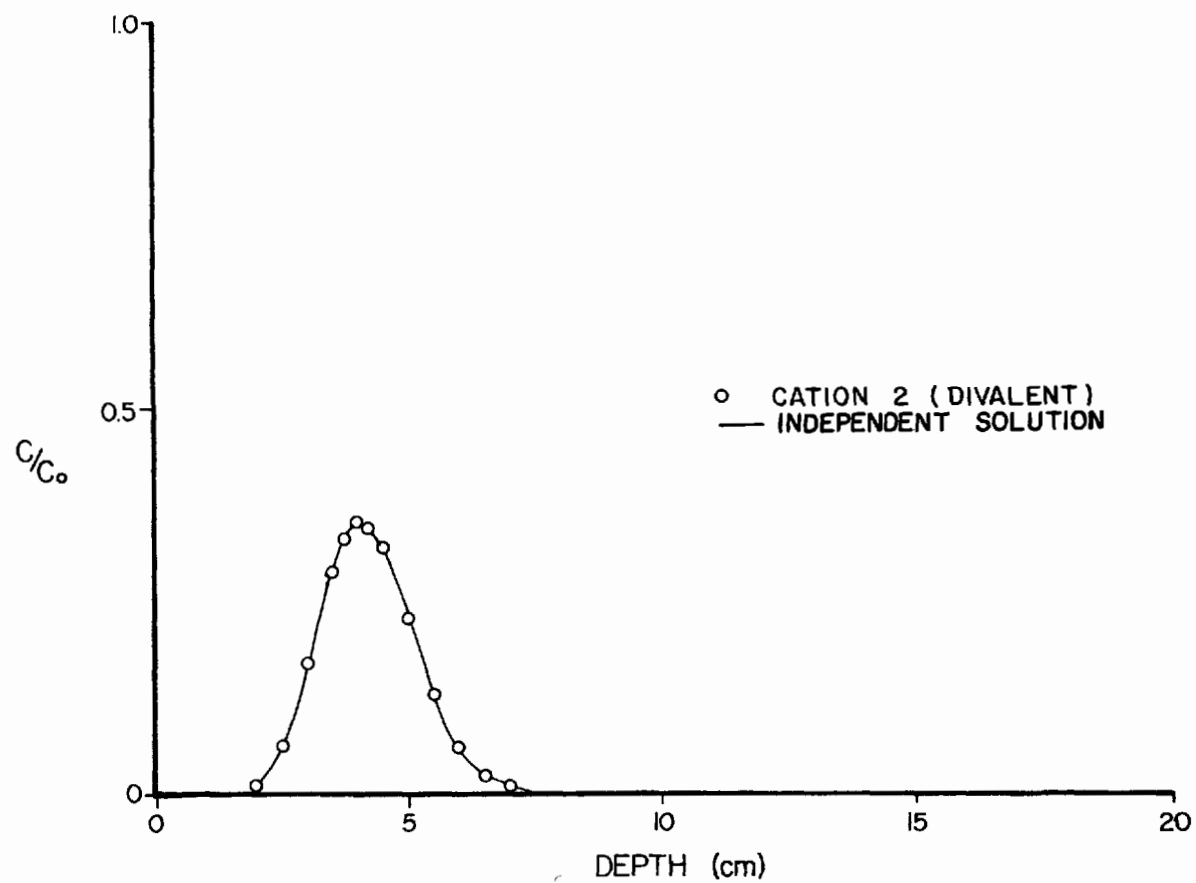


Figure 114. Simulated concentration pulse for cation 2 and for the conditions of run R-6.

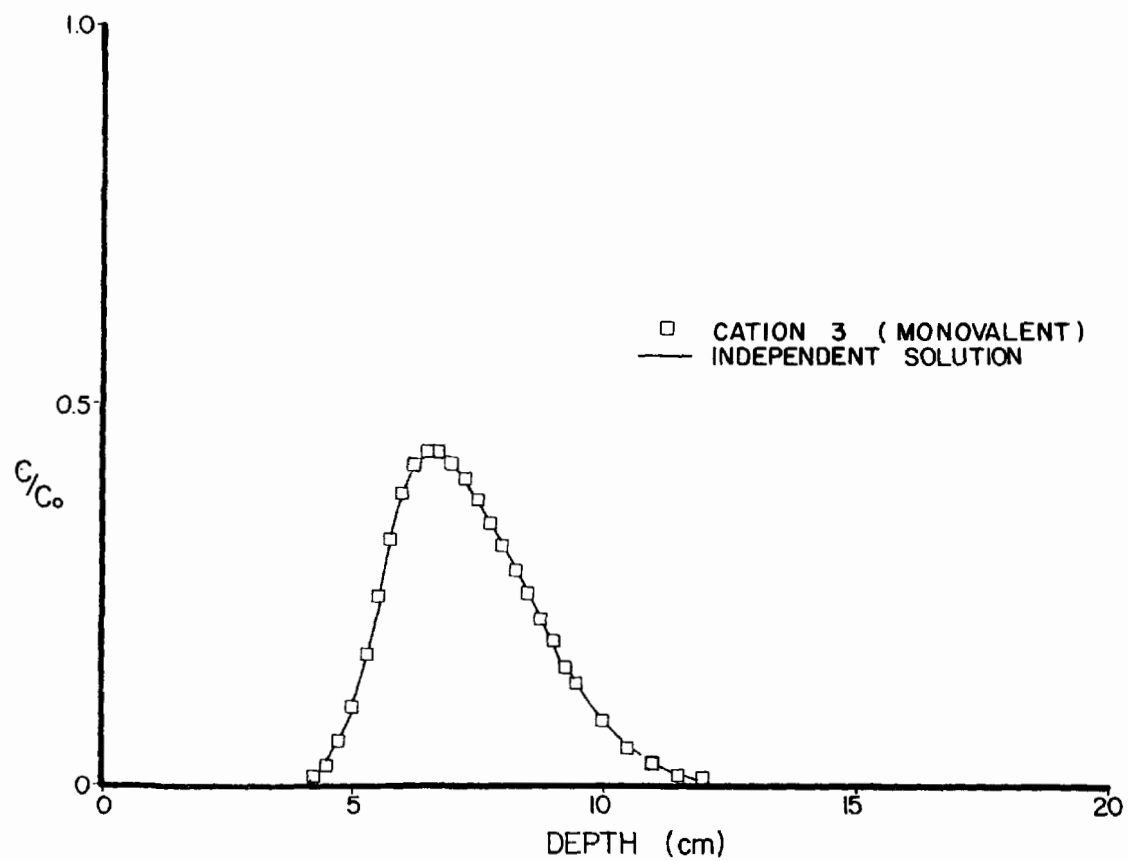


Figure 115. Simulated concentration pulse for cation 3 for the conditions of run R-7.

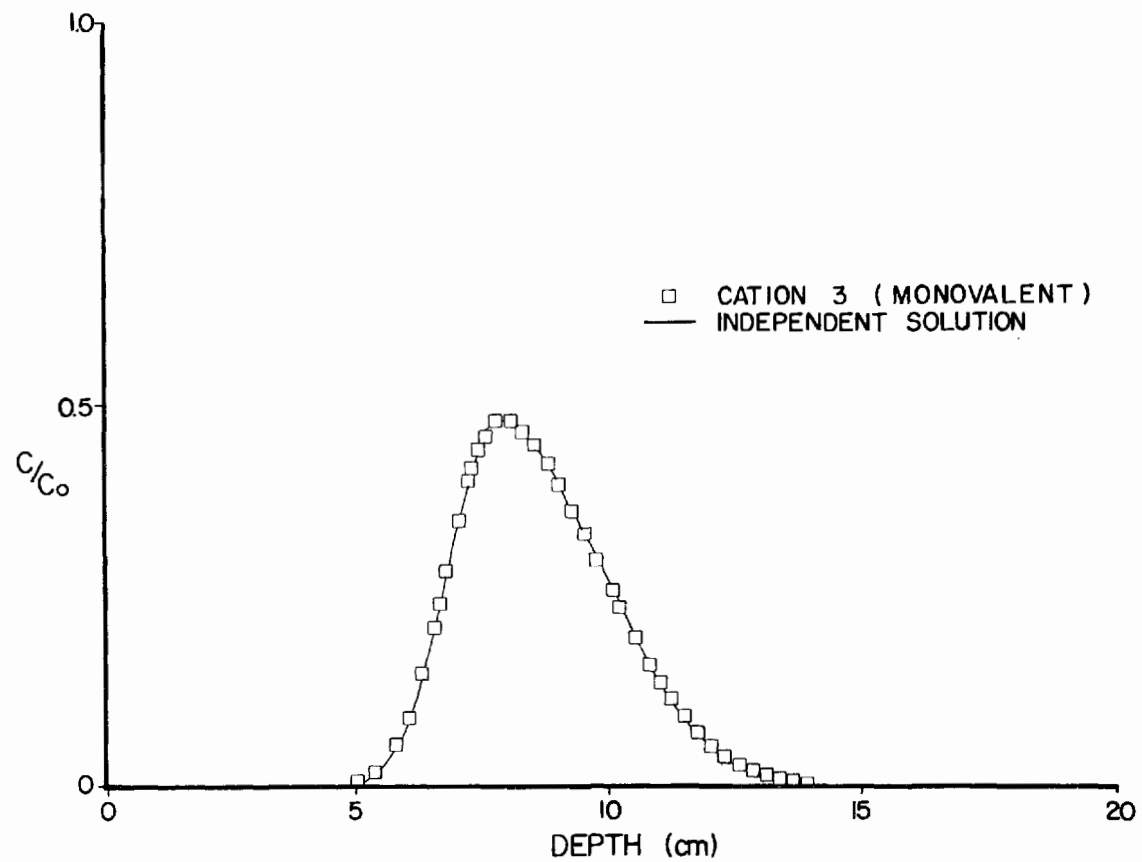


Figure 116. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-8.

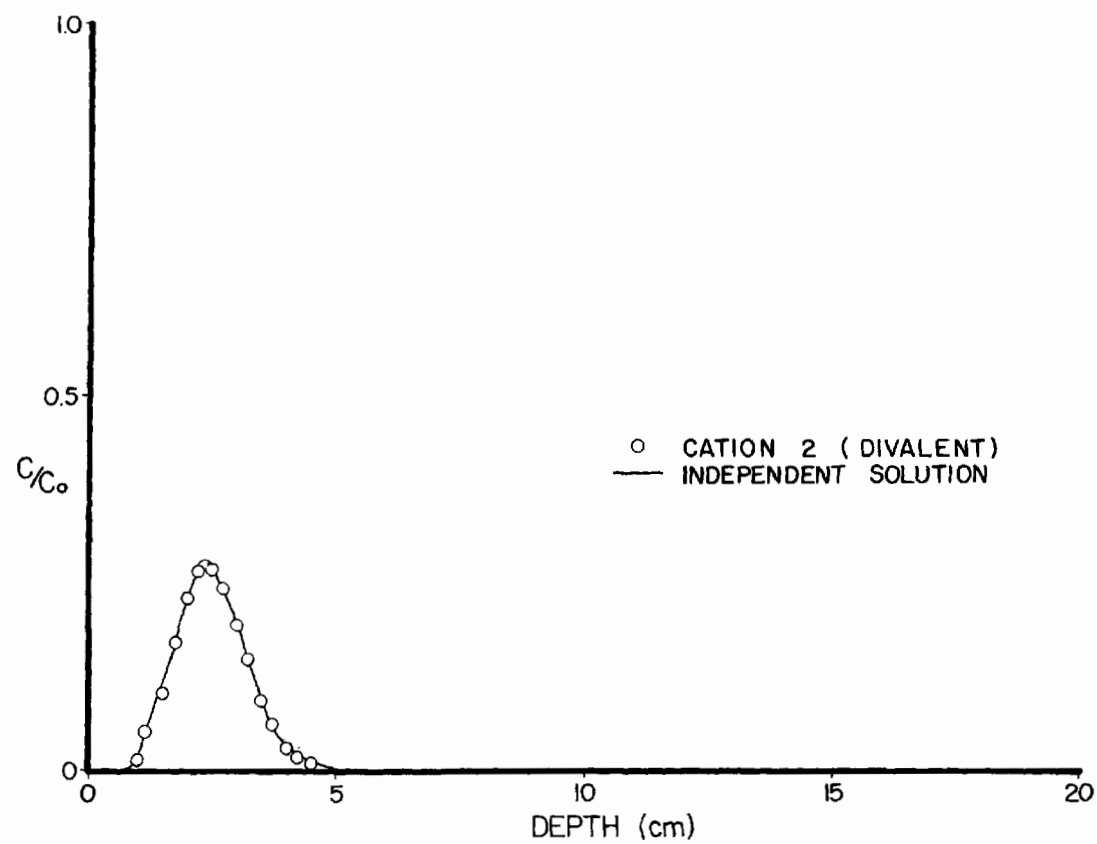


Figure 117. Simulated concentration pulse for cation 2 for the conditions of run R-9.

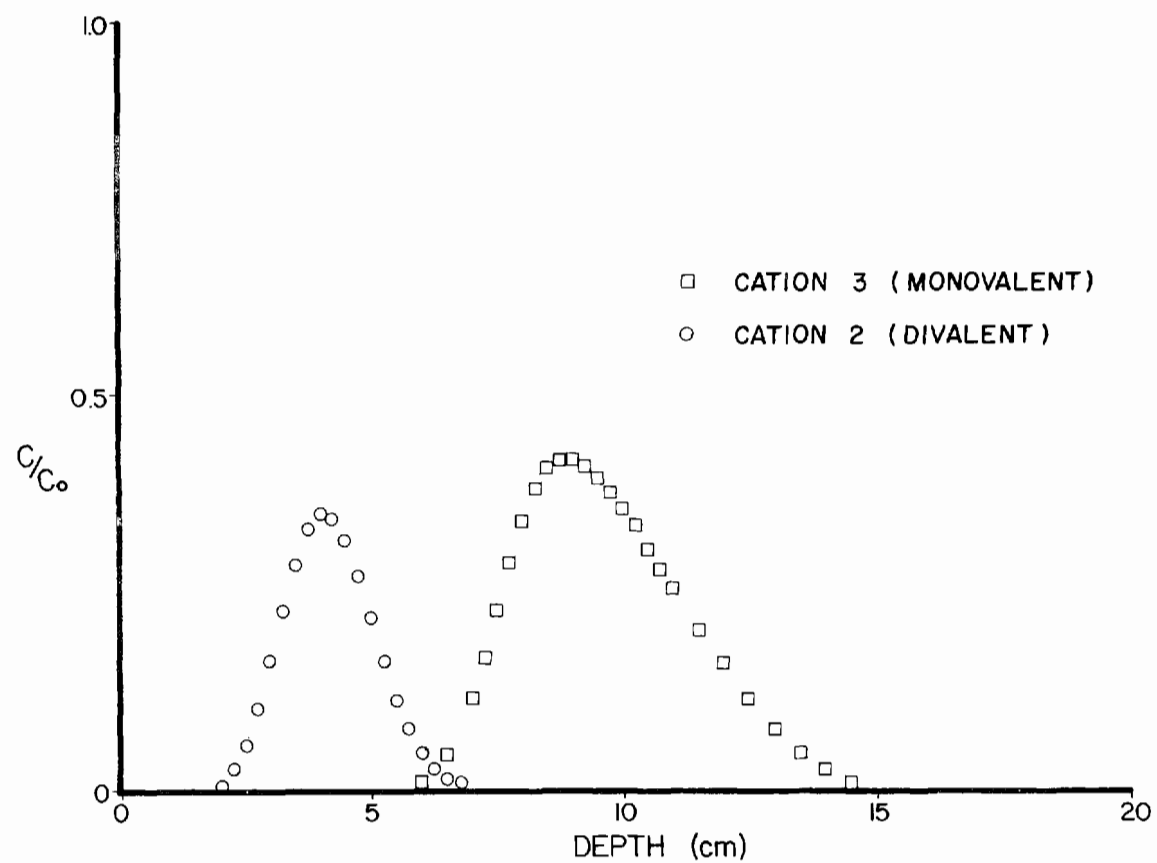


Figure 118. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-10.

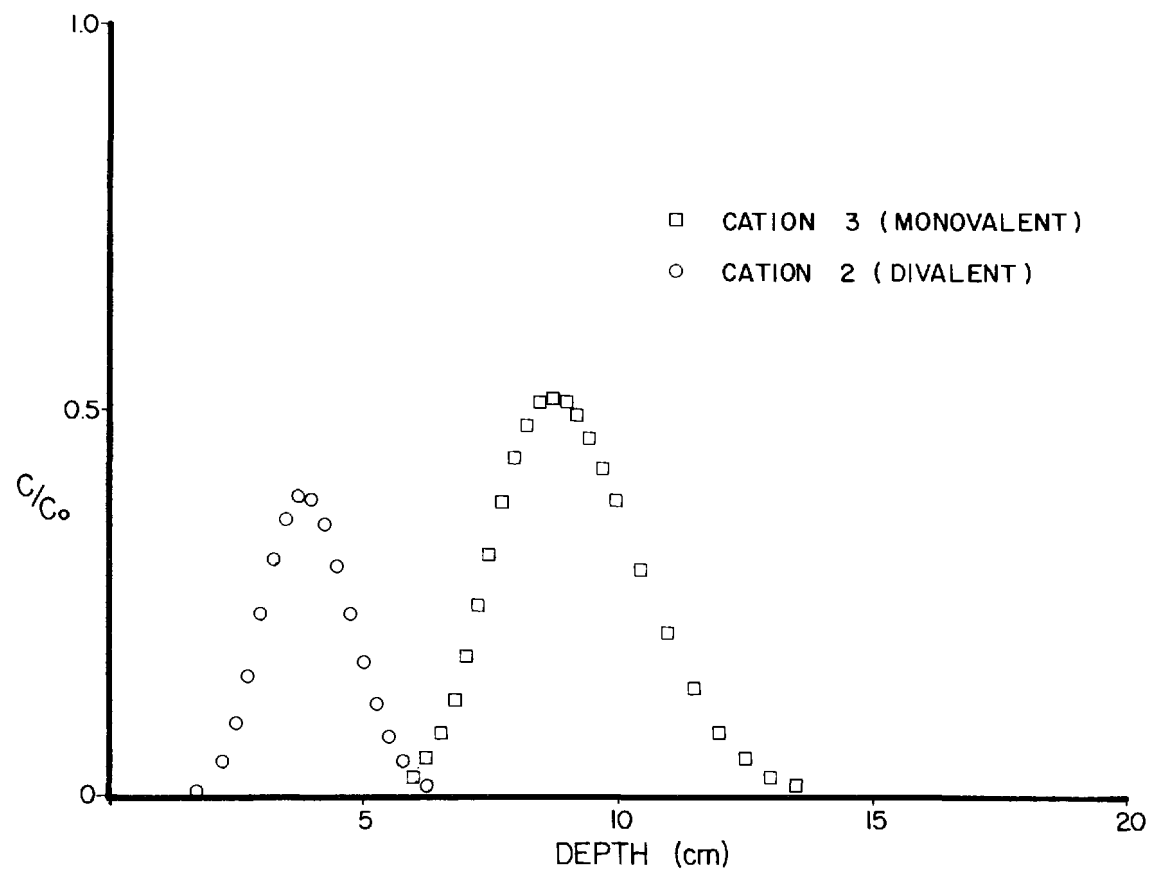


Figure 119. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-11.

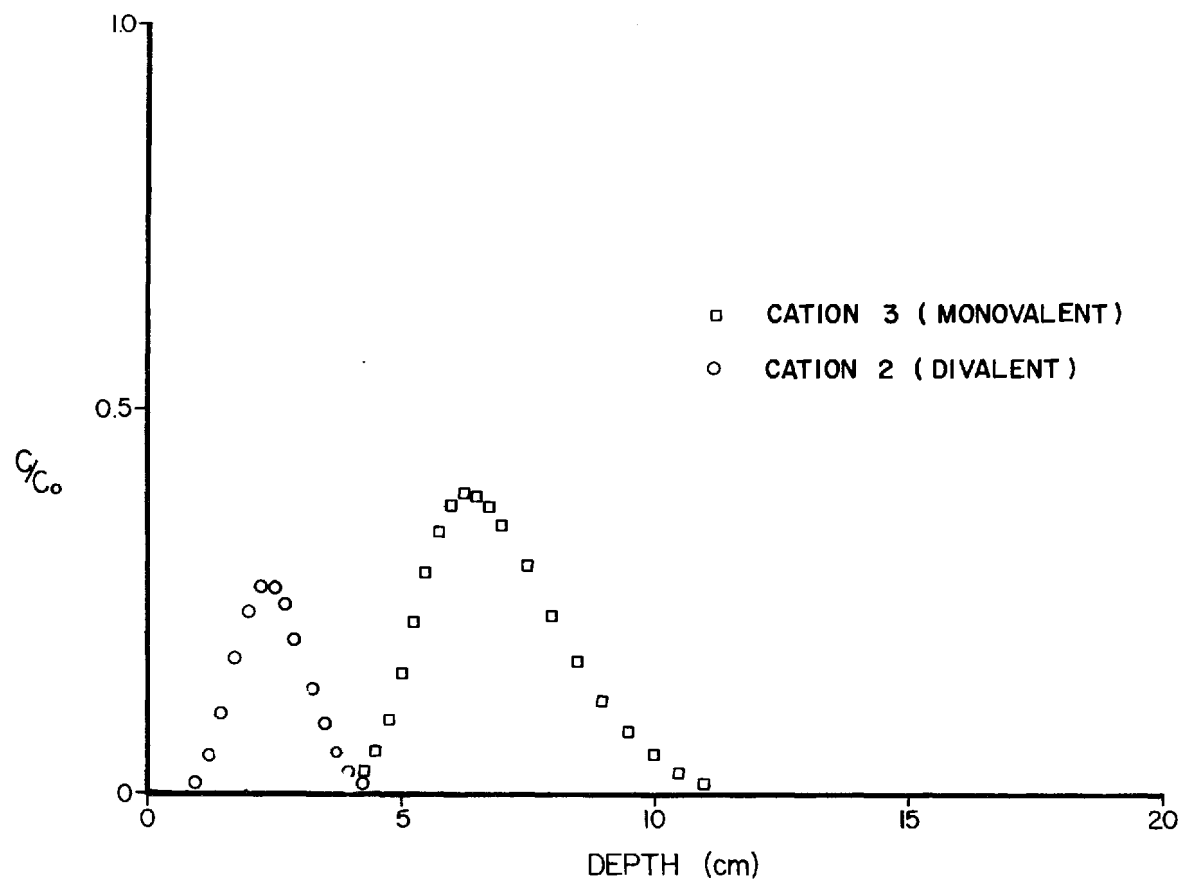


Figure 120. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-12.

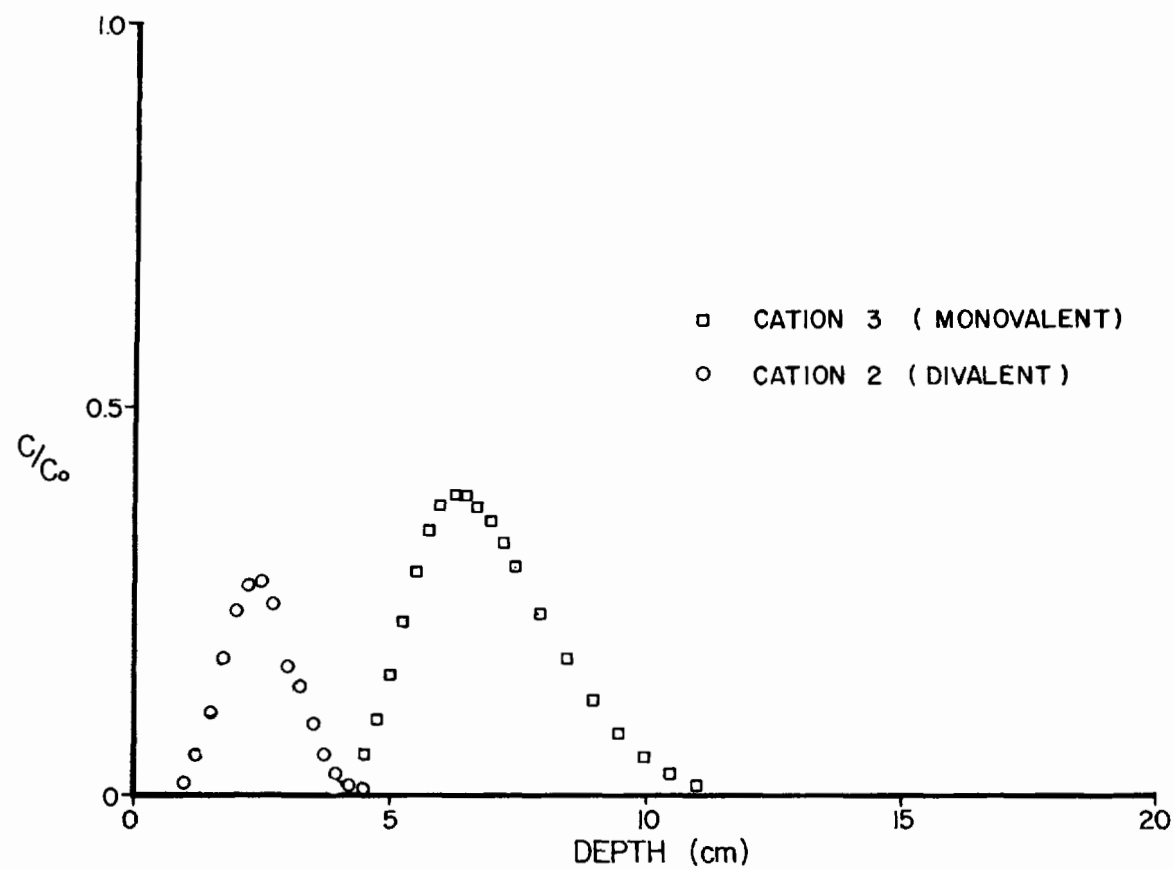


Figure 121. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-13.

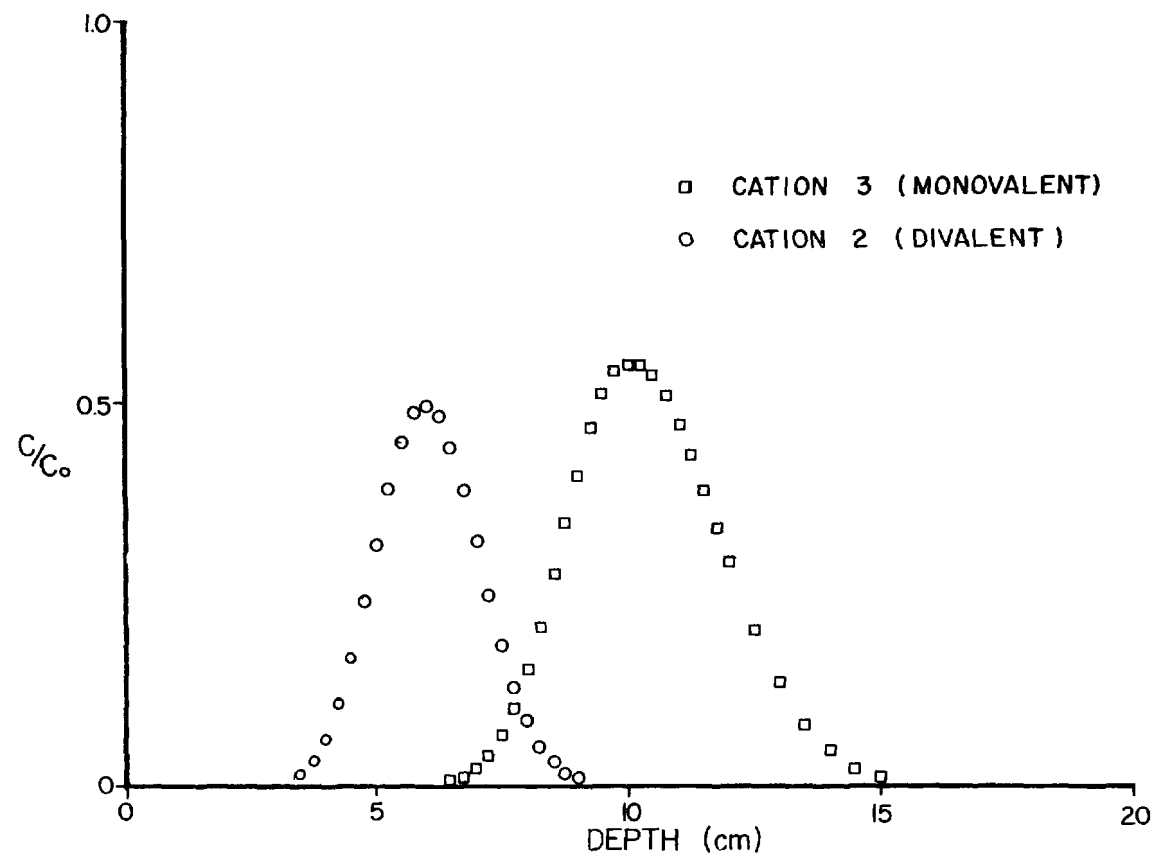


Figure 122. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-14.

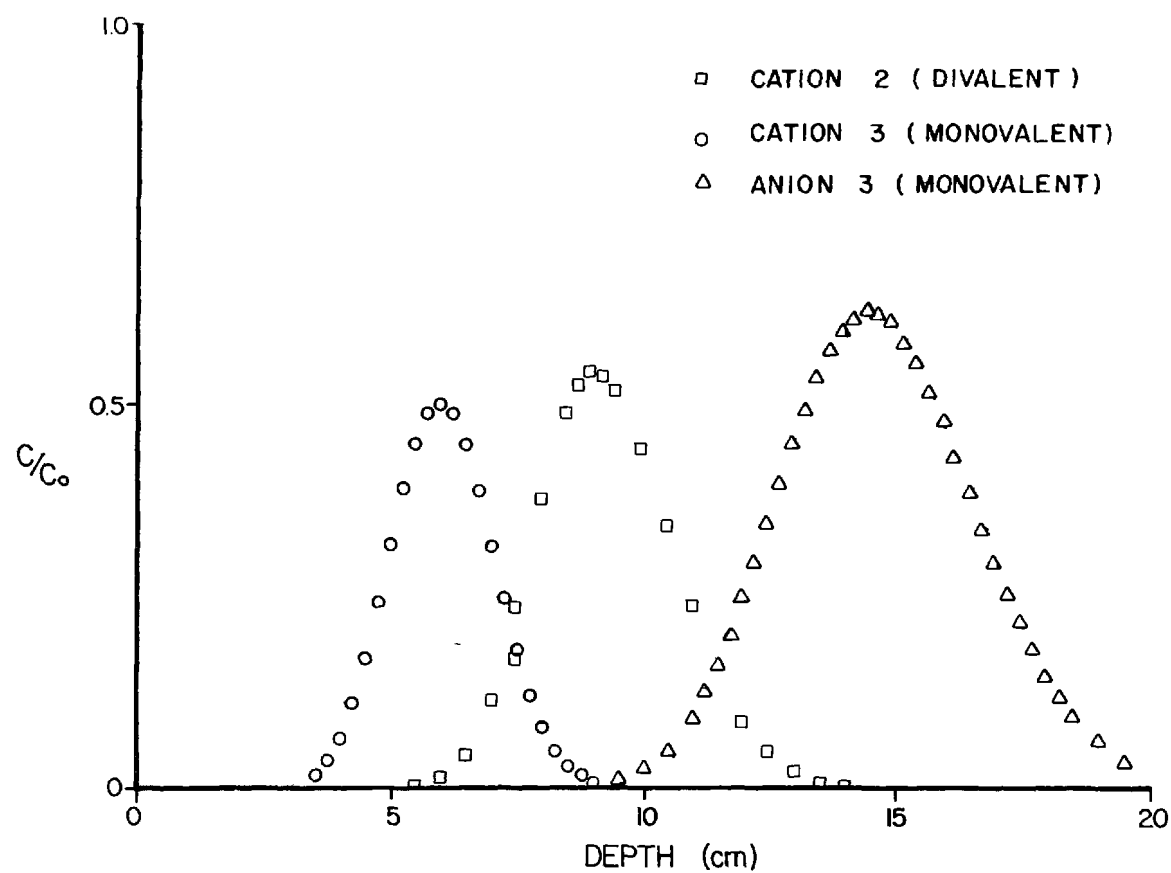


Figure 123. Simulated concentration pulses for cations 2 and 3 and anion 3 for conditions of run R-15.

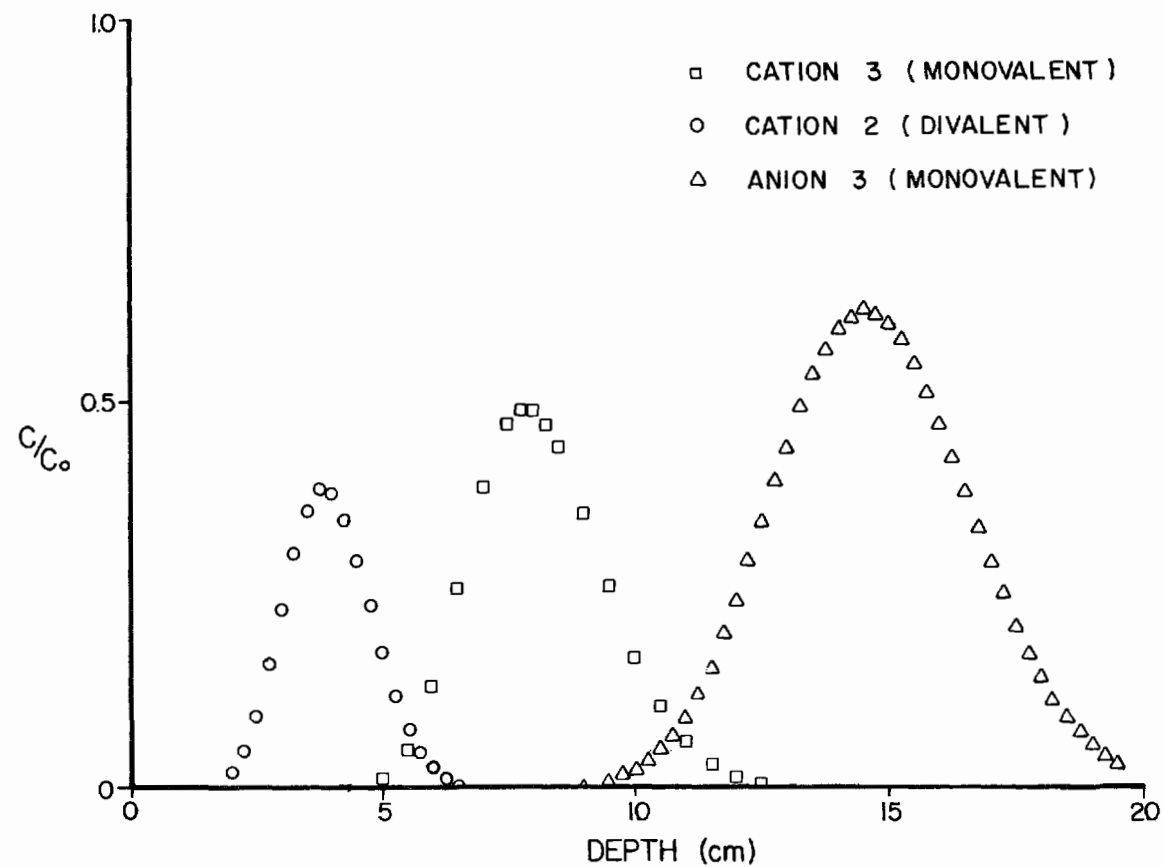


Figure 124. Simulated concentration pulses for cations 2 and 3 and anion 3 for conditions of run R-16.

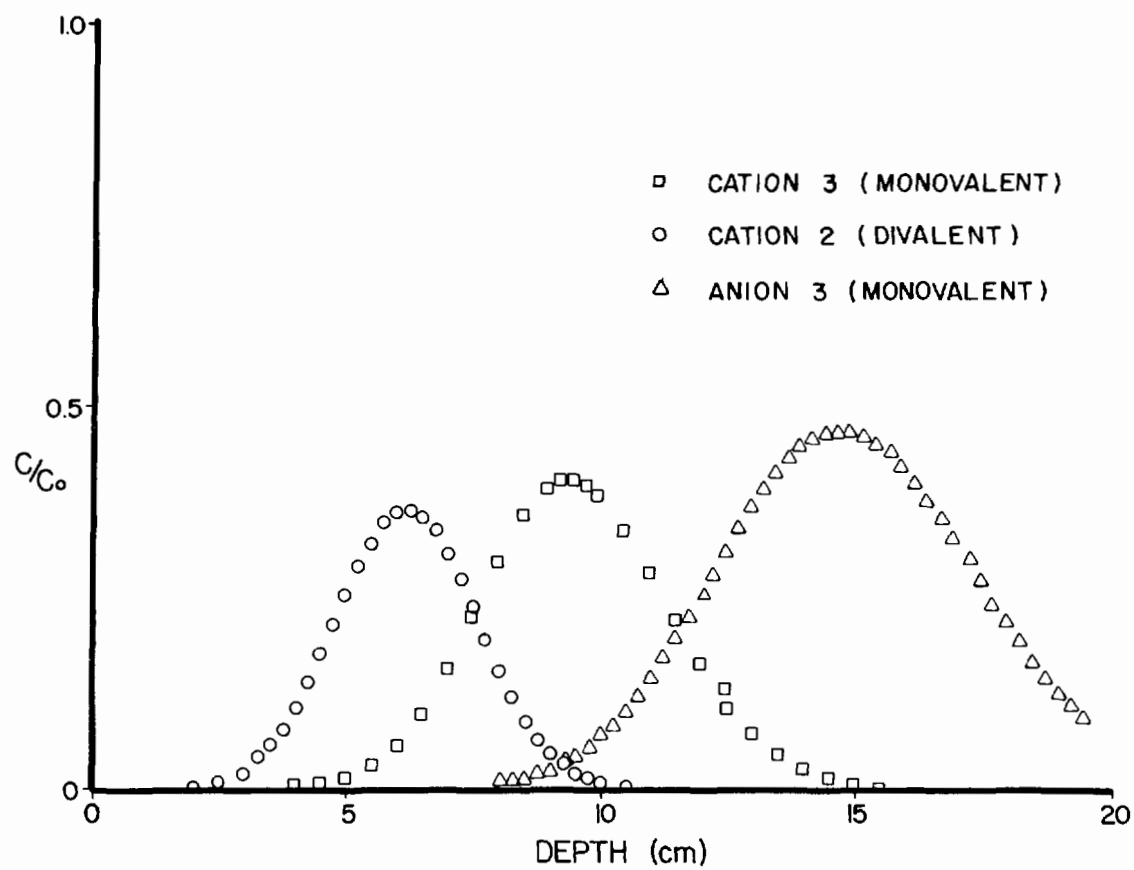


Figure 125. Simulated concentration pulses for cations 2 and 3 and anion 3 for conditions of run R-17.

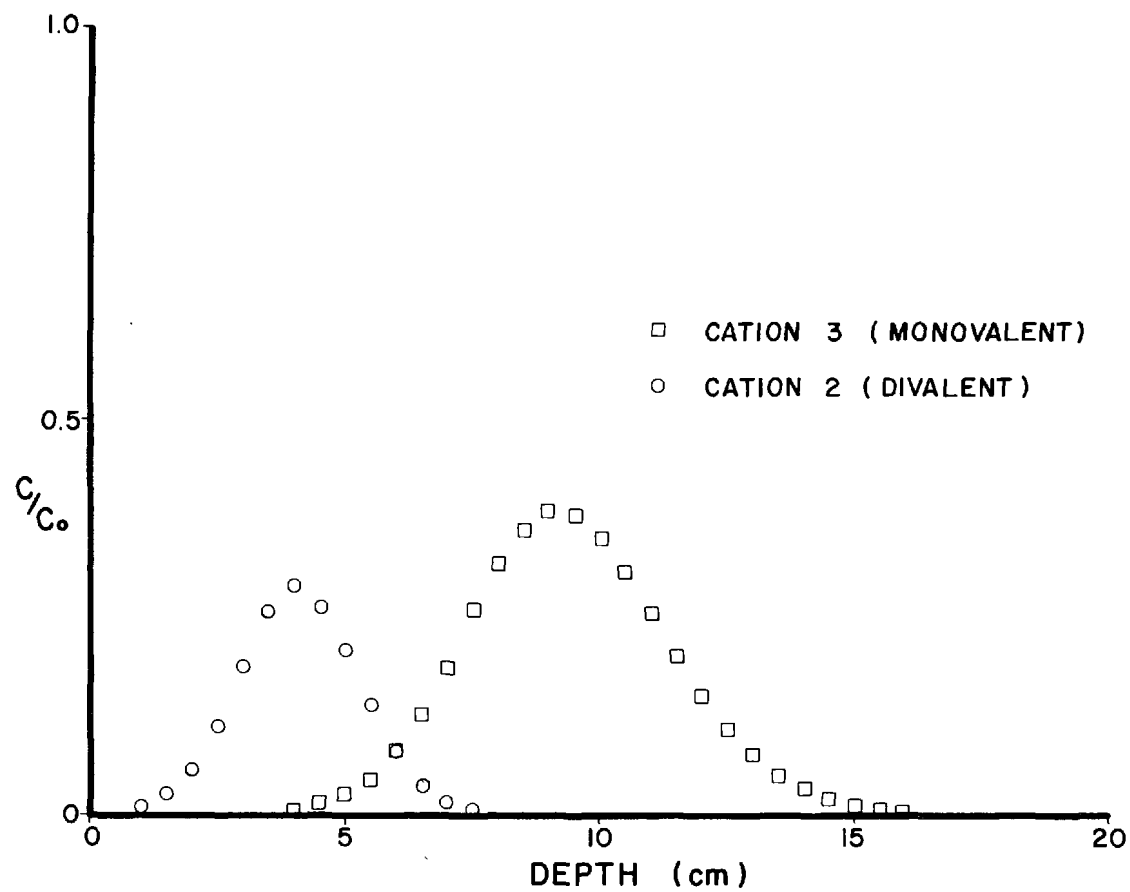


Figure 126. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-18.

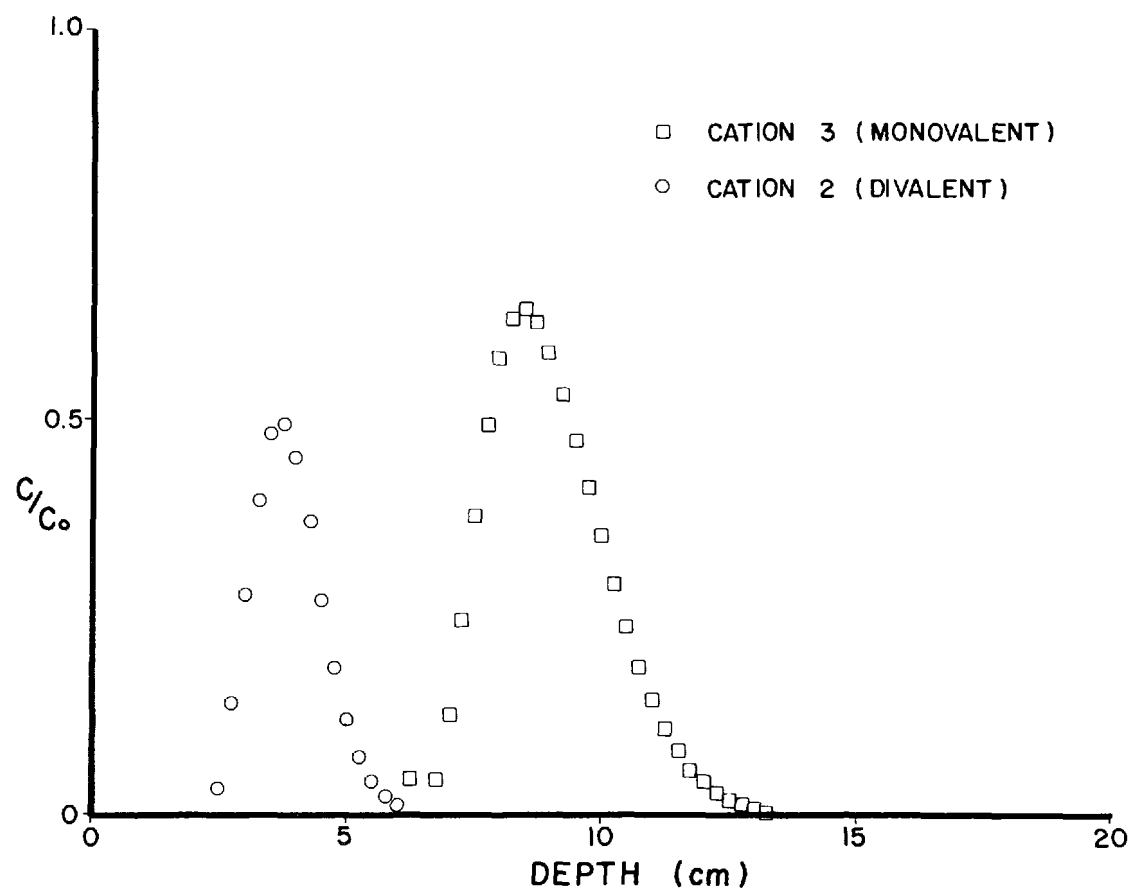


Figure 127. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-19.

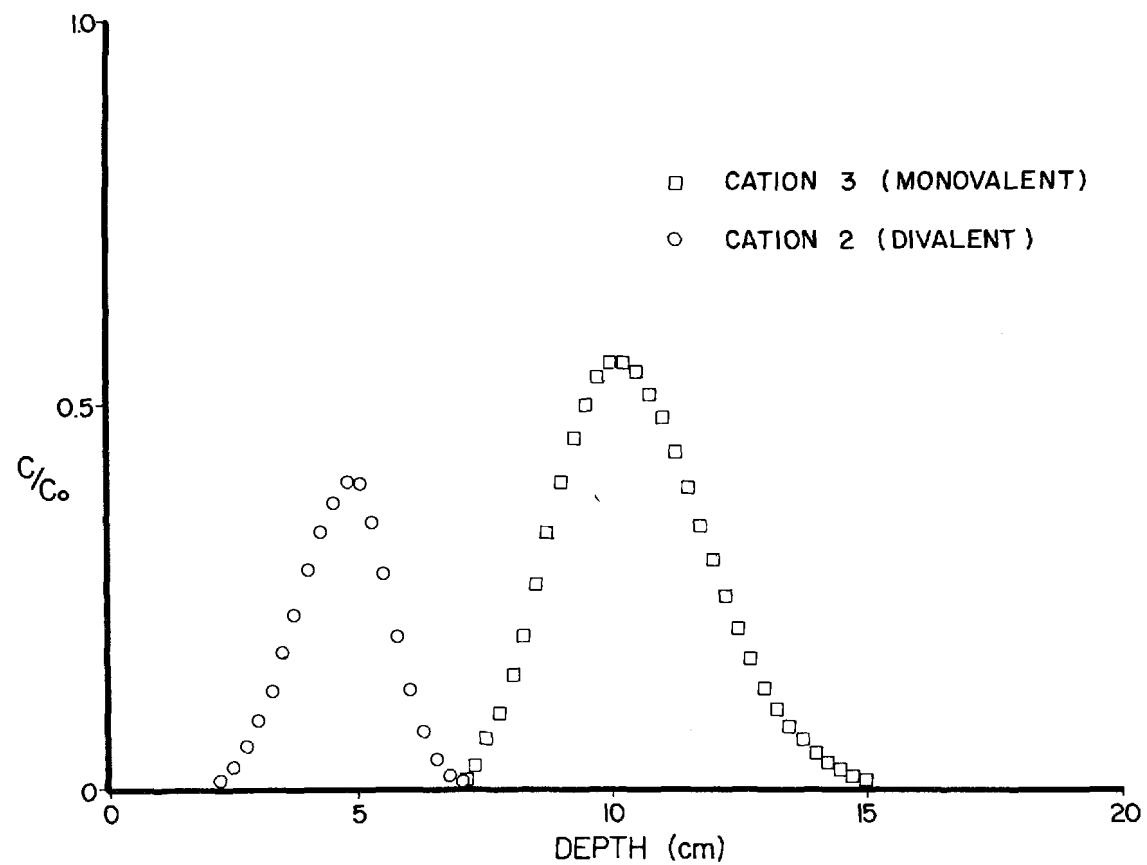


Figure 128. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-20.

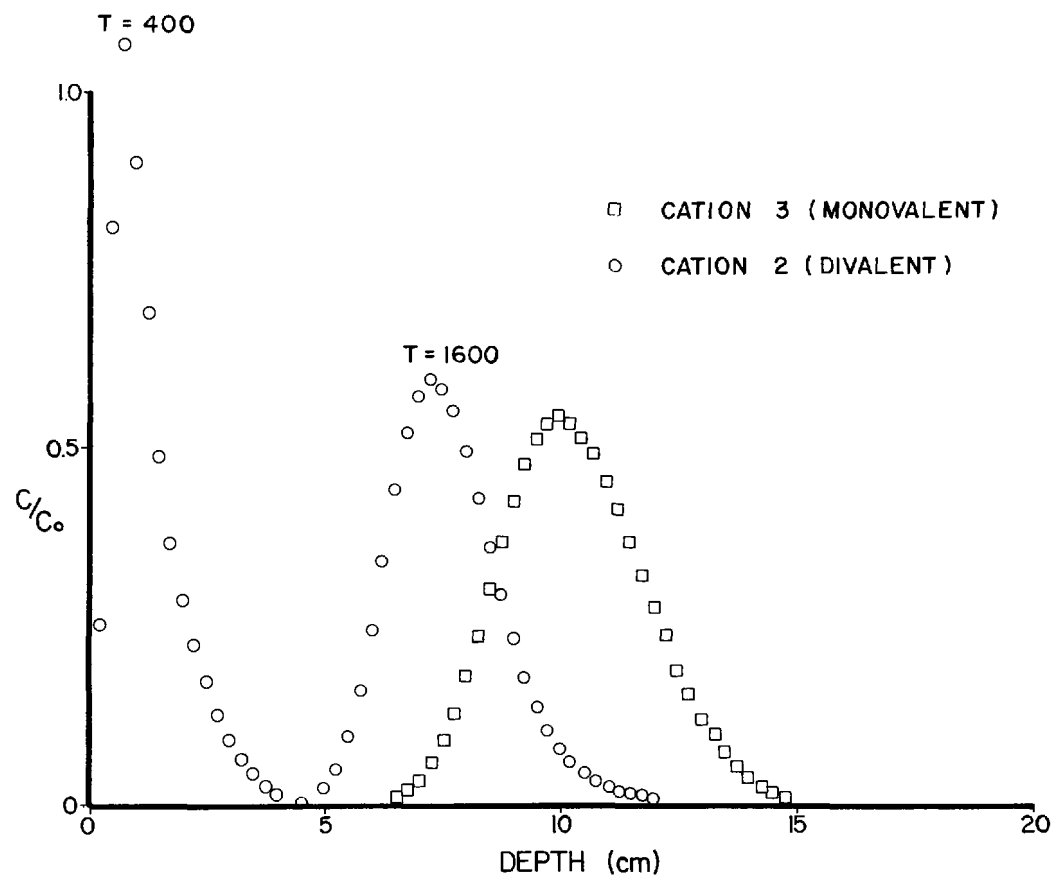


Figure 129. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-21.

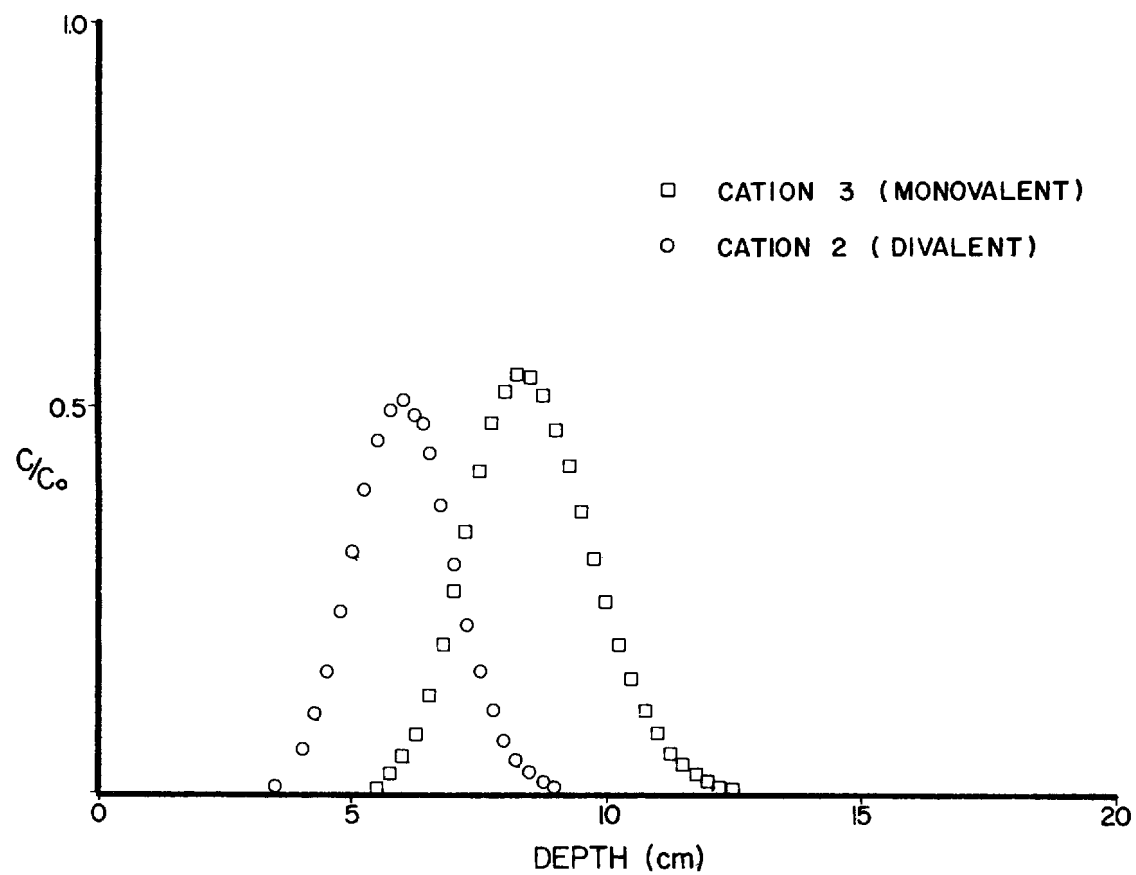


Figure 130. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-22.

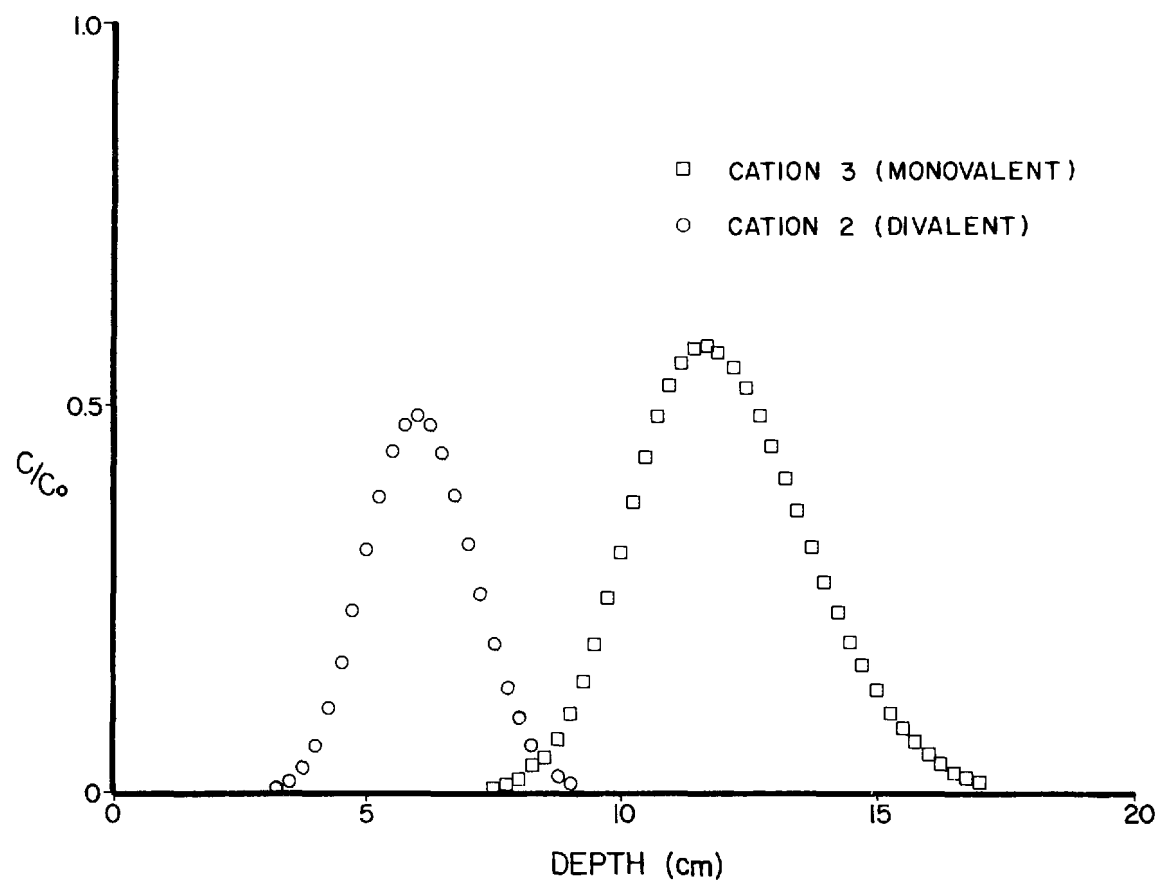


Figure 131. Simulated concentration pulses for cations 2 and 3 for the conditions of run R-23.

were made with $C_{2S} = 0.13$ and cation 3 absent. For runs R-4 and R-5 cation 2 was omitted and C_{2S} was 0.26. The results from R-1 are for $\Delta Z = 0.5$. There is reasonable agreement between the results obtained from the model and those from the independent method, although there is an insufficient number of points to adequately define the simulated pulse configuration after 400 minutes of simulated time. For the larger value of ΔZ , the pulses simulated with the model show considerable smearing and deviation from those obtained by the independent method. Run R-3 was made with $\beta = 0.2$. The results indicate almost no sensitivity to β in this range.

Similar sensitivity to grid spacing, Δz , can be observed in Figure 113 for runs R-4 and R-5 with monovalent cation 3. For $\Delta Z = 1.0$ and $\beta = 0.1$ (R-3) the agreement between the model predictions and the independent method predictions is poor. Much better agreement can be seen for $\Delta Z = 0.5$ and $\beta = 0.2$.

Runs R-6 and R-7 were made with $C_{1I} = 0.05$. For run R-6, C_{2S} was 0.05 with C_3 absent and for R-7, C_{3S} was 0.10 with C_2 absent. Runs R-8 and R-9 were made with $C_{1I} = 0.025$. For R-9 C_{2S} was 0.025 and for R-8, C_{3S} was 0.05. For each of these runs ΔZ was 0.25 and β was 0.5. In each case there is excellent agreement between the results calculated with the model and those obtained from the independent solution method as can be observed in Figures 114 through 117.

Due to the good agreement between model predictions, for $\Delta Z = 0.25$ and $\beta = 0.5$, and those obtained independently, and to the reasonably detailed pulse definitions obtained with $\Delta Z = 0.5$, these values were selected for the remaining runs.

To aid in the analysis of the various effects which were investigated, smooth curves were drawn through the calculated C_2/C_{2S} , C_3/C_{3S} and A_3/A_{3S} points which represent the pulses which appear in Figures 114 through 127. From these graphs estimates were made of the values of certain dimensionless numbers, which to quantify certain characteristics of the simulated pulses that can be observed qualitatively from the figures. The relative pulse heights were calculated according to:

$$h_r = C_{\max}/C_o$$

where C_{\max} represents the estimated maximum at the time of observation value of C_2 , C_3 , or A_3 , and C_S represents the corresponding initial concentration, C_{2S} , C_{3S} , or A_{3S} in the incoming slug of solution.

The relative distance traveled by each pulse was calculated according to:

$$D_r = (D_{c_{\max}} + V \cdot t_p/2)/d_s = (d_{c_{\max}} + d_{tp}/2)/d_s$$

where $d_{c_{\max}}$ is the value of the z coordinate where pulse height was deter-

mined. The distance, d_s , is the distance traveled by an imaginary point in the soil solution from time, $t = 0$, up to the time of observation. For $V = 0.01$ cm/min. and time of observation = 1600 min., d_s has the value of 16.0 cm. The distance, $d_{tp}/2 = Vt_p/2$, allows $t_p/2$ minutes for the center of the original solution slug to reach the column surface. For all of the runs with $V \cdot t_p/2 = 1.5$ cm., two other numbers were recorded to indicate the relative symmetry and spread of the pulses. The relative half-pulse widths S_R and S_L were calculated according to:

$$S_L = [d_{c_{max}} - (d_{c_{max/2}})_L] / (d_{tp}/2)$$

and

$$S_R = [d_{c_{max}} - (d_{c_{max/2}})_R] / (d_{tp}/2)$$

where $(d_{c_{max/2}})_L$ is the z-coordinate of the point on the left side of the pulse where the concentration is $C_{max/2}$, and $(d_{c_{max/2}})_R$ is the corresponding z-coordinate on the right side of the pulse.

The values of d_r , h_r , S_L , and S_R as determined from the simulated pulses observed at 1600 min. for runs R-6 through R-18 are shown for cations 2 and 3 and anion 1 in Table 71.

Effect of a second cation in the slug solution--The tendency of cation 2 to be adsorbed in preference to cation 3 is reflected in Figures 114 and 117, corresponding to runs R-6 through R-9. The cation 3 pulses (Figures 115 and 116) exhibit more spreading, greater distances of travel and greater relative heights than the cation 2 pulses (Figure 114 and 117) for either value of C_{II} represented. The competition of cation 1 on the cation exchange complex keeps relatively greater amounts of cation 3 in solution to be influenced by the solution transport mechanisms of convection and diffusion.

The effect on the cation 3 pulse of including cation 2 in the incoming solution slug can be observed by comparing d_r , h_r , S_L , and S_R (Table 71) for cation 3 from run R-10 with the corresponding values from run R-7. A value of $C_{II} = 0.05$ was used for both runs, while the value of C_{3S} was 0.1 in both cases. For run R-10 cation 2 was included with $C_{2S} = 0.05$. For run R-7, $d_r = 0.59$, while for run R-10, $d_r = 0.66$. The relative heights are 0.49 and 0.43, respectively, for the two runs, and the relative half-widths are $S_L = 0.83$ and $S_R = 1.47$ for R-7, and $S_L = 1.03$ and $S_R = 1.60$ for R-10. Thus, adding cation 2 to the slug solution increases the average velocity of the cation 3 pulse for the 1600 minute simulation period and increases the apparent dispersion of the cation 3 pulse, as manifested by decreased height and increased spread of the pulse. The ratio S_L/S_R , for the cation 3 pulse, is 0.56 for run R-7 and 0.64 for run R-10, indicating that the cation 3 pulse is more symmetric in the presence of cation 3 than in the absence of cation 2 for the conditions of those runs.

TABLE 71. CHARACTERISTICS OF THE ION PULSES FOR THE RUNS LISTED IN TABLE 70. THE PARAMETERS GIVEN INCLUDE THE RELATIVE DISTANCE THE PULSE TRAVELED (d_r), THE RELATIVE PULSE HEIGHT (h_r), THE RELATIVE TAILING PULSE WIDTH AT HALF LENGTH (S_L) AND THE RELATIVE LEAD PULSE WIDTH AT HALF HEIGHT (S_r).

Run	Cation 2				Cation 3				Anion 3			
	d_r	h_r	S_L	S_r	d_r	h_r	S_L	S_r	d_r	h_r	S_L	S_r
R 6	0.35	0.35	0.73	0.73								
R 7					0.59	0.49	0.83	1.47				
R 8					0.44	0.44	0.67	1.43				
R 9	0.25	0.27	0.53	0.53								
R10	0.35	0.37	0.70	0.70	0.66	0.43	1.03	1.60				
R11	0.34	0.39	0.67	0.67	0.64	0.52	0.97	1.23				
R12	0.24	0.29	0.53	0.53	0.49	0.39	0.87	1.27				
R13	0.24	0.29	0.53	0.53	0.49	0.39	0.87	1.27				
R14	0.47	0.50	0.80	0.80	0.73	0.56	1.07	1.30				
R15	0.48	0.51	0.80	0.80	0.66	0.55	0.93	1.17	1.00	0.62	1.53	1.53
R16	0.33	0.39	0.66	0.66	0.59	0.50	0.97	1.17	1.00	0.62	1.53	1.53
R17	0.48	0.37	0.97	1.07	0.68	0.41	1.40	1.50	1.02	0.47	1.97	2.00
R18	0.35	0.30	0.87	0.87	0.67	0.39	1.40	1.53				
R19	0.33	0.50	0.57	0.57	0.62	0.66	0.67	1.13				
R20	0.40	0.41	0.83	0.57	0.73	0.56	1.07	1.30				
R21	0.55	0.60	0.73	0.97	0.70	0.54	1.07	1.37				
R22	0.47	0.51	0.77	0.77	0.62	0.54	0.87	1.00				
R23	0.47	0.49	0.83	0.83	0.83	0.58	1.23	1.43				

The asymmetry of the cation 3 pulse, in the absence of cation 2 (R-7), is due to the preferential adsorption of cation 1 over cation 3. Lai and Jurinak (1972), using simulated concentration fronts to illustrate the effects of preferential adsorption on solution profiles of one cation entering a soil column which was initially saturated with a different cation, demonstrated that the fronts tend to be more diffuse when the original cation is adsorbed in preference to the influent cation. The leading edge of the cation 3 pulse is somewhat analogous to such a front and is therefore more diffuse than the trailing edge of the pulse.

A comparison of Figures 118 and 114 and of d_r , h_r , S_L , and S_R for runs R-10 and R-6 show that the presence of cation 3 has little effect on the cation 2 pulse for the conditions of those runs. For run R-6, $d_r = 0.35$, $h_r = 0.35$, $S_L = 0.73$, and $S_R = 0.73$. The corresponding values for the cation 2 pulse from run R-10 are 0.35, 0.37, 0.70, and 0.70, respectively. In both cases, the cation 2 pulse is apparently symmetric, and there is no difference in the values of d_r obtained for the two runs. The symmetry of the cation 2 pulses reflects the non-preferential adsorption of cation 1 over cation 2, and vice-versa. This quality is "built-in" to all runs for which $E_{12} = 1.0$, since from equation (44) it can be seen that the ratio of the adsorbed phase concentrations, Y_1/Y_2 is equal to the ratio of solution concentrations, C_1/C_2 , when the exchange coefficient E_{12} is unity.

Effect of solution normality--The conditions for runs R-1 through R-23 (Table 70), excluding runs R-10, R-12, and R-13, are such that the total cationic concentrations, expressed in meq/ml, of the initial soil solution is equal to the total cationic concentration of the slug solution. For example, for run R-11, the total cationic concentration of the initial soil solution is $C_T = 2 \cdot 0.050 = 0.100$ meq/ml.

The effect of varying C_T can be observed by comparing the pulses shown in Figure 119 (run R-11) with those presented in Figure 122 (run R-14). For run R-14, C_T is 0.200 meq/ml. The values of d_r , h_r , S_L , and S_R , for cation 2, are 0.34, 0.39, 0.67, and 0.67, respectively, for run R-11 and 0.47, 0.50, 0.80, and 0.80, respectively, for run R-14. For cation 3, the values of d_r , h_r , S_L , and S_R are 0.64, 0.52, 0.97, and 1.23, respectively, for run R-11, and 0.73, 0.56, 1.07, and 1.30, respectively, for run R-14. Thus, for both cations, the effect of increasing C_T is manifested by increases in each of the four parameters. Since increasing C_T , with other factors constant, results in an increase in the proportion of ions present in the solution phase, as well as an increase in the total mass of each ion, the result is a more solution-phase dominated system. The increases in the proportion of cations 2 and 3 which are present in the solution phase are reflected by the increases in h_r , S_L and S_R for the cation 2 and cation 3 pulses. The decreased effect of cation adsorption on the pulses for the larger value of C_T is also reflected in relative distances of travel for the two pulses which are closer to unity for $C_T = 0.2$ meq/ml than for $C_T = 0.1$ meq/ml.

Effect of ionic activity--The effects of ionic activity are included in the model through two mechanisms. One such mechanism is the influence of the activity coefficient, γ , on the ion-pair concentrations X_{11} and X_{21} , as indicated by equations (49) and (50). The other is the influence of γ on the

exchange relationships between cation 1 and cations 3, 4, and 5, as can be seen from equations (56) through (58). The effects due to the latter mechanism can be observed by comparing Figure 119 (run R-11) with Figure 124 (run R-16) and Figure 122 (run R-14) with Figure 123 (run R-15). For runs R-11 and R-16, the total cationic concentration is 0.1 meq/ml, with $C_{1I} = 0.05$ moles/liter, $C_{2S} = 0.025$ moles/liter and $C_{3S} = 0.05$ moles/liter. Run R-11 was made with γ held constant at 1.0 for all depths and times. For run R-16, anions 2 and 3 were included with $A_{2I} = 0.1$ moles/liter and $A_{3S} = 0.1$ moles/liter to provide a total anionic concentration of 0.1 meq/ml for both the original soil solution and the incoming slug solution. The activity coefficient, γ , was calculated according to equation (61) for run R-16.

For cation 2, the values of d_r , h_r , S_L , and S_R are 0.34, 0.39, 0.67, and 0.67, respectively, for run R-11, and 0.33, 0.39, 0.66, and 0.66, respectively, for run R-16. Hence, for the conditions which are common to runs R-11 and R-16, the assumption of unit ionic activity (run R-11) results in a cation 2 pulse which differs little from the pulse simulated with the effects of activity included. For cation 3, d_r , h_r , S_L , and S_R are 0.64, 0.52, 0.97, and 1.23, respectively, for run R-11, and 0.59, 0.50, 0.97, and 1.17, respectively, for run R-16, indicating slight decreases in d_r and h_r , no change in S_L and a decrease in S_R for the case where γ is calculated.

For higher values of total cationic and anionic concentrations, 0.20 meq/ml for runs R-14 and R-15, the effect of ionic activity on the cation 3 pulse is more pronounced. Run R-14 was made with $\gamma = 1.0$ for all depths and times. For run R-15, γ was calculated as a function of the solution concentrations. The values of d_r , h_r , S_L , and S_R are 0.73, 0.56, 1.07, and 1.30, respectively, for run R-14, and the corresponding values for run R-15 are 0.66, 0.55, 0.93, and 1.17, respectively, indicating lower values for d_r , h_r , and S_R when γ is calculated rather than held constant. These effects are qualitatively similar to those observed from runs R-11 and R-16, where the total cationic and anionic concentrations are both 0.1 meq/ml. The value of S_L is lower for γ calculated than for γ held constant at 1.0. Since this effect on S_L is reversed from that observed for runs R-11 and R-16, there is apparently some interaction between the level of solution concentrations and the effect of solution activity on S_L .

For cation 2, the values of d_r , h_r , S_L , and S_R are essentially the same for both runs R-14 and R-15, again indicating little observable effect of solution activity on the cation 2 pulse.

The lower values of relative pulse height and relative distance of travel of the cation 3 pulses which were observed for runs R-15 and R-16 are indicative of decreased preferential adsorption of cation 1 over cation 3 when γ is calculated as opposed to having the constant value, 1.0. The coefficient, γ , occurs in the numerator of the right-hand side of equation (33), which determines the ratio of concentrations in the adsorbed phase, Y_1/Y_3 as a function of $C_1^{1/2}/C_3$. A reduction in the magnitude of γ , for particular values of C_1 and C_3 , therefore results in a reduced value of Y_1/Y_3 . Since for all non-zero values of the solution concentrations of ions which are present the value of γ is less than 1.0 (see equation 61), the preferential adsorption of cation 1 is diminished when γ is calculated rather than assigned

the constant value, 1.0. Nevertheless, the effects of ionic activity on the cation 3 pulse are small compared to the effects of changing the total cationic concentration by a factor of two.

Effect of varying θ and CEC When only cations 1, 2, and 3 are considered simultaneously, equation (54), which expresses conservation of charge on the soil cation exchange complex, can be written:

$$2 \cdot Y_1 + 2 \cdot Y_2 + Y_3 = \frac{\rho_b \cdot \text{CEC}}{100 \cdot \theta} .$$

This equation constitutes the only mechanism through which influence of the cation exchange capacity, CEC, is included in the model. The moisture content, θ , influences model results through equation (88) and also through its effect on the combined diffusion and dispersion coefficient, D_{ci} , as can be seen from equation (78). However, for steady-flow conditions, where θ is constant with depth and time, the value of θ may be changed without affecting the value of the apparent diffusion coefficient, D_{ci}/θ , provided the volumetric flux, q , is also adjusted so that $v = q/\theta$ remains the same. Therefore, for runs made with the same value of V , differences in results from runs using different values of θ are due to equation (88). Moreover, the value of θ by some multiplicative factor should produce the same difference in results between two runs as increasing the value of CEC by the same factor.

The effect of increasing CEC from 10.0 to 20.0 meq/100g, for $\theta = 0.50$, can be observed by comparing Figure 120 (run R-12) with Figure 118 (run R-10). The effect of decreasing θ from 0.50 to 0.25, for CEC = 10.0, can be seen by comparing Figure 121 (run R-13) with Figure 118. The values of C_{1I} , C_{2S} , and C_{3S} are 0.05, 0.05, and 0.10, respectively, for all three runs.

The values of d_r , h_r , S_L , and S_R for run R-10 (CEC = 10.0 and $\theta = 0.50$) are 0.35, 0.37, 0.70, and 0.70, respectively, for cation 2, and 0.66, 0.43, 1.03, and 1.60, respectively, for cation 3. The corresponding values for both runs R-12 (CEC = 20.0 and $\theta = 0.50$) and R-13 (CEC = 10.0 and $\theta = 0.25$) are 0.24, 0.29, 0.53, and 0.53, for cation 2, and 0.49, 0.39, 0.87, and 1.27 for cation 3. Thus an increase in CEC, with θ constant, or a decrease in θ , with CEC and V constant, produces effects which are qualitatively similar to effects due to changes in the total cationic concentration, C_T , which were pointed out earlier. A reduction in θ , with CEC and C_T constant, represents both a reduction in total mass for the three ions in the system and a reduction of the ratio of the ion masses in the solution phase to those in the adsorbed phase. An increase in CEC represents both an increase of the total mass of each ion and an increase of the ratio of the ion masses in the adsorbed phase to those in the solution phase. Thus decreasing θ or increasing CEC results in a more adsorbed-phase dominated system, whereas decreasing C_T also results in more adsorbed-phase dominated systems.

Effect of varying r , the mean pore velocity to apparent diffusion coefficient ratio--The effect of varying the mean pore velocity to apparent diffusion coefficient ratio, r , can be observed by comparing the pulses shown in Figures 126 (run R-18) and 127 (run R-19) with those presented in Figure 119

(run R-11). For all three runs the value of C_{1R} , C_{2S} , and C_{3S} are 0.050, 0.025, and 0.050 moles/liter, respectively. For run R-11 ($r = 10.0$), the values of d_r , h_r , S_L , and S_R are 0.34, 0.39, 0.67, and 0.67, respectively, for cation 2, and 0.64, 0.52, 0.97, and 1.23, respectively, for cation 3. The corresponding values for run R-18 ($r = 5.0$) are 0.35, 0.30, 0.87, and 0.87, respectively, for cation 2, and 0.67, 0.39, 1.40, and 1.53, respectively, for cation 3. For cation 2, the increase in d_r due to changing r from 10.0 to 5.0 represents only 3.0% of the value of d_r corresponding to $r = 10$. For cation 3 the percent increase in d_r is 4.7. Changing r has a much greater effect on the relative heights and relative half-widths of the pulses than on their relative distances of travel. Due to the decrease in r from 10.0 to 5.0 there is a 23.0% reduction in h_r and an increase of 23.0% for both S_L and S_R for cation 2. For cation 3 there is a decrease in h_r of 25.0%, an increase in S_L of 44.4% and an increase in S_R of 24.4%.

For run R-19 ($r = 20.0$), the values of d_r , h_r , S_L , and S_R are 0.33, 0.50, 0.57, and 0.57, respectively, for cation 2, and 0.62, 0.66, 0.67, and 1.13, respectively, for cation 3. Changing r from 10.0 to 20.0 results in a 3.0% reduction in d_r for cation 2 and a 3.1% reduction in d_r for cation 3. For cation 2 a 28.2% increase in h_r and a 15% decrease in S_L and S_R resulted from the change in r from 10.0 to 20.0. For cation 3, the corresponding percent increases in h_r was 46.2. The values of S_L and S_R were decreased by 31.1% and 8.1%, respectively.

Thus, for both cations 2 and 3 the results of changing r are manifested primarily by changes in relative pulse height and in the relative half-widths of the pulses. The most diffuse (lowest h_r and highest S_L and S_R) pulses were obtained for the lowest value of r , as would be expected, due to the greater influence of apparent diffusion for low values of r .

Effect of varying the exchange coefficients, E_{12} and E_{13} --As was previously indicated, the mass-action equation (44) and the Gapon equation (45) are such that cations 1 and 2 are adsorbed preferentially over cation 3, when the values of the exchange coefficients, E_{12} and E_{13} , are both 1.0. The effect of varying E_{12} can be observed by comparing Figures 128 (run R-20) and 129 (run R-21) with Figure 122 (run R-14). For each of the three runs the values of C_{1R} , C_{2S} and C_{3S} are 0.10, 0.05 and 0.10 moles/liter, respectively. The values of E_{12} for runs R-14, R-20 and R-21 are 1.0, 0.5 and 2.0, respectively.

With $E_{12} = 1.0$ (run R-14), the values of d_r , h_r , S_L and S_R are 0.47, 0.50, 0.80 and 0.80, respectively, for cation 2, and for cation 3, their respective values are 0.73, 0.56, 1.07 and 1.30. The corresponding values for $E_{12} = 0.5$ (run R-20) are 0.40, 0.41, 0.83 and 0.57, for cation 2, and 0.73, 0.56, 1.07 and 1.30 for cation 3. The decrease in the values of E_{12} thus had no observable effect on the cation 3 pulse in terms of the four calculated parameters.

The decrease in E_{12} from 1.0 to 0.5 is manifested in the cation 2 pulse by decreases in h_r , d_r , and S_R and by an increase in S_L . The more diffuse trailing edge (Figure 128) is due to the preferential adsorption of cation 2 over cation 1, for $E_{12} < 1.0$. The increased influence of adsorption for the

lower value of E_{12} is also reflected in the decreased relative height and relative distance¹² of travel of the cation 2 pulse.

The effect of varying E_{13} can be observed by comparing Figures 130 (run R-22) and 131 (run R-23) with Figure 122 (run R-14). For $E_{13} = 0.5$ (run R-22), the values of d_r , h_r , S_L , and S_R are 0.47, 0.51, 0.77, and 0.77, respectively, for cation^r2, and 0.62, 0.54, 0.87, and 1.00, respectively, for cation 3.

For $E_{13} = 2.0$ (run R-23), the values of d_r , h_r , S_L , and S_R are 0.47, 0.49, 0.83, and 0.83, respectively, for cation^r2 and 0.83, 0.58, 1.23, and 1.43, respectively, for cation 3. Just as the variation of E_{12} had little effect on the cation 2 pulse, the variation of E_{13} produced only small changes in the observed characteristics of the cation 2 pulse. On the other hand, decreasing E_{13} from 1.0 to 0.5 produced significant decreases in d_r , h_r , S_L , and S_R for the cation 3 pulse, while increasing E_{13} from 1.0 to 2.0 had the opposite effect on each of the cation 3 pulse characteristics.

Comparison of cation 2, cation 3 and anion 3 pulses--For all of the runs, R-1 through R-23, the relative distances of travel, d_r , for the cation 2 pulse are less than the corresponding value for the cation 3 pulse. In all cases d_r for both pulses is less than 1.0. The cation 2 pulses are generally symmetric, with $S_L/S_R = 1.0$, while the cation 3 pulses are skewed to the right, with $S_L/S_R < 1.0$. Exceptions to the symmetry of the cation 2 pulses were noted for values of $E_{12} \neq 1.0$. With one exception ($E_{12} = 2.0$) the relative heights of the cation¹² pulses are less than the relative heights of the cation 3 pulses.

For the conditions of runs R-15 through R-17, the characteristics of the two cation pulses can be compared with those of anion 3 pulses. Run R-16 (Figure 124) was made with lower values of initial soil solution and slug solution concentrations ($C_{1I} = 0.05$, $C_{2S} = 0.025$, $C_{3S} = 0.05$, and $A_{2I} = A_{3S} = 0.1$) than those used for run R-15 ($C_{1I} = 0.1$, $C_{2S} = 0.05$, $C_{3S} = 0.1$, and $A_{2I} = A_{3S} = 0.2$), but with the same value of r ($r = 10.0$) for both runs. Run R-17 (Figure 125) was made with the same values of initial soil solution and slug solution concentrations as run R-15 (Figure 123) but with $r = 5.0$ instead of 10.0. The values of the ion pulse characteristics for each of the three runs can be found in Table 71.

It is evident from Figures 122 through 124 that the anion 3 pulses are further advanced and have greater spread and greater relative heights than either of the cation pulses. The value of d_r for the anion 3 pulse is 1.0 for runs R-15 and R-16 and 1.02 for run R-17, indicating that the apparent velocity of the anion 3 pulse, as determined by the position of the peak concentration, is about the same as the mean solution pore velocity. The slightly higher value of d_r for run R-17 indicates a shift similar to that observed for the cation 2 and cation 3 pulses. Indeed, for $r = 10.0$ d_r is 0.33 for cation 2 and 0.70 for cation 3, while for $R = 5.0$ d_r for cation 2 is 0.35 and 0.72 for cation 3.

None of the characteristics of the anion 3 pulse show any sensitivity to the differences in concentrations between runs R-15 and R-16, whereas it was

previously indicated that the cation pulses are strongly affected by such differences.

Reducing r from 10.0 (Figure 122) to 5.0 (Figure 124) resulted in changes in the anion 3 pulse which are qualitatively similar to the changes observed in the cation pulses for the same reduction in r . The relative height of the anion 3 pulse decreased from 0.12 to 0.47. The relative half-widths increased from $S_L = 1.52$ and $S_R = 1.52$ to 1.97 and 2.00, respectively.

Observed increases in pulse height--Shown in Figure 128 are results corresponding to run R-21 for cations 1 and 2 after 1600 minutes of simulated time and for cation 2 after 400 minutes of simulated time. The predicted relative pulse height for cation 2, corresponding to 400 minutes, is greater than 1.0, indicating a temporary local increase in the concentration of cation 2 above C_{2S} for this run. At first, it was thought that the indicated increase in concentration was numerically induced by the computational procedure in a manner similar to the overshoot observed and discussed earlier for finite-difference solutions to equation (4). However, it was previously shown that overshoot associated with finite-difference approximations to equation (4) is sensitive to the grid-spacing, ΔZ , and/or the time step size, Δt , used in conjunction with a particular value of $r = v/D$. Additional runs made with varying combinations of smaller values of Δt and ΔZ than those used for run R-21 failed to verify that numerically induced overshoot was the cause of the increased concentration observed for run R-21. Runs with $\Delta Z = 0.125$ and $\beta = 0.05$ produced results very similar to those shown in Figure 126 ($\Delta Z = 0.25$ and $\beta = 0.5$), and in no case was the maximum predicted concentration after 400 minutes less than that indicated in Figure 126.

An additional run was made with $C_{2S} = 0.1$ moles/liter, $C_{3S} = 0.0$ moles/liter, $A_{2I} = 0.2$ moles/liter and $A_{3S} = 0.2$ moles/liter and with the values of all the other parameters identical to those used for run R-21. The cation 2 and anion 3 pulses observed after 400 minutes of simulated time are shown in Figure 132. The relative heights of both pulses are less than 1.0. If the excessive value of the concentration of cation 2 observed in Figure 126, for $C_{2S} = 0.05$ moles/liter, was due to poor response of the finite-difference approximations to the discontinuity in concentrations at $t = 0$ and $Z = 0$, the adverse effect should have been more pronounced with $C_{2S} = 0.10$ moles/liter. Moreover, the effect should have also been observed in the anion 3 pulse. Also, the results for cation 2 shown in Figure 131 were found to agree with results obtained from the independent numerical solution to the two-cation problems represented by that run.

For the conditions of run R-21, observations of the cation 2 and cation 3 pulses after each time step from $t = 0$ up to $t = 400$ minutes indicated that h_i for the cation 3 pulse also exceeded 1.0 at early times. These observations indicate that similar phenomena may have occurred for the conditions of some of the other runs but were simply not observed.

A plausible explanation of the temporary increases in concentrations of cations 2 and 3 can be given as follows: as the solution containing cations 2 and 3 enters the soil column, the two influent cations begin to replace cation 1 on the exchange complex, and the solution concentrations of both

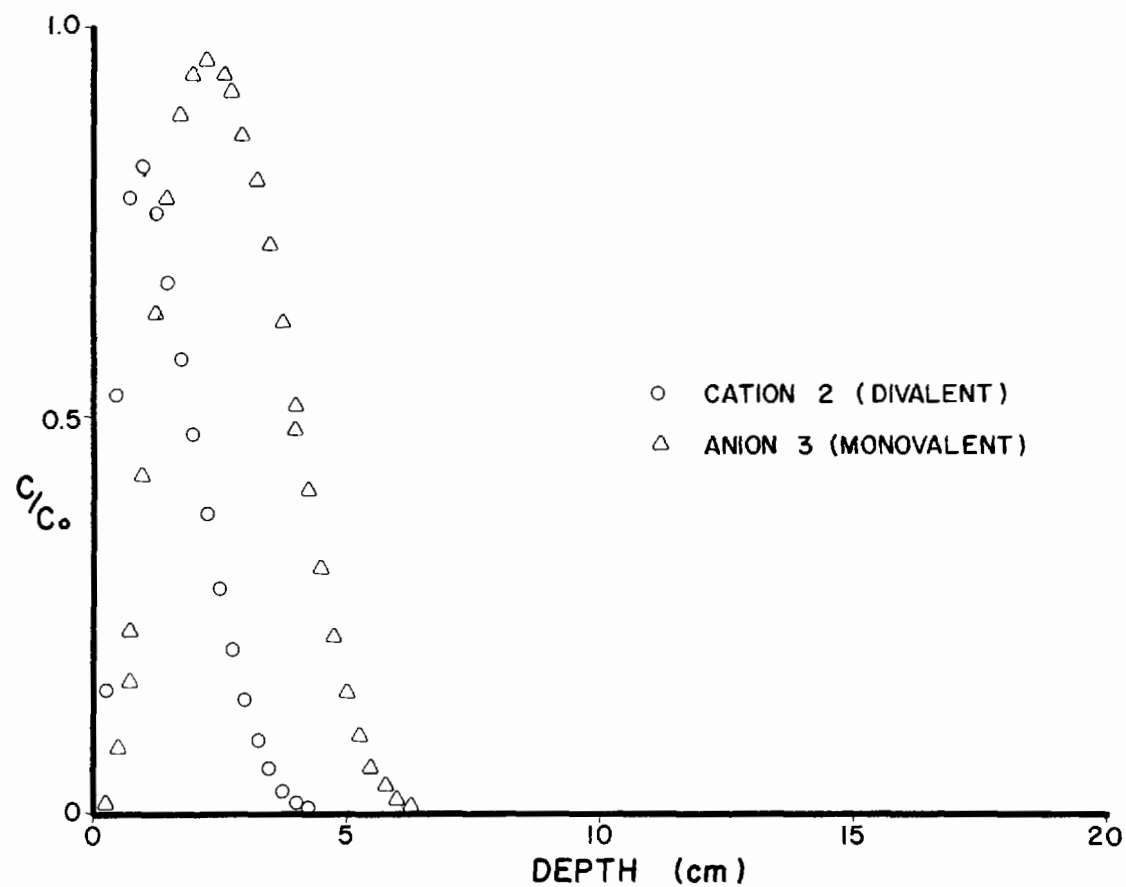


Figure 132. Simulated concentration pulses for cation 2 and anion 3. The conditions are the same as run R-21 except that $C_{3s} = 0.0$, $C_{2s} = 0.1$ and $A_{3s} = 0.2$. Observation time is $T = 400$ minutes.

cations begin to increase at shallow depths in the column. Since cation 3 is less preferred on the exchange complex than cation 2, its solution concentration approached C_{3S} , the slug solution concentration, more rapidly than the concentration of cation 2 approaches C_{2S} .

Provided the pulse time t_p is long enough, the concentration of cation 3 eventually reaches C_{3S} . Whether the concentration of cation 3 continues to increase after it reaches C_{3S} , or instead, begins to decrease depends not only on the flux gradient but also on release or adsorption of cation 3 on the exchange complex. The adsorption of cation 3 on the exchange complex, at the expense of cation 2, provides a potential source of cation 3 to the solution. Thus the solution concentration of cation 3, at a given depth in the column, may continue to rise even when $C_3 > C_{3S}$. However, such a rise cannot continue indefinitely since the exchange complex source is limited and since diffusion and/or dispersion effects oppose increases of C_3 above C_{3S} .

Summary--

Several simulation runs were made using the computer model of ion transport and chemical equilibrium. Simulated concentration pulses were used to compare results obtained from the model with results obtained from an independent numerical method of solution of two-cation problems. The model results agreed with results from the independent method.

Qualitative assessments were made of the effects of changes in the values of certain model parameters on the simulated concentration pulses. To aid in this analysis, four pulse characteristics: relative distance of travel, d_r , relative pulse height, h_r , and relative half-widths of the pulses, S_L and S_R , were defined and calculated for each simulated pulse. Specific effects considered were: effect of a second cation in the slug solution, effect of total cationic concentration, effect of solution activity, effect of mean pore velocity to apparent diffusion coefficient ratio, effect of cation exchange capacity and volumetric moisture content, and effect of exchange coefficients.

For the runs made, the greatest changes in the relative distance of travel, d_r , for the cation 2 pulse occurred as a result of varying the total cationic concentration ($\Delta d_r = 0.13$, where Δd_r represents the absolute value of the change in d_r due to the change in concentration), CEC or θ ($\Delta d_r = 0.11$), and E_{12} ($\Delta d_r = .08$). Little or no change in d_r for the cation 2 pulse resulted from changing E_{13} ($\Delta d_r = 0.0$), including the effect of the activity coefficient, γ ($\Delta d_r = 0.01$), including cation 2 in the incoming slug solution ($\Delta d_r = 0.0$), or changing 4 ($\Delta d_r = 0.01$).

The greatest changes in d_r for the cation 3 pulse occurred as a result of varying CEC and θ ($\Delta d_r = .17$), changing the total cationic concentration ($\Delta d_r = 0.09$) and including cation 2 in the incoming slug solution ($\Delta d_r = 0.07$). Smaller changes in d_r resulted from changes in E_{12} ($\Delta d_r = 0.03$), changes in r ($\Delta d_r = 0.03$), and including the effects of γ ($\Delta d_r = 0.03$).

The greatest changes in relative height for both the cation 2 and cation 3 pulses occurred as a result of varying r ($\Delta h_r = .11$ for cation 2 and $\Delta h_r = .14$ for cation 3). Varying the total cationic concentration had an equally pronounced effect on the height of the cation 2 pulse ($\Delta h_r = 0.11$) but a smaller effect on the height of the cation 3 pulse ($\Delta h^r = 0.06$).

No change in the relative height of the cation 2 pulse resulted from including the effects of γ in the model at either level of total cationic and anionic concentrations used. Little or no change in h_r for the cation 3 pulse resulted from changing E_{13} ($\Delta h_r = 0.021$), changing E_{12} , ($\Delta h_r = 0.02$), or including the effects of γ at the low level of total cationic and anionic concentrations ($\Delta h_r = 0.01$). The effects on h_r on other changes were intermediate between the extremes indicated above for both cations.

The factors which produced the greatest changes in the half-widths of the cation 2 pulses were a change in the total cationic concentration ($\Delta S_L = \Delta S_R = 0.13$), a change in CEC or θ ($S_L = S_R = 0.17$), a change in r ($\Delta S_L = \Delta S_R = 0.2$) and a change in E_{12} ($\Delta S_L = 0.03$ and $\Delta S_R = 0.23$). Among the factors having the greatest effects on the half-widths of the cation 3 pulses were changes in r ($\Delta S_L = 0.43$ and $\Delta S_R = 0.30$), changes in CEC or θ ($\Delta S_L = 0.16$ and $\Delta S_R = 0.33$), changes in E_{13} ($\Delta S_L = 0.20$ and $\Delta S_R = 0.30$), including cation 2 in the slug solution ($\Delta S_L = 0.20$ and $\Delta S_R = 0.13$) and changing the total cationic concentration ($\Delta S_L = 0.14$ and $\Delta S_R = 0.17$).

By comparison, including the effects of γ resulted in no change in S_L or S_R for cation 2 and resulted in only small changes in S_L and S_R for cation 3 ($\Delta S_L = 0.03$ and $\Delta S_R = 0.07$ at the low level of solution normality and $\Delta S_L = 0.07$ and $\Delta S_R = 0.03$ at the high level of solution normality). Including cation 2 in the incoming slug solution also produced little change in either S_L or S_R for cation 2 ($\Delta S_L = S_R = 0.03$), as did changing E_{13} ($\Delta S_L = \Delta S_R = 0.03$). Changing E_{12} likewise produced only small changes in S_L and S_R for cation 3 ($\Delta S_L = 0$ and $\Delta S_R = 0.07$).

For most of the runs, the cation pulses were nearly symmetric having equal S_L and S_R values. Asymmetric cation 2 pulses resulted when values of the exchange coefficient, E_{12} , were different from 1.0. For $E_{12} = 0.5$, the cation 2 pulses were skewed to the left with $S_L > S_R$. For $E_{12} = 2.0$, the cation 2 pulses were skewed to the right, with $S_L < S_R$. On the other hand, the cation 3 pulses were asymmetric and skewed to the right ($S_R > S_L$) for all of the runs made.

For both cations 2 and 3, the respective heights and half-widths of the pulses were appreciably affected by changes in r , whereas the relative distance of travel was only slightly perturbed by changes in r . In contrast, changes in the total cationic concentration and changes in CEC or θ resulted

in appreciable changes in all four of the calculated pulse characteristics for both cations. Similarly, including cation 2 in the slug solution with cation 3 resulted in appreciable changes in d_r , h_r , S_L and S_R for cation 3. On the other hand, the addition of cation 3 to the slug solution containing cation 2 had little effect on any of the cation 2 pulse characteristics.

Comparisons among divalent cation (cation 2), monovalent cation (cation 3), and monovalent anion (anion 3) pulse characteristics revealed that the anion pulse was characterized by the greatest distance of travel and greatest spread (highest values of S_L and S_R) of the three ion pulses. The cation 2 pulse was generally characterized by the shortest distance of travel, smallest relative height, and least spread of the three ions. The only observed exception to the above general trend occurred for the case, $E_{12} = 2.0$, where the cation 2 pulse had a greater relative height (but smaller distance of travel) than the cation 3 pulse.

For the conditions of one of the runs, it was found that the relative heights of the cation 2 and cation 3 pulses each exceeded 1.0 for short periods of time. The results from additional test runs indicated that the temporary increases in pulse height were due to some interaction between cations 2 and 3, rather than due to numerical overshoot.

Conclusions--

From the results of the simulation runs, the following conclusions were drawn:

- (1) Based on comparison of model results with those from an independent method, the combined multi-equation and chemical equilibrium approach (represented by the model) provides a valid solution procedure for multi-ion transport problems where chemical equilibrium can be assumed.
- (2) The comparatively minor effects of the presence of the monovalent cation (3) on the characteristics of the divalent cation (2) pulse indicates that the presence (in small quantities) of less preferred cations may have a negligible effect on the transport of more strongly adsorbed cations for certain applications. However, the effects of strongly adsorbed cations on the movement of less preferred cations probably cannot be ignored.
- (3) The relatively minor responses of both cation pulses to the inclusion of a calculated activity coefficient indicate that a precise determination of the activity coefficient is probably unnecessary when only the effect on adsorption is important. This is not necessarily true for instances where ion pairing or solubility-precipitation mechanisms are important.
- (4) The effects of apparent diffusion were shown to be important with respect to the height and spread of both cation pulses for the runs for which the velocity to apparent diffusion coefficient ratio was varied.
- (5) Since varying the exchange coefficient for either of the cations (monovalent or divalent) produced only minor changes in the characteristics

of the pulse for the ion not associated with that coefficient, the accuracy of exchange coefficients for cations other than those being monitored in a given experiment may not be critical.

The above conclusions (2) - (5) are tentative due to the limited number of runs which have been made. They are strictly applicable only to the type of transport problem represented by the runs. However, the conclusions drawn from this set of runs are indicative of further investigations that may prove fruitful with respect to information about multi-ion transport phenomena. A different type of transport problem which should receive attention in the future is a pulse problem where the slug solution contains only one cation but where the soil initially contains two cations in varying ratios.

Determination of Equilibrium Coefficients

Preliminary Experiment--

The preliminary experiment on a Beaumont clay (sample 1) to ascertain Ba^{++} interferences indicated considerable antagonism for Na^+ , K^+ and Ca^{++} analyses (Figures 133, 134 and 135, respectively). However, Mg^{++} was not greatly affected by the high concentration of Ba^{++} (Figure 136). Cation compositions on the soil were determined by comparison to standard dilution curves using $BaCl_2$ as the diluent to circumvent laborious corrections. This was justified due to the linearity of the interference with increased cation concentration. Solution concentrations were determined by comparison to the standard dilution curves employing water as the diluent. It was assumed that the salts, other than Ba , comprising the solution matrix were too low in concentration to interfere with the respective cationic analyses.

Solution and adsorbed cation concentrations at equilibrium for the various treatments are given in Table 72. The solution concentrations shown here were adjusted to 46% moisture by weight from the moisture contents used in the experiment. The effective CEC of the soil can be expressed as the sum of the individual cations adsorbed. Total cations summed over the 17 treatments averaged 47.38 meq/100g with a standard deviation of 1.23 meq/100g. The small standard deviation indicates that the 4 cations measured adequately described the cationic distribution for the soil. Also there was a complete conservation of charge; or, an equivalent increase in one cation necessitated an equivalent decrease of one or more of the other cations.

Generally, an increase in the solution concentration due to a treatment input resulted in an increase in the amount adsorbed. Correlation coefficients were positive and relatively high except for Ca . The negative and relatively low value for Ca suggested that adsorbed Ca decreased with increased solution Ca . An inspection of the data (Table 73) shows that even when Ca was applied at the 100 ppm level the increase on the exchange complex was quite small. The greatest increase occurred at the 100 ppm treatment of Na , K and Ca . Due to the relatively high correlation values, an analysis of covariance was determined to evaluate the significance of the different treatments on adsorbed cations (Appendix O). Results of this test indicated that no real differences existed for the cations adsorbed at the different solution concentrations, although the error for adsorbed values was adjusted for differences in the solution values. Thus, the variability between solu-

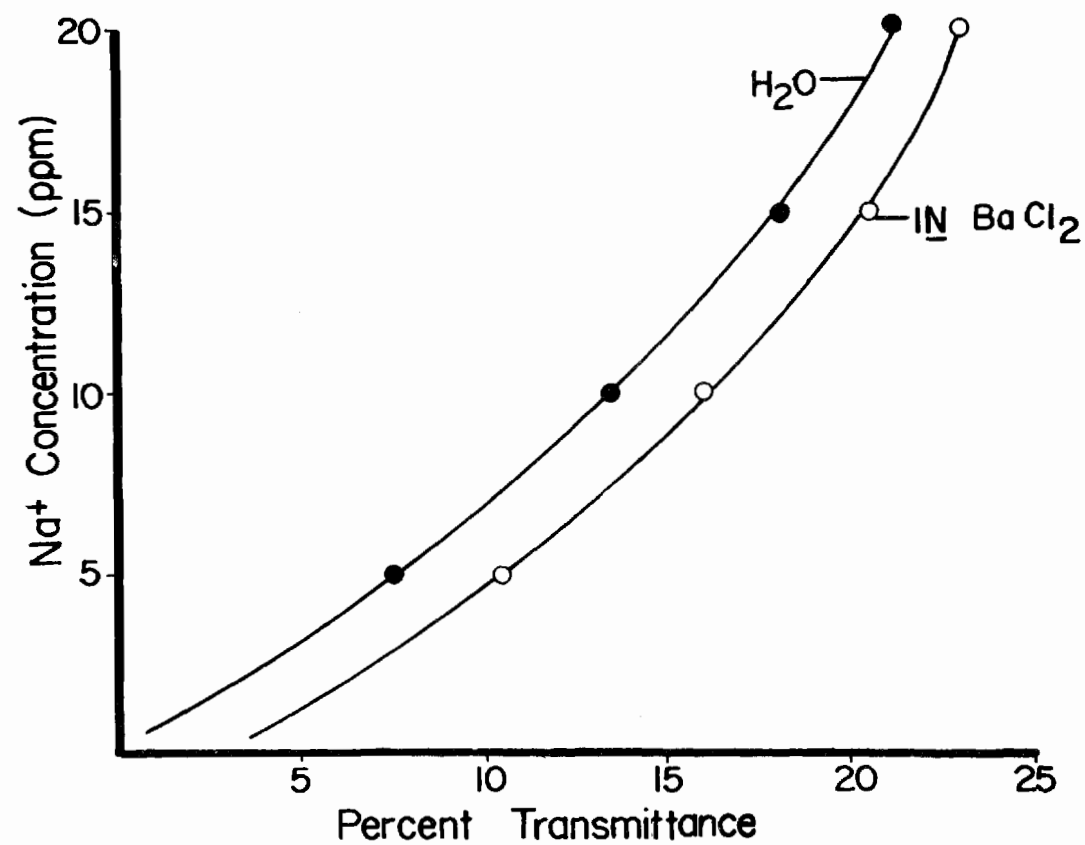


Figure 133. Standard dilution curves for Na⁺ employing distilled deionized H₂O, and 1 N BaCl₂ as diluents for soil sample 1.

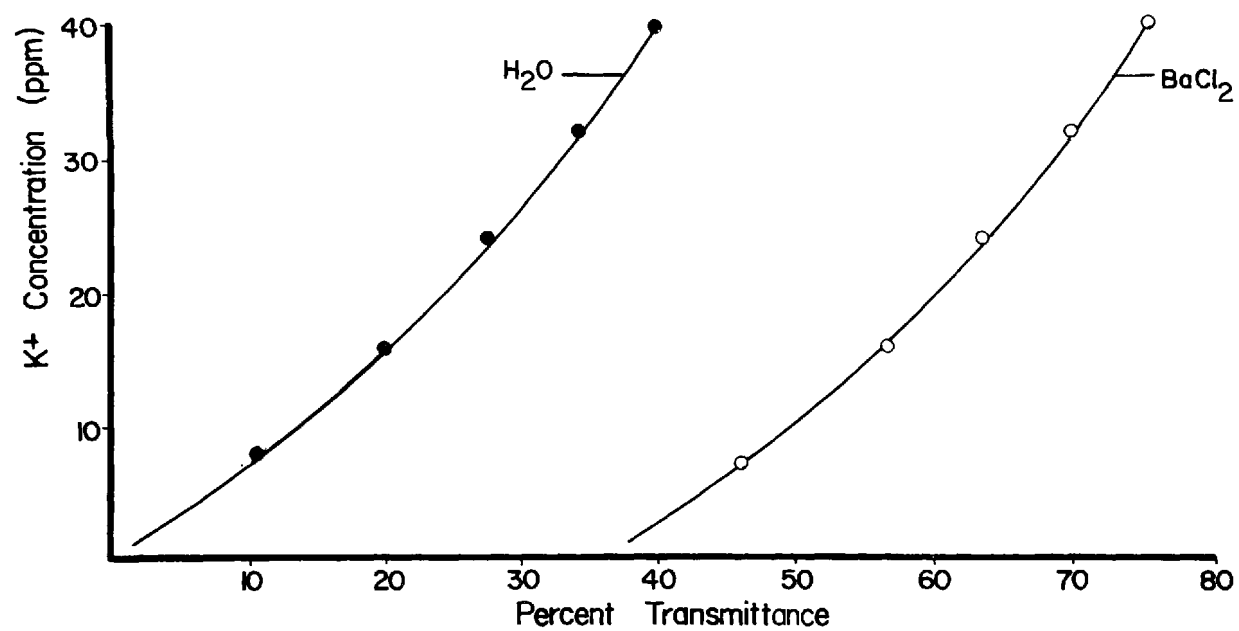


Figure 134. Standard dilution curves for K⁺ employing distilled deionized H₂O, and 1 N BaCl₂ as diluents for soil sample 1.

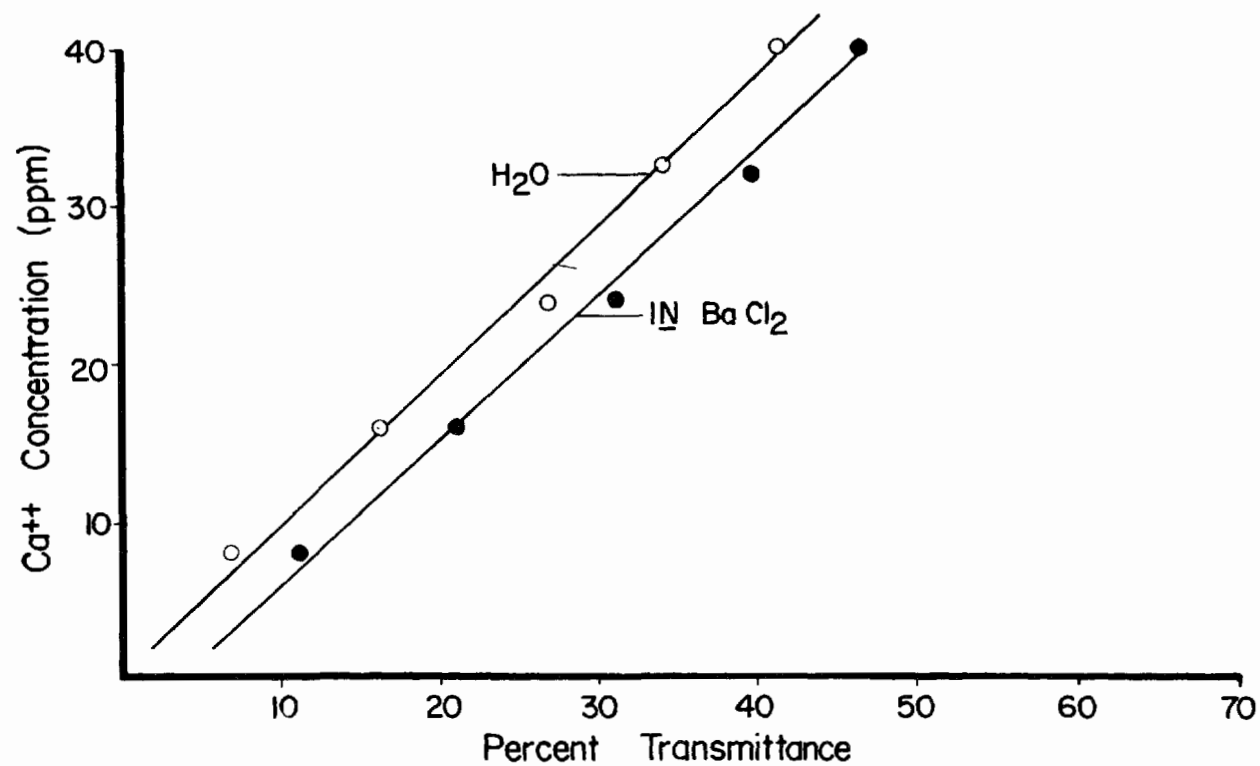


Figure 135. Standard dilution curves for Ca⁺⁺ employing distilled deionized H₂O, and 1 N BaCl₂ as diluents for soil sample 1.

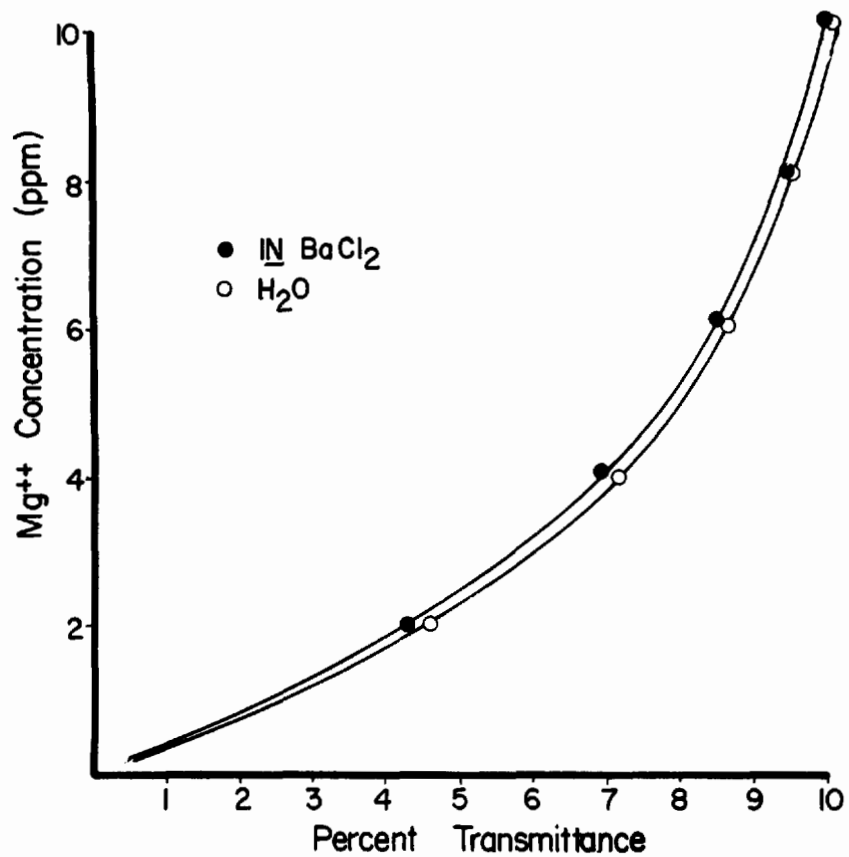


Figure 136. Standard dilution curves for Mg⁺⁺ employing distilled deionized H₂O, and 1 N BaCl₂ as diluents for soil sample 1.

TABLE 72. EQUILIBRIA SOLUTION AND ADSORBED CATION CONCENTRATIONS, OF A BEAUMONT CLAY SOIL, ESTABLISHED AT VARIOUS SOLUTION CATIONIC TREATMENTS IN SAMPLE 1

Treatment	Solution Cations				Exchangeable Cations				Total
	Na	K	Ca	Mg	Na	K	Ca	Mg	
ppm	mmoles/liter				meq/100g				
none	8.48	0.77	1.04	1.55	0.41	0.56	29.16	15.34	45.47
50 Na + 50 K	30.81	6.98	8.12	5.24	1.65	1.59	28.53	15.01	46.78
100 Na + 100 K	54.14	15.64	16.93	8.34	2.88	2.51	27.74	14.73	47.86
50 Na + 50 Ca	11.11	2.33	13.51	6.79	2.54	0.49	30.64	14.87	48.54
100 Na + 100 Ca	67.06	3.64	41.18	14.07	2.30	0.44	30.76	14.22	47.72
50 Na + 50 Mg	38.38	3.34	27.55	16.98	1.33	0.45	26.78	18.31	46.87
100 Na + 100 Mg	60.60	4.36	52.37	40.74	2.59	0.40	24.56	20.52	48.07
50 K + 50 Ca	9.60	10.04	19.14	9.31	0.36	1.39	29.95	14.64	46.34
100 K + 100 Ca	11.34	18.21	44.37	13.58	0.28	2.40	30.47	14.26	47.41
100 K + 100 Mg	11.11	19.72	53.94	44.14	0.29	2.22	24.38	19.96	46.76
50 Ca + 50 Mg	9.69	3.40	43.50	25.71	0.36	0.45	27.95	17.52	46.28
100 Ca + 100 Mg	13.13	3.99	98.60	58.69	0.20	0.42	25.61	18.91	45.14
100 Na + 100 K + 100 Mg	67.67	19.64	57.42	47.04	2.26	2.34	24.11	19.95	48.66
100 Na + 100 Ca + 100 Mg	67.47	4.72	95.70	58.20	2.28	0.39	25.87	18.96	47.50
100 Na + 100 K + 100 Ca	58.88	19.70	46.40	17.95	2.66	2.33	32.76	11.02	48.77
100 K + 100 Ca + 100 Mg	13.64	22.09	98.89	53.35	0.18	2.23	25.59	19.39	47.39
100 K + 100 Na + 100 Ca + 100 Mg	59.59	21.97	101.79	39.29	2.63	2.24	24.38	20.65	49.90

tion values was too great even with the adjustment. The reason for this was probably due to the fact that Na, K and Mg were adsorbed at the expense of Ca only to a point. That point was determined by the amounts of Ca released, and the competitiveness of Ca for readsorption.

Multiple linear regressions were determined for a specific cation adsorbed as a function of the solution concentrations, as described by the following equation:

$$Y \text{ (cation adsorbed)} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4$$

where:

$$\begin{aligned} x_1 &= \text{Na}^+ \text{ in solution} \\ x_2 &= \text{K}^+ \text{ in solution} \\ x_3 &= \text{Ca}^{++} \text{ in solution} \\ x_4 &= \text{Mg}^{++} \text{ in solution.} \end{aligned}$$

TABLE 73. CORRELATION COEFFICIENTS DETERMINED FOR ADSORBED CATION CONCENTRATIONS AS A FUNCTION OF CORRESPONDING SOLUTION CONCENTRATION IN SOIL SAMPLE 1

Cationic Specie	Correlation Coefficient
Na	0.83
K	0.94
Ca	-0.58
Mg	0.78

A summarization of these calculations is presented in Table 74. Sodium adsorbed was positively affected by Na in solution and negatively affected by Mg in solution. However, the low regression coefficient for Na in solution suggests that Na is not preferentially adsorbed in the soil except for a few exchange sites. This is completely consistent with what was observed in the natural cationic distribution with no treatment. Although the Na solution value was much greater than any of the other 4 cations, it was adsorbed by less than 1.0% of the exchange sites. Conversely, K adsorbed appeared to be largely a function of K in solution with a small active competition from Ca. The magnitude of the K adsorbed was approximately 2.4 meq/100g at the 100 ppm K treatment levels regardless of the other cations in combination, suggesting a site specificity for K in the Beaumont clay soil at about 5% of the effective CEC (Table 72). However, only 1% of the exchange sites were occupied by K in the natural soil (Table 72, no treatment). This is probably due to the low solution values which prevail in the area, and points out the need for K fertilization.

Calcium, as shown in Table 72, was positively affected by Ca in solution,

but negatively affected by K and Mg in solution, particularly that of Mg. Magnesium adsorbed was largely a function of the Mg in solution, tempered somewhat by the K and Ca solution levels. Naturally occurring ratios

TABLE 74. MULTIPLE LINEAR REGRESSION COEFFICIENTS FOR THE CATIONS ADSORBED AS A FUNCTION OF SOLUTION CONCENTRATIONS IN SOIL SAMPLE 1.

Cation adsorbed		X_1 (Na in solution)	X_2 (K in solution)	X_3 (Ca in solution)	X_4 (Mg in solution)
Y	b_0	b_1	b_2	b_3	b_4
Na	0.562	0.038	-0.002	-0.001	-0.014
K	0.464	0.000	0.119	-0.007	-0.001
Ca	30.393	-0.006	-0.029	0.055	-0.181
Mg	14.433	-0.003	-0.022	-0.035	0.167

(Table 72, no treatment) appear to be inconsistent with the results of the equilibrium experiment. Calcium occupies 64% of effective CEC compared to 34% for Mg, yet the solution values are essentially the same. The equilibrium study suggests that Mg would be preferentially adsorbed, or at least more strongly adsorbed than Ca. Perhaps Ca comprised a much greater percentage of the primary minerals from which the soil was weathered, and with very little K or Mg in solution, the ratio has remained high for Ca.

Adsorbed values for the various cations were calculated by the equations summarized in Table 74, and correlated with the values experimentally observed (Figures 137 - 140). The good correlations suggest that the equations adequately describe the equilibrium obtained under laboratory conditions.

Experiment with Field Soil--

The second equilibrium study was conducted on Beaumont clay soil (sample 2) collected within the field plot area. Treatments consisted of various concentrations of monovalent cations (Table 75), since this better approximated fertilizer amendments employed in the field study. These values were adjusted to 46% gravimetric moisture content.

As noted in the previous experiment, the total cations adsorbed remained relatively constant over the various treatments and averaged 20.55 meq/100g with a standard deviation of 1.26 meq/100g. Samples receiving the NH_4^+ treatments were not used in the average since NH_4^+ was not determined and obviously occupied some of the exchange sites.

Cationic concentrations of Na and K in solution were highly correlated to the corresponding amounts adsorbed (Table 76). Calcium and magnesium were negatively correlated indicative of the fact that they were exchanged by the

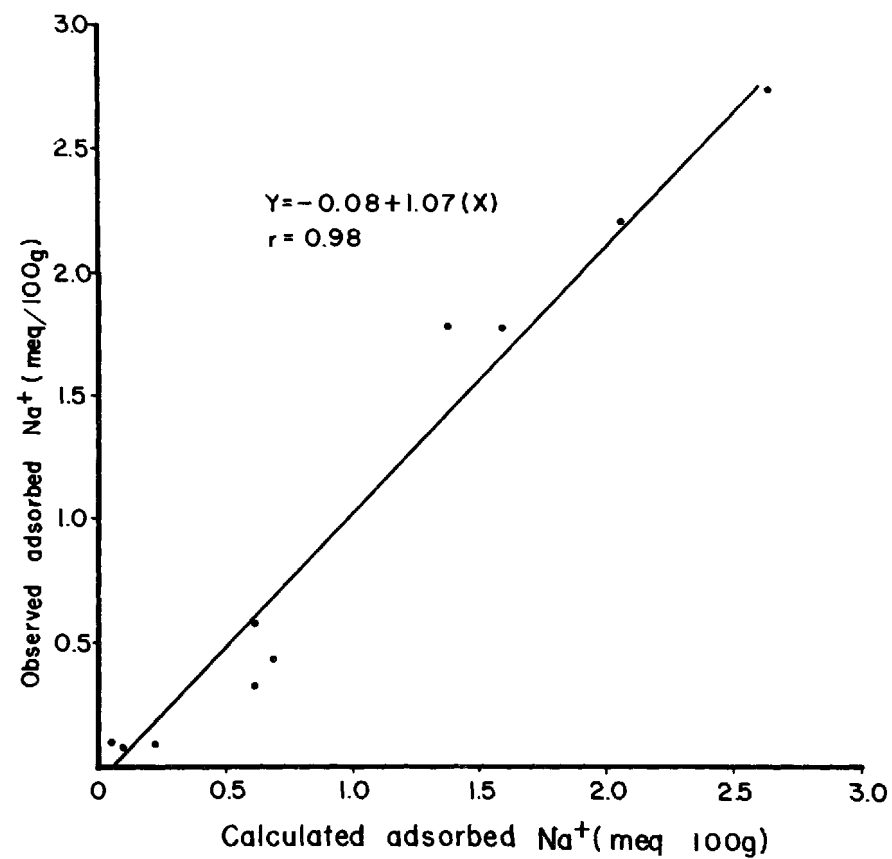


Figure 137. Linear correlation of calculated and experimentally observed Na^+ adsorbed for soil sample 1.

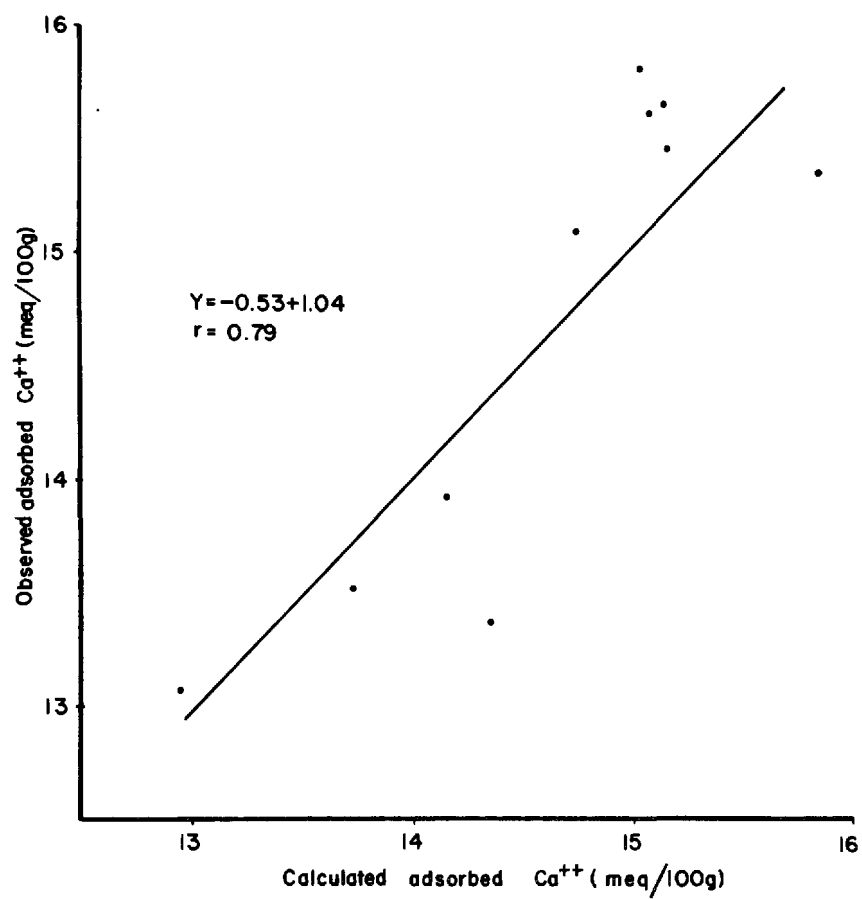


Figure 138. Correlation of calculated and experimentally observed Ca^{++} adsorbed for soil sample 1.

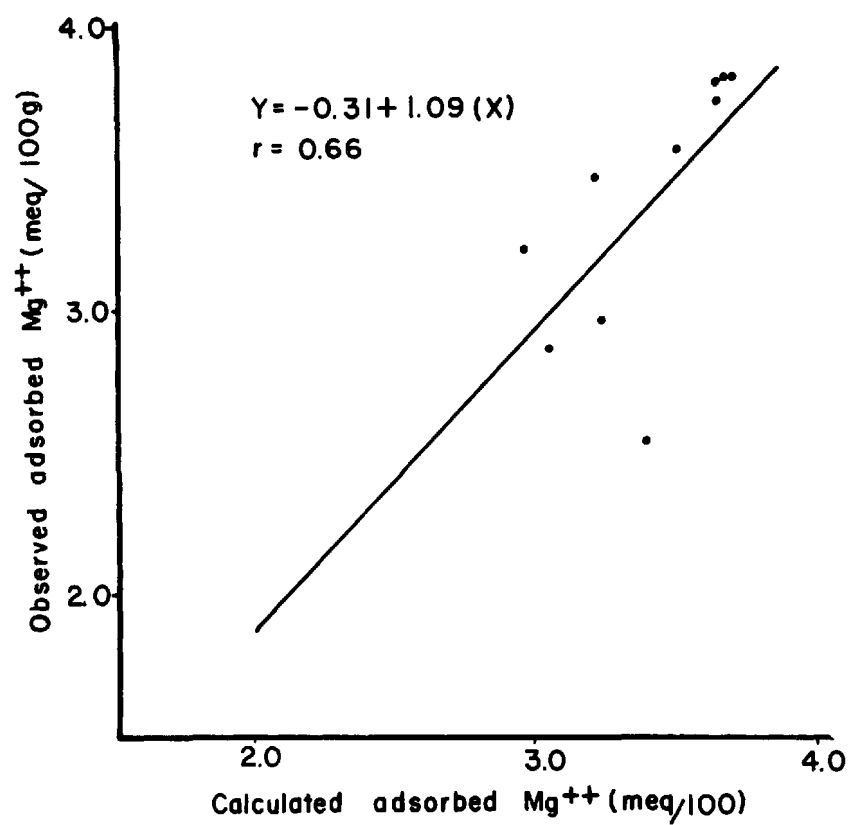


Figure 139. Linear correlation of calculated and the experimentally observed Mg^{++} adsorbed for soil sample 1.

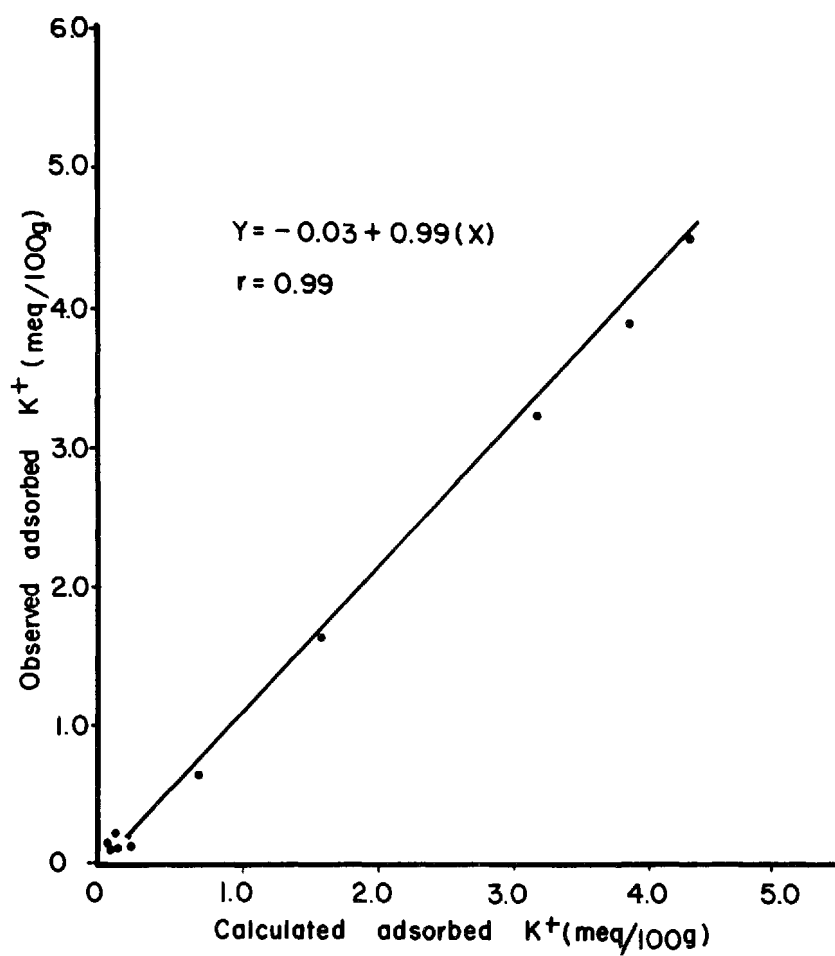


Figure 140. Correlation of calculated K^+ adsorbed and that determined experimentally for soil sample 1.

TABLE 75. EQUILIBRIA SOLUTION AND ADSORBED CATION CONCENTRATIONS OF A BEAUMONT CLAY SOIL, ESTABLISHED AT VARIOUS SOLUTION CATIONIC TREATMENTS IN SAMPLE 2

Treatment ppm	Solution Cations		Ca ⁺⁺	Mg ⁺⁺	Adsorbed Cations				Total
	Na ⁺	K ⁺			Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	
	mmoles/liter				meq/100 g				
none	1.88	0.64	1.42	1.00	0.31	0.21	13.37	3.74	17.63
80 Na ⁺	41.90	1.39	3.97	1.51	1.77	0.15	15.82	3.83	21.57
120 Na ⁺	62.11	1.57	7.71	2.27	1.77	0.12	15.66	3.83	21.38
160 Na ⁺	88.73	2.03	9.35	2.83	2.22	0.12	15.46	3.66	21.46
240 Na ⁺	132.12	2.38	13.38	4.25	2.66	0.13	15.36	3.57	21.72
130 K ⁺	2.96	30.23	21.09	5.00	0.10	1.67	15.10	3.48	20.35
260 K ⁺	3.25	72.68	41.95	8.69	0.09	3.27	13.93	3.23	20.52
390 K ⁺	3.25	124.43	58.96	10.77	0.08	4.55	13.06	2.89	20.58
40 Na ⁺ + 65 K ⁺	24.63	11.24	11.45	3.31	0.44	0.65	15.66	2.55	19.30
85 Na ⁺ + 325 K ⁺	54.22	86.05	54.42	9.92	0.58	3.95	13.52	2.98	21.03
60 NH ₄ ⁺	2.46	1.98	16.04	4.11	0.12	0.10	15.66	3.69	-----
120 NH ₄ ⁺	3.94	2.50	34.58	7.18	0.11	0.07	14.64	3.40	-----
180 NH ₄ ⁺	2.56	2.67	46.49	9.35	0.09	0.06	13.62	3.06	-----

Na and K treatments.

An analysis of covariance was determined to evaluate the significance of the Na, K, and NH_4 treatments on the adsorbed cations (Appendix O, Table O-2). Results indicated that the treatments had no significant influence on the adsorbed cation distribution. This suggests that the solution values must exceed those obtained in this study to influence the distribution, where divalent cations dominate the base saturation.

TABLE 76. CORRELATION COEFFICIENTS FOR ADSORBED CATION CONCENTRATIONS AS A FUNCTION OF CORRESPONDING SOLUTION CONCENTRATIONS IN SOIL SAMPLE 2

Cationic Specie	Correlation coefficient
Na^+	0.93
K^+	0.99
Ca^{++}	-0.72
Mg^{++}	-0.64

Multiple linear regression analyses were determined for each cation adsorbed as a function of the solution concentrations. These data are summarized in Table 77. Adsorbed Na^+ increased with increased Na^+ and K^+ in solution but decreased as the solution Ca^{++} and Mg^{++} increased. This suggests that at the level of Na^+ applied in this study there would be considerable antagonism or competition from exchanged Ca^{++} and Mg^{++} . This is consistent with what one would expect due to differences in valence. However, it appears incongruent with the trends observed for K. The coefficients obtained for the solution cations suggest that K^+ adsorption pivoted around Ca^{++} desorption, but with considerable competition with Mg^{++} for adsorption sites. The coefficients from the multiple linear regressions suggested considerable antagonism of Ca^{++} by Mg^{++} , and vice versa upon exchange by the monovalent treatments' ions.

Values for the adsorbed ions were calculated using the coefficients (Table 76) and solution concentrations (Table 75) and linearly correlated to those actually observed (Figures 141, 142, 143, and 144). The calculated values for Na and K adsorbed agreed closely with the observed values. Calculated values for Ca and Mg deviated considerably from those observed, suggesting that the equations developed do not adequately describe sorption-desorption trends for the divalent cations, and precludes the extrapolation of these equations to the field results.

TABLE 77. MULTIPLE LINEAR REGRESSION COEFFICIENTS FOR THE CATIONS ADSORBED AS A FUNCTION OF SOLUTION CONCENTRATIONS IN SOIL SAMPLE 2

Cation Adsorbed		S_1 (Na in solution)	X_2 (K in solution)	X_3 (Ca in solution)	X_4 (Mg in solution)
y	b_0	b_1	b_2	b_3	b_4
Na ⁺	0.737	0.023	0.025	-0.042	-0.125
K ⁺	0.116	-0.007	-0.003	0.095	-0.075
Ca ⁺⁺	14.509	0.003	-0.018	-0.071	0.451
Mg ⁺⁺	3.844	0.003	0.001	0.038	-0.296

EVALUATION OF EXCHANGE COEFFICIENTS

The concentrations of ions in the solution in equilibrium with the soil samples and the concentrations on the exchange sites were used to calculate the exchange coefficients. For calcium-sodium exchange, the coefficients were calculated by a least squares fit to the following equation:

$$\frac{Ca_{abs}}{Na_{abs}} = K\gamma \sqrt{\frac{Ca_{sol}}{Na_{sol}}}$$

where:

$$\gamma = e^{-1.171\sqrt{2(Ca+Na) + .5(Na+K) + C1}}$$

Corresponding equations were used for Ca-K, one Ca-NH₄. For the Ca-Mg exchange the following relation was used:

$$\frac{Ca_{abs}}{Mg_{abs}} = K \frac{Ca_{sol}}{Mg_{sol}}$$

Solution concentrations utilized to calculate these values were not adjusted for moisture content. The values used to calculate the Ca-NH₄ exchange were calculated by differences from the data shown in Table 77.

The exchange coefficients and correlation coefficients for both soil samples are given in Table 78. Obvious differences occur between the exchange coefficients for the two samples of the same soil. The K_{Ca-K} was

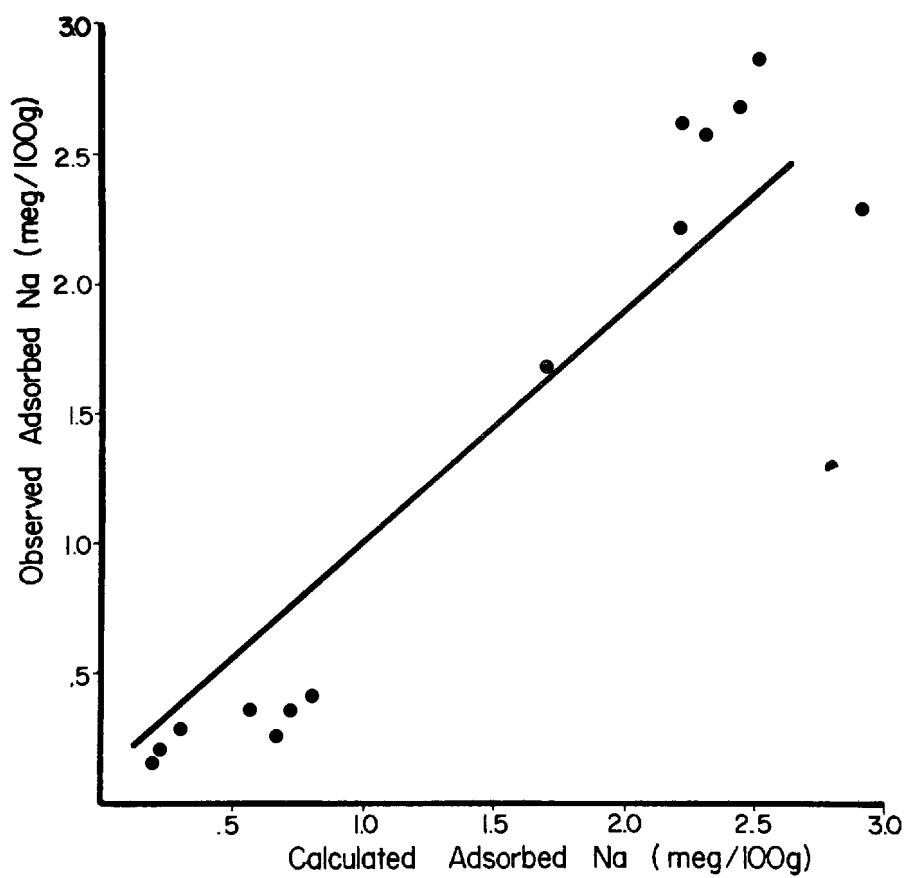


Figure 141. Linear correlation of calculated and experimentally observed adsorbed Na for soil sample 2.

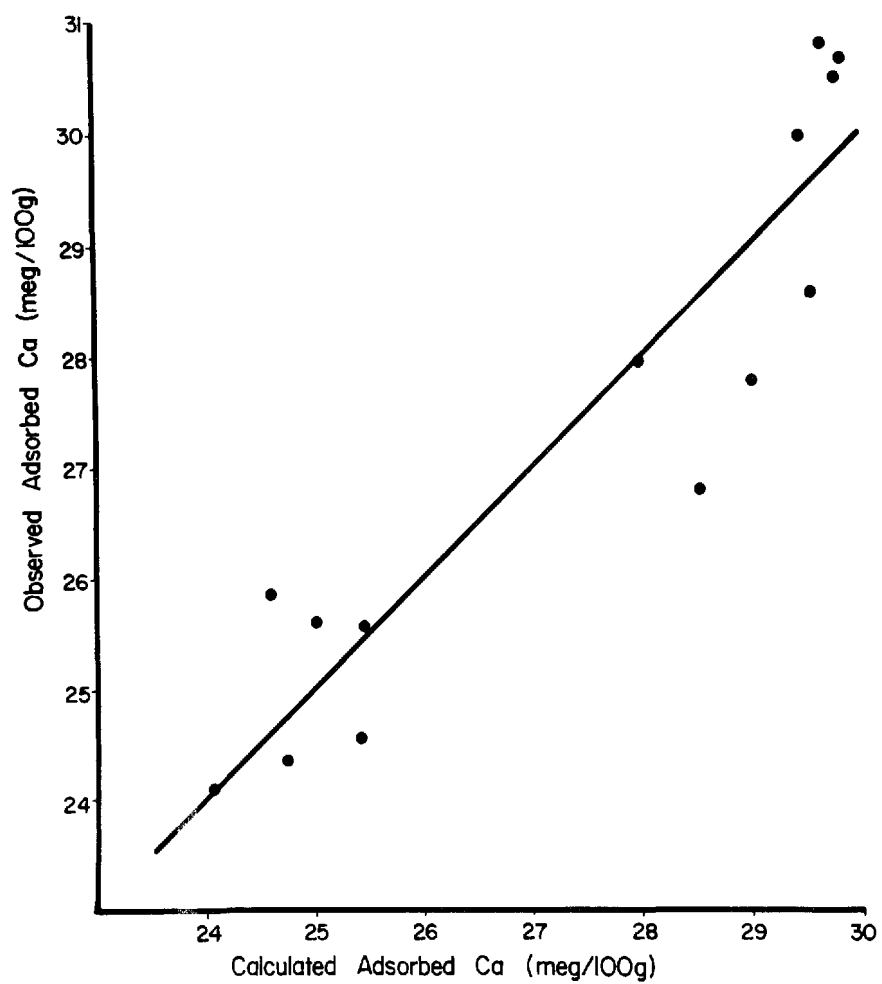


Figure 142. Linear correlation of calculated and experimentally observed adsorbed Ca for soil sample 2.

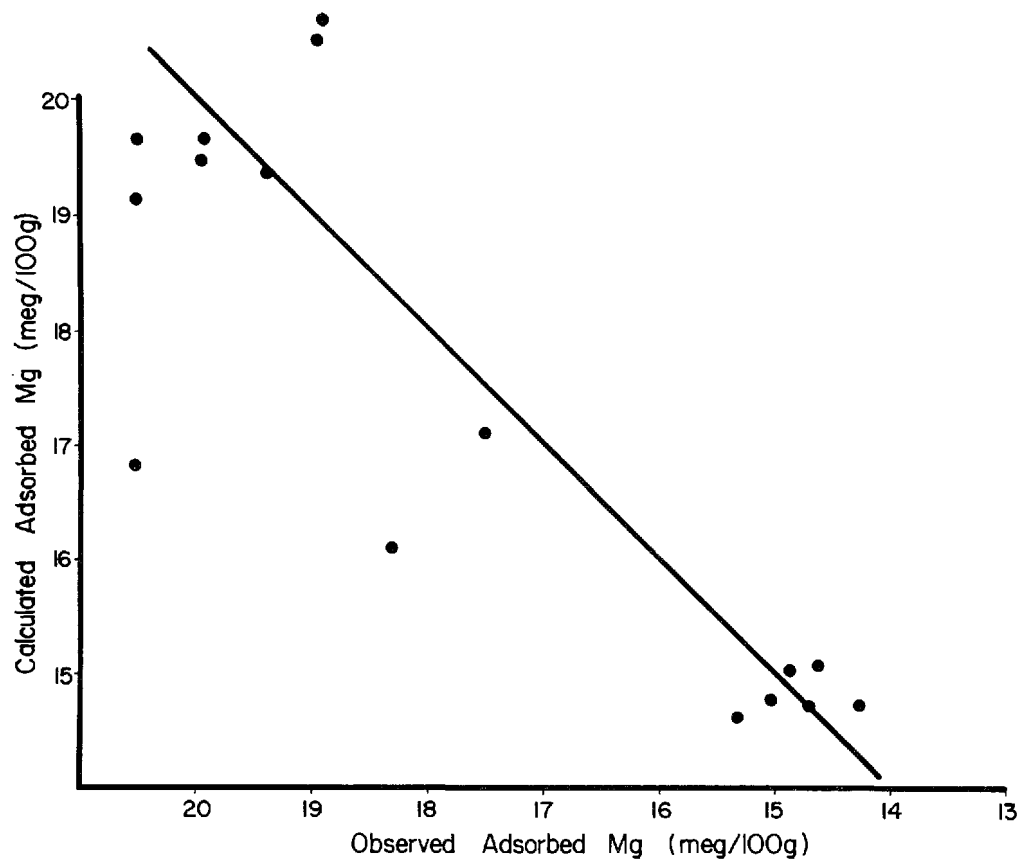


Figure 143. Linear correlation of calculated and experimentally observed adsorbed Mg for soil sample 2.

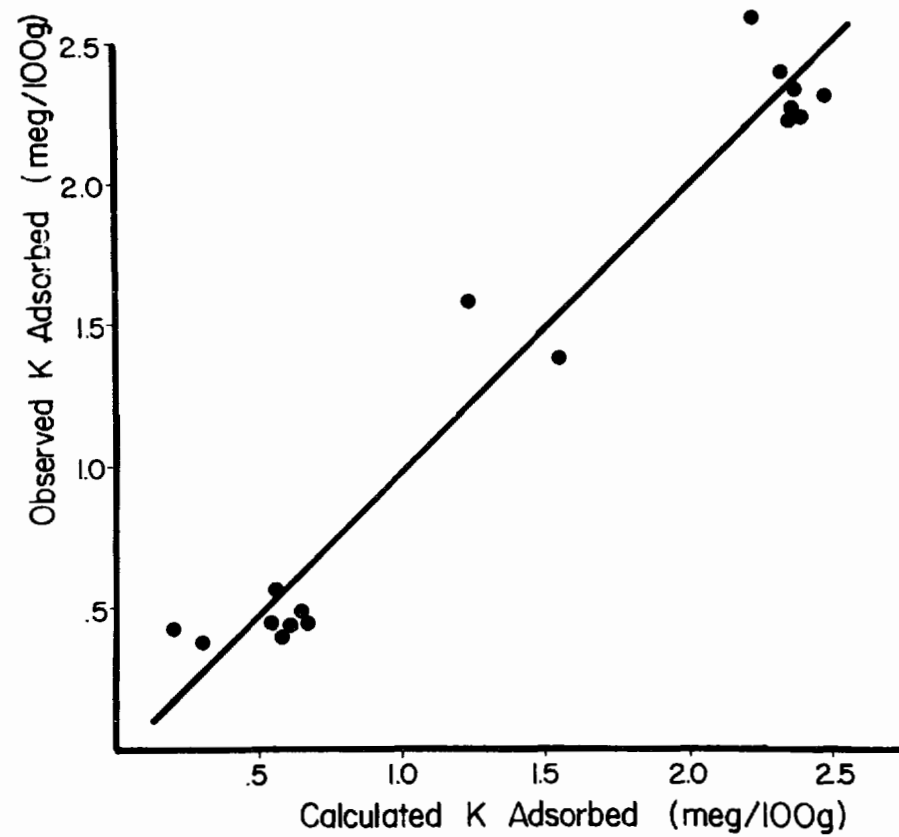


Figure 144. Linear correlation of calculated and experimentally observed adsorbed K for soil sample 2.

twice as large in sample 1 as it was in sample 2, while K_{Ca-K} was twice as large in sample 2 than it was in sample 1. Only the values of K_{Ca-Mg} are in reasonable agreement between the two soils. The correlations were highly significant for all but the K_{Ca-Mg} coefficients. The poorer correlations for these exchanges may be attributed to the narrow range of exchanges which were investigated.

The exchange coefficients for sample 2 were utilized in the present calculations since this soil was collected from the field of interest.

TABLE 78. EXCHANGE COEFFICIENTS CALCULATED FROM THE ION EQUILIBRIUM STUDIES ON SAMPLES 1 AND 2 OF BEAUMONT CLAY.

Soil 1	r
$K_{Ca-Na} = 1.07 (m/l)^{\frac{1}{2}}$	0.964**
$K_{Ca-K} = 0.231 (m/l)^{\frac{1}{2}}$	0.945**
$K_{Ca-Mg} = 0.851$	0.212
Soil 2	r
$K_{Ca-Na} = 0.526 (m/l)^{\frac{1}{2}}$	0.889**
$K_{Ca-K} = 0.539 (m/l)^{\frac{1}{2}}$	0.958**
$K_{Ca-NH_4} = 0.429 (m/l)^{\frac{1}{2}}$	
$K_{Ca-Mg} = 1.04$	0.502*

*Significant at the 1% level.

**Significant at the 5% level.

Simulations of Irrigation Return Flow

After the SOIL and EQUIL parts of the model were thoroughly tested, they were utilized in the paddy model to simulate the changes in ion concentrations in the flood and irrigation return flow water. The input data required for the model are listed in Appendix M. For these simulations the actual data collected in the field was used insofar as possible. The simulation was conducted utilizing data from the top 24 cm of soil. The bulk density and soil-water content data shown in Figures 21 and 22 were used as was the root distribution shown in Figure 23. Values of K_i calculated from data in the literature shown in Table 64 were used. The recommended fertilizer rates as given in Table 2 were used. The beginning salt contents of the surface

soil for the 1975 season given in Table 21 were used. Since detailed data were not available for each cm increment, the same values were used in each depth increment. The ions from the fertilizer application at the time of planting were spread through the top 5 cm of soil at the beginning of the calculations. Eighty percent of the fertilizer applied just prior to the flood was put in the solution in the first soil increment. Twenty percent was dissolved in the flood water at the beginning of the simulation. This was done to simulate the distribution which resulted as the salts dissolved from the crystals on the soil surface and were leached directly into the soil. The water balance during the 1975 season for the intermittent flow plots given in Appendix F were utilized in the simulation. Evaporation from the water surface was assumed to be 25% of the evapotranspiration initially and decreases to 10% as the crop canopy developed.

The largest changes in the concentration of ions in the water followed fertilizer application, therefore emphasis was placed on simulating these changes. A series of simulations were run but only a few samples of the results will be shown here to demonstrate points of agreement and disagreement between the data and the model.

The results of a simulation using the 1974 data from the impounded recommended rate plots are shown in Figures 145-147 during the period when the plots were flooded.

The general agreement between the simulation and the concentration of the Ca^{++} , Na^+ , and Cl^- shown in the figures is good. The model adequately simulated the increase of Ca^{++} and Na^+ early in the season and the dilution which occurred after heavy rainfall such as that of June 9. The release of Ca^{++} and Na^+ when the second fertilizer application was made on June 19 is also well simulated. The influence of several rainfalls which occurred later in the season can be seen in the simulation but sampling was not frequent enough to pick up the small fluctuations. The model did not simulate height of the peak in Ca^{++} concentration which occurred at panicle differentiation application. The chloride concentration was closely simulated throughout the season except for the period between June 20 and 24 when the simulation was about one-third greater than measured values.

Similar success was achieved with magnesium and sulfate. The agreement between the nitrate concentration and that simulated was not very good undoubtedly because of the nitrogen transformation for which the mechanisms are now being investigated by others.

The utility of the model for simulating the water quality is evident. The concentration of specific ions in the return flow resulting from rainfall overflow or from deliberate release of water can be simulated at any time throughout the season. Efforts should be made in the future to use the model to simulate the quality of irrigation return flow from different soils under different climatic and irrigation management regimes.

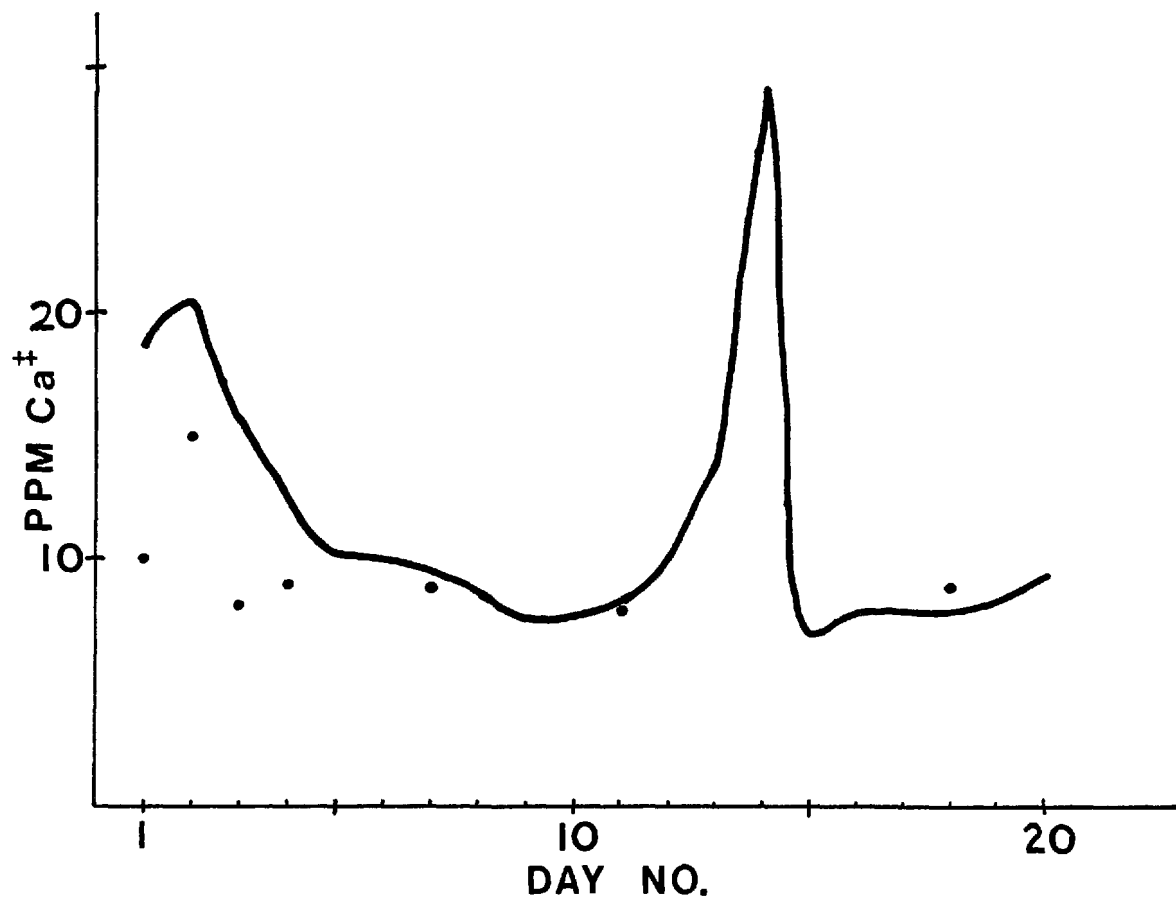


Figure 145. Simulated Ca^{++} concentration in floodwater from impounded recommended plots during 1975. The data points are the actual field data.

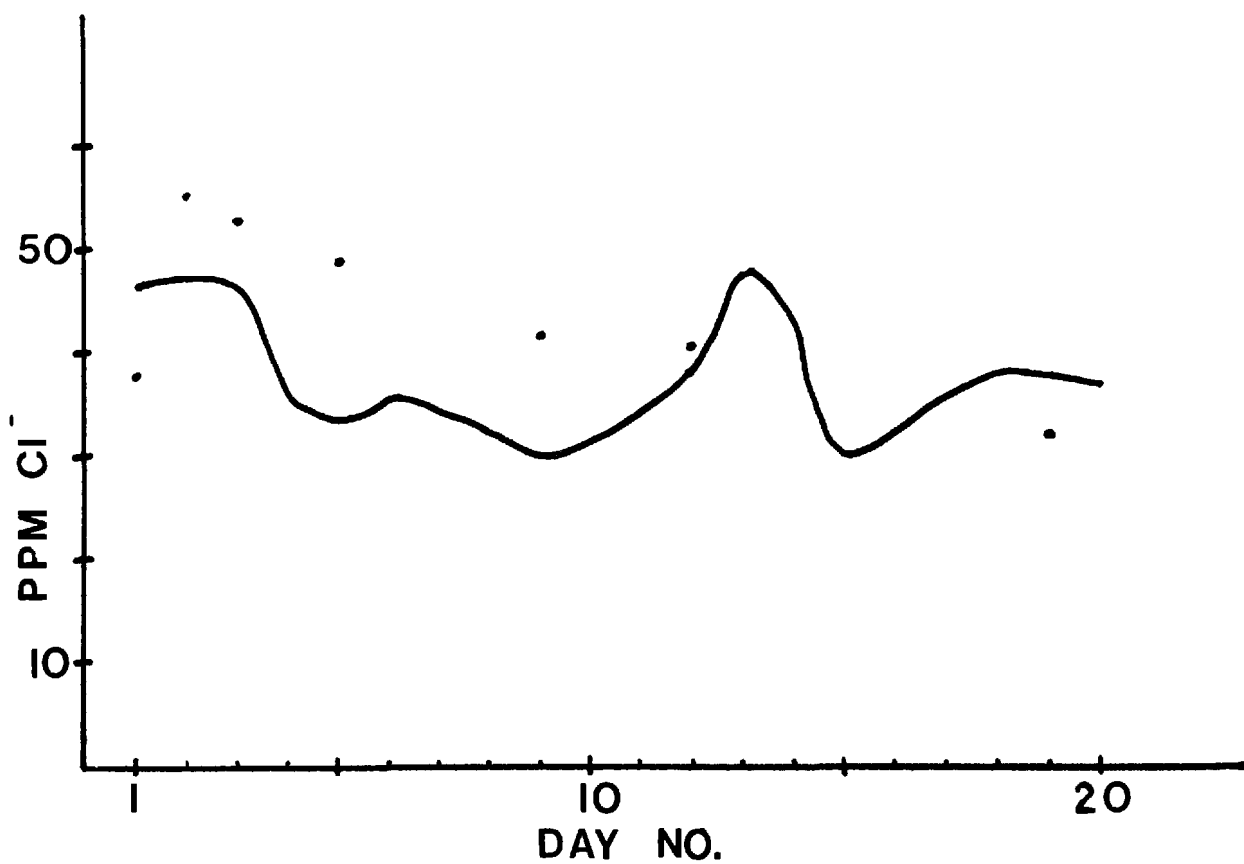


Figure 146. Simulated Cl^- concentration in floodwater from impounded recommended plots during 1975. The data points are the actual field data.

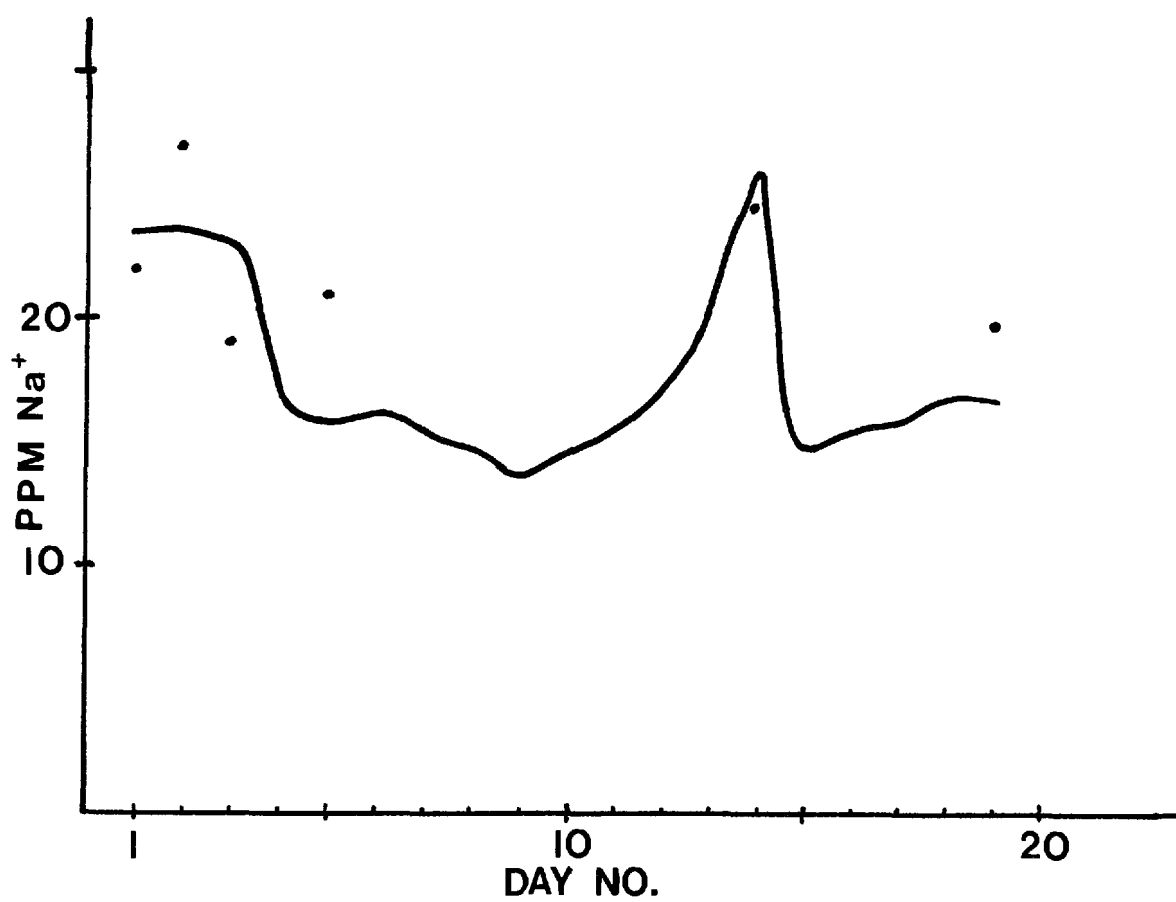


Figure 147. Simulated Na^+ concentration in floodwater from impounded recommended plots during 1975. The data points are the actual field data.

REFERENCES

- Abram, F. S. H. 1960. An Automatic Dosage Apparatus. Laboratory Practice, November. p. 797.
- Alabaster, J. S. 1969. Survival of Fish in 164 Herbicides, Insecticides, Fungicides, Wetting Agents, and Miscellaneous Substances. Int. Pest Control 11:29-35.
- Aldrich, R. J. 1953. Herbicides-Residues in Soil. J. Agr. Food Chem. 1:257-260.
- Ashton, F. M. and T. J. Sheets. 1959. The Relationship of Soil Adsorption of EPTC to Oats Injury in Various Soil Types. Weeds 7:88-90.
- Audus, L. T. 1951. The Biological Detoxification of Hormone Herbicides in Soil. Plant Soil 3:170-192.
- Bailey, G. W. and J. L. White. 1970. Factors Influencing the Adsorption, Desorption, and Movement of Pesticides in Soil. Residue Rev. 32:29-92.
- Barr, A. J., J. A. Goodnight, J. P. Sall, and J. T. Helwig. 1976. A Users Guide to SAS-76. SAS Institutes Inc. Raleigh, North Carolina.
- Barrows, H. L. and V. J. Kilmer. 1963. Plant Nutrient Losses from Soils by Water Erosion. Advance Agron. 15:303-316.
- Bartha, R. 1971. Fate of Herbicide-Derived Chloroanilines in Soil. J. Agr. Food Chem. 19:385-387.
- Bartha, R. and L. Bordeleau. 1969. Cell-Free Peroxidases in Soil. Soil Biol. Biochem. 1:139-143.
- Bartha, R., R. P. Lanzilotta, and D. Prammer. 1967. Stability and Effects of Some Pesticides in Soil. J. Applied Microbiology 15:67-75.
- Bartha, R. and D. Prammer. 1967. Pesticide Transformations to Aniline and Azo Compounds in Soil. Science 156:1617-1618.
- Benoit, D. A. and F. A. Puglisi. 1973. A Simplified Flow-Splitting Chamber and Siphon for Proportional Diluters. Water Res. 7:1915-1916.
- Biggar, J. W., D. R. Nielsen, and K. K. Tanji. 1966. Comparison of Computed and Experimentally Measured Ion Concentrations in Soil Column Effluents. Trans. Am. Soc. Ag. Eng. 9:784-787.

- Biggar, J. W. and D. R. Nielsen. 1967. Miscible Displacement and Leaching Phenomenon. In: Irrigation of Agricultural Lands, R. M. Hagen, H. R. Haise, and T. W. Edminster (ed.). Agronomy Monograph No. 11, pp. 254-274.
- Black, C. A., D. D. Evans, J. L. White, L. E. Ensminger and F. E. Clark. 1965. Methods of Soil Analysis, Part 1: Physical and Mineralogical Properties, Including Statistics of Measurement and Sampling. Am. Soc. of Agron., Agronomy Monograph No. 9, 770 pp.
- Bollag, J. M. and S. Liu. 1971. Degradation of Sevin by Soil Microorganisms. Soil Biol. Biochem. 3:337-345.
- Bordeleau, L. M. and R. Bartha. 1972a. Biochemical Transformations of Herbicide-Derived Anilines in Culture Medium and in Soil. Can. J. of Microbiol. 18:1857-1864.
- Bordeleau, L. M. and R. Bartha. 1972b. Biochemical Transformations of Herbicide-Derived Anilines: Purification and Characterization of Causative Enzymes. Can. J. of Microbiol. 18:1865-1871.
- Bradfield, R. 1941. Calcium in the Soil: I. Physical-Chemical Relations. Soil Sci. Soc. Amer. Proc. 6:8-15.
- Brenner, H. 1962. The Diffusion Model of Longitudinal Mixing in Beds of Finite Length. Numerical Values. Chem. Engr. Sci. 17:229-243.
- Bresler, E. 1972. Interacting Diffuse Layers in Mixed Mono Devalent Ionic Systems. Soil Sci. Soc. Am. Proc. 36:891-896.
- Bresler, E. 1973. Simultaneous Transport of Solutes and Water Under Transient Unsaturated Flow Conditions. Water Resources Research 9:975-986.
- Bresler, E. and R. J. Hanks. 1969. Numerical Method for Estimating Simultaneous Flow of Water and Salt in Unsaturated Soils. Soil Sci. Soc. Am. Proc. 33:827-832.
- Burge, W. D. 1972. Microbial Populations Hydrolyzing Propanil and Accumulation of 3,4-Dichloroaniline and 3, 3', 4, 4'-Tetrachloroazobenzene in Soils. Soil Biol. Biochem. 4:379-386.
- Burge, W. D. 1973. Transformation of Propanil-Derived 3, 4-Dichloroaniline in Soil to 3, 3', 4, 4'-Tetrachloroazobenzene as Related to Soil Peroxidase Activity. Soil Sci. Soc. Amer. Proc. 37:392-395.
- Butler, L. I. and L. M. McDonough. 1971. Determination of Residues of Carbofuran and Toxic Metabolites by Electron Capture Gas Chromatography after Derivative Formation. J. Agr. Food Chem. 54:1357-1360.
- Butler, L. I. and L. M. McDonough. 1970. Specific GLC Method for Determining Residues of Carbaryl by Electron Capture Detection after Derivative Formation. J. Agr. Food Chem. 53:495-498.

- Butler, P. A. 1963. Commercial Fisheries Investigations. USDI Fish and Wildlife Service Circ. 167:11-25.
- Carlson, A. R. 1972. Effects of Long Term Exposure to Carbaryl on Survival Growth and Respiration of Fathead Minnows, Pimephales promelas. Jour. Fish Research Board of Can. 29(5):583-587.
- Carnahan, B., H. A. Luther, and J. O. Wilkes. 1969. Applied Numerical Methods. John Wiley and Sons, New York. 604 pp.
- Caro, J. H., H. P. Freeman, D. E. Glotfelty, B. C. Turner, and W. M. Edwards. 1973. Dissipation of Soil-Incorporated Carbofuran in the Field. J. Agr. Food Chem. 21:1010-1015.
- Carslaw, H. S., and J. C. Jaeger. 1959. Conduction of Heat in Solids. Oxford University Press. Great Britain. 510 pp.
- Carson, C. D. and J. B. Dixon. 1972. Potassium Selectivity in Certain Montmorillonitic Soil Clays. Soil Sci. Soc. Amer. Proc. 35:838-843.
- Carter, F. L. and J. B. Graves. 1973. Measuring Effects of Insecticides on Aquatic Animals. Louisiana Agric. 16:14.
- Chaiyara, S., V. Ratananu, and R. Harrel. 1975. Acute Toxicity of Insecticides, Toxaphene and Carbaryl and Herbicides, Propanil and Molinate to Four Species of Aquatic Organisms. Bull. Environ. Contam. Toxicol. 14:281.
- Chandler, J. H., Jr., H. O. Sanders and D. F. Walsh. 1974. An Improved Chemical Delivery Apparatus for Use in Intermittent-Flow Bioassays. Bull. of Environmental Contamination and Toxicology 12(1):123-128.
- Chaudhari, N. M. 1971. An Improved Numerical Technique for Solving Multi-dimensional Miscible Displacement Equations. J. Soc. Petroleum Engrs. 11:277-284.
- Chisaka, H. and P. C. Kearney. 1970. Metabolism of Propanil in Soils. J. Agr. Food Chem. 18:854-859.
- Coats, K. H. and B. D. Smith. 1964. Deadend Pore Volume and Dispersion in Porous Media. Soc. Petrol. Engrs. Jour. 4:73-84.
- Cope, O. B. 1974. Sport Fishery Investigation. USDI Fish and Wildlife Service Circ. 226. pp. 51-53.
- Corke, C. T. and F. R. Thompson. 1970. Effects of Some Phenylamide Herbicides and Their Degradation Products on Soil Nitrification. Can. J. Microbiol. 16:567-571.
- Crosby, D. G. and R. K. Tucker. 1966. Toxicity of Aquatic Herbicides to Daphnia magna. Science, 154:289-291.

- Danckwerts, P. V. 1953. Continuous Flow Systems. Distribution of Residence Times. Chem. Engr. Sci. Genie Chimique. 2:1-13.
- Delaune, R. D. and W. H. Patrick, Jr. 1970. Urea Conversion to Ammonia in Waterlogged Soils. Soil Sci. Soc. Amer. Proc. 34:603-607.
- de Vall, W. B. 1943. The Correlation of Soil pH with Distribution of Woody Plants in the Gainesville Area. Proc. Fla. Acad. of Sci. 6:9-24.
- deWit, C. T. and H. van Keulen. 1972. Simulation of Transport Processes in Soils. Centre for Agric. Publishing and Documentation, Wageningen, Netherlands. 11 pp.
- Dutt, G. R., M. Shaffer and W. J. Moore. 1972a. Computer Simulation Model of Dynamic Bio-Physico-Chemical Processes in Soils. Ariz. Agr. Expt. Sta. Tech. Bull. 196. 128 pp.
- Dutt, G. R. and K. K. Tanji. 1962. Predicting Concentrations of Solutes in Water Percolated Through a Column of Soil. J. Geophys. Research 67:3437-3439.
- Dutt, G. R., R. W. Terkelstou and R. S. Rauschkolb. 1972b. Prediction of Gypsum and Leaching Requirements for Sodium-Affected Soils. Soil Sci. 114:93-103.
- Dyer, K. L. 1965. Unsaturated Flow Phenomena in Panoche Sandy Clay Loam as Indicated by Leaching of Chloride and Nitrate Ions. Soil Sci. Soc. Amer. Proc. 29:121-126.
- E. I. du Pont de Nemours and Co., Inc. 1974. Technical Data Sheet. Biochemicals Dept. Wilmington, Delaware.
- Edwards, C. A. 1966. Insecticide Residues in Soils. Residue Rev. 13:83-132.
- Eldridge, E. F. 1963. Irrigation as a Source of Water Pollution. J. Water Pollution Contr. Fed. 35:614-625.
- Engvild, K. C. and H. L. Jensen. 1969. Microbiological Decomposition of Herbicide Pyrazon. Soil Biol. Biochem. 1:295-300.
- Environmental Protection Agency. 1971. Methods for Chemical Analysis of Water and Wastes. Water Quality Office, Analytical Quality Control Laboratory. Cincinnati, Ohio. 312 pp.
- Erickson, A. E. and B. G. Ellis. 1971. The Nutrient Content of Drainage Water from Agricultural Land. Mich. Agr. Exp. Sta. Tech. Bull. 31. 16pp.
- Evans, G. N. 1971. Evaporation from Rice at Griffith, New South Wales. Agr. Meteorol. 8:117-127.
- FMC Corp. (undated). (Technical bulletin entitled, Furadan). Agricultural Chem. Div. Middlepoint, New York.

- Fabacher, D. L. and H. Chambers. 1974. Resistance to Herbicides in Insecticide-Resistant-Mosquito Fish, *Gambusia affinis*. *Environmental Letters*. 7:15-20.
- Farmer, W. J., K. Igue, W. F. Spenser, and J. P. Martin. 1972. Volatility of Organo-Chlorine Insecticides from Soil. I. Effect of Concentration, Temperature, Air Flow Rate, and Vapor Pressure. *Soil Sci. Soc. Amer. Proc.* 36:443-444.
- Faust, S. D. 1964. Pollution of the Water Environment by Organic Pesticides. *Clinical Pharmacology and Therapeutics* 5:677-686.
- Flaigg, N. G. 1953. The Effect of Irrigation Return Flow on Water Supplies. *Southwest Water Works Jour.* 34:9-16.
- Flinchum, W. T., J. W. Stansel, and D. G. Westfall. 1973. Effect of Time and Rate of Molinate on the Growth and Production of Bluebelle Rice. Texas Agr. Exp. Sta. Prog. Rpt. PR-3167. Texas A&M University, College Station, Texas.
- Fried, J. J. and M. A. Combarous. 1971. Dispersion in Porous Media. *Advan. Hydrosci.* 7:169-282.
- Frissel, M. J. and P. Reiniger. 1974. Simulation of Accumulation and Leaching in Soils. Centre for Agric. Publishing and Documentation, Wageningen, Netherlands. 116 pp.
- Garder, A. O., Jr., D. W. Peaceman, and A. L. Pozzi, Jr. 1964. Numerical Calculation of Multidimensional Miscible Displacement by the Method of Characteristics. *Soc. Petrol Eng. J.* 4:26-36.
- Garman, W. H. 1970. Agricultural Nutrient Budget. In: Nutrient Mobility in Soils: Accumulation and Losses. SSSA Spec. Publ. No. 4. *Soil Sci. Soc. Amer.* pp. 61-74.
- Garman, W. H. 1973. Agriculture's Place in the Environment: Considerations for Decision Making. *J. Env. Quality* 2:327-333.
- Getzin, L. W. 1973. Persistence and Degradation of Carbofuran in Soil. *Env. Ento.* 2:461-467.
- Gilliam, J. W., R. B. Daniels, and J. F. Lutz. 1974. Nitrogen Content of Shallow Water in the North Carolina Coastal Plain. *Jour. of Env. Quality* 3:147-151.
- Hanway, J. J. and J. M. Laflin. 1974. Plant Nutrient Losses from Tile Outlets Terraces. *Jour. of Env. Quality* 3:335-355.
- Hayne, H. L., H. H. Moorefield, A. J. Borash, and J. W. Keays. 1958. Toxicology of Sevin of Goldfish. *Joun. Eco. Ento.* 51:540.

- Helling, C. S., P. C. Kearney, and M. Alexander. 1971. Behavior of Pesticides in Soils. *Advan. Agron.* 23:147-240.
- Hodgson, R. H. 1971. Influence of Environment on Metabolism of Propanil in Rice. *Weed Sci.* 19:501-507.
- Holden, A. V. 1972. The Effects of Pesticides on Life in Fresh Waters. *Proc. Roy. Soc. Lond. Ser. B.* 180:383-394.
- Hossner, L. H. and D. P. Phillips. 1973. Extraction of Soil Solution from Flooded Soil Using a Porous Plastic Filter. *Soil Sci.* 115:87-88.
- Householder, A. S. 1953. Principles of Numerical Analysis. McGraw-Hill Book Co. New York. 274 pp.
- James, R. V. and Jacob Rubin. 1972. Accounting for Apparatus-Induced Dispersion in Analysis of Miscible Displacement Experiments. *Water Resour. Res.* 8:717-721.
- Johnson, D. P. and H. A. Stansbury. 1965. Adaptation of Sevin Insecticide (Carbaryl) Residue Method to Various Crops. *J. Agr. Food Chem.* 13:235-238.
- Karinen, J. F., J. G. Lamberton, N. E. Stewart, and L. C. Terriere. 1967. Persistence of Carbaryl in the Marine Estuarine Environment, Chemical and Biological Stability in Aquarium Systems. *J. Agr. Food Chem.* 15:148-155.
- Kato, I., Y. Naito, R. Taniguchi and F. Kamota. 1965. Studies on the Evapotranspiration of Crops. II. On the Transpiration Amount of Paddy Rice Plants in Paddy Field and Upland Field Conditions. *Bull. of the Tokai-Kinki Natl. Agr. Exp. Sta., No. 12.*
- Katz, M. 1961. Acute Toxicity of Some Organic Insecticides to Three Species of Salmonids and to the Three-Spine Stickleback. *Trans. Ame. Fish Soc.* 90:264-268.
- Kaufman, D. D. 1967. Degradation of Carbamate Herbicides in Soil. *J. Agr. Food Chem.* 15:582-591.
- Kaufman, D. D., P. C. Kearney, D. W. VonEndt, and D. E. Miller. 1970. Methyl Carbamate Inhibition of Phenyl Carbamate Metabolism in Soil. *J. Agr. Food Chem.* 18:513-519.
- Kazano, H., P. C. Kearney, and D. D. Kaufman. 1972. Metabolism of Methyl Carbamate Insecticides in Soils. *J. Agr. Food Chem.* 20:975-979.
- Kearney, P. C., R. G. Nash, and A. R. Isensee. 1969. Persistence of Pesticide Residues in Soils. In: *Chemical Fallout*. M. W. Miller and G. G. Berg (ed.). Charles C. Thomas, Publisher. Springfield, Ill. pp. 54-67.

- Kearney, P. C., R. J. Smith, Jr., J. R. Plimmer, and F. S. Guardia. 1970. Propanil and TCAB Residues in Rice Soils. *Weed Sci.* 18:464-465.
- Kilmer, V. J., J. W. Gilliam, J. F. Lutz, R. T. Joyce and C. D. Eklund. 1974. Nutrient Losses from Fertilized Grassed Watersheds in Western North Carolina. *Jour. of Env. Quality* 3:214-219.
- Kilmer, V. J. 1972. The Relationship of Soil and Fertilizer Phosphorus to Water Quality. In: *Effects of Intensive Fertilizer Use on the Human Environment*. FAO Soils Bulletin 16:108-125.
- Kilmer, V. J. and R. T. Joyce. 1971. Fertilizer Use in Relation to Water Quality with Special Reference to Southeastern United States. In *Proceedings of the Pacific Northwest Fertilizer Conference*, Bozeman, Montana. p. 87-98.
- Kilmer, V. J. and J. C. Barber. 1974. Fertilizer Use and Misuse. Presented at the Nitrogen in Soil and Water Symp. Hesteler, Ontario.
- Kirda, C., D. R. Nielsen, and J. W. Biggar. 1973. Simultaneous Transport of Chloride and Water During Infiltration. *Soil Sci. Soc. Amer. Proc.* 37:339-345.
- Knarr, R. D. 1970. Determination of Ordram and Its Impurities in Technical Material by Gas-Liquid Chromatography. Stauffer Chemical Co. WRC-70-31.
- Korn, S. 1973. The Uptake and Persistence of Carbaryl in Channel Catfish. *Trans. Amer. Fish. Soc.* 102:137-139.
- Krupp, H. K. and D. E. Elrich. 1969. Density Effects in Miscible Displacement Experiments. *Soil Sci.* 107:372-380.
- Kumai, M., and T. Chiba. 1953. On the Heat Energy Balance of the Paddy Field. *J. Agr. Met. Japan* 8:117-119.
- Kung, 1965. Determining Water Requirement of Rice by Field Measurement in Thailand. *Int. Rice Comm. Newsletter* 14:5-18.
- Lai, S. H. and J. J. Jurinak. 1972. Cation Adsorption in One-Dimensional Flow Through Soils: A Numerical Solution. *Water Resour. Res.* 8:99-107.
- Law, J. P. 1971. National Irrigation Return Flow Research and Development Program, EPA 13030 GJS 12/71. U.S. Environmental Protection Agency, Ada, Oklahoma. 23 pp.
- Law, J. P., J. M. Davidson and L. W. Reed. 1970. Degradation of Water Quality in Irrigation Return Flows. *Okla. State Univ. Ag. Exp. Sta. Bull.* B-684. 26 pp.
- Law, J. P. and G. V. Skogerboe. 1972. Potential for Controlling Quality of Irrigation Return Flows. *J. Env. Quality* 1:140-145.

- Lichtenstein, E. P. 1970. Fate and Movement of Insecticides in and from Soil. In: Pesticides in the Soil Ecology Degradation and Movement. Intl. Symp. at Michigan State University.
- Lourence, F. J. and W. O. Pruitt. 1971. Energy Balance and Water Use of Rice Grown in the Central Valley of California. Agron. J. 63:827-832.
- Macek, K. M. and W. A. McAllister. 1970. Insecticide Susceptibility of Some Common Fish Family Representatives. Trans. Amer. Fish. Soc. 99:20-27.
- Martin, J. P. and K. Haider. 1971. Microbial Activity in Relation to Soil Humus Formation. Soil Sci. 111:54-63.
- McGauhey, P. H. 1968. Quality Changes Through Agricultural Use. Engineering Management of Water Quality. McGraw-Hill Book Co., New York. pp. 58-66.
- McGowan, M. 1972. Toxicology Laboratory Report, T-4028. (personal communication). Stauffer Chem. Co.
- McKee, J. E. and H. W. Wolf. 1963. Water Quality Criteria 2nd ed. California State Water Resources Control Board Publication 3-A. pp. 548.
- Meek, B. D., L. B. Grass, and L. W. Willardson. 1970. Nitrate Transformations in a Column with a Controlled Water Table. Soil Sci. Soc. Amer. Proc. 34:235-239.
- Monteith, John L. 1973. Principles of Environmental Physics. American Elsevier Publishing Company, Incorporated. New York. p. 94.
- Morin, J., D. Goldberg, and I. Seginer. 1967. A Rainfall Simulator with a Rotating Disk. Trans. of the ASAE 10:74-79.
- Mount, D. I. and R. E. Warner. 1965. A Serial-Dilution Apparatus for Continuous Delivery of Various Concentrations of Materials in Water. U.S. Public Health Serv. Pub. #999-WP-23. 16 pp.
- Newman, A. S. and C. R. Downing. 1958. Herbicides and the Soil. J. Agr. Food Chem. 6:352-353.
- Newman, A. S., J. R. Thomas, and R. L. Walker. 1952. Disappearance of 2, 4-Dichlorophenoxyacetic Acid and 2, 4, 5-Trichlorophenoxyacetic Acid from Soil. Soil Sci. Soc. Amer. Proc. 16:21-24.
- Nielsen, D. R., R. D. Jackson, J. W. Cary, and D. D. Evans (eds). 1972. Soil Water. American Society of Agronomy and Soil Science Society of America. Madison, Wisconsin. 175 pp.
- Nightingale, H. I. and W. C. Bianchi. 1974. Ground-Water Quality Related to Irrigation with Imported Surface of Local Ground Water. J. Environ. Quality 3:356-361.

- Parlange, J. Y. and J. L. Starr. 1971. Linear Dispersion in Finite Columns. Soil Sci. Amer. Proc. 39:817-819.
- Patrick, W. H., Jr., R. D. Delaune and F. J. Peterson. 1974. Nitrogen Utilization by Rice Using ¹⁵N-Depleted Ammonium Sulfate. Agr. Jour. 66:819-820.
- Patrick, W. H., Jr., and D. S. Mikkelsen. 1971. Plant Nutrient Behavior in Flooded Soil. Fertilizer Technology and Use. 2nd ed. Soil Sci. Soc. Amer. Madison, Wis. 190 pp.
- Plimmer, J. R., P. C. Kearney, H. Chisaka, J. B. Yount, and U. I. Klingebiel. 1970. 1, 3-Bis (3, 4-Dichlorophenyl) Triazene from Propanil in Soils. J. Agr. Food Chem. 18:859-861.
- Ponnamperuma, F. N., A. E. Martinez and T. Loy. 1966. Influence of Redox Potential and Partial Pressure of Carbon Dioxide of pH Values and the Suspension Effect of Flooded Soils. Soil Sci. 101:421-431.
- Ponnamperuma, F. N. 1965. In: "The Mineral Nutrition of the Rice Plant," John Hopkins Press, Baltimore, Maryland. pp. 295-328.
- Price, H. S., J. S. Cavendish and R. S. Verga. 1968. Numerical Methods of High-Order Accuracy for Diffusion-Convection Equations. Soc. Petrol. Eng. J. 8:293-303.
- Reed, G. B., and J. H. Orr. 1943. Cultivation of Anaerobes. J. Bacteriol. 43:309-320.
- Reiniger, P. and G. H. Bolt. 1972. Theory of Chromatography and Its Application to Cation Exchange in Soils. Neth. J. Agric. Sci. 20:301-313.
- Research Group of Evapotranspiration. 1967. Evapotranspiration from Paddy Field. J. Agr. Met., Tokyo 4-22:149-158.
- Rible, J. M. and L. E. Davis. 1955. Ion Exchange in Soil Columns. Soil Sci. 79:41-47.
- Richtmeyer, R. D. 1957. Difference Methods for Initial Value Problems. Interscience Pub., Inc. New York. 189 pp.
- Rosen, J. D. and M. Siewierski. 1971. Synthesis and Properties of 4 (3, 4-Dichloroaniline)-2, 2'-4'-Trichloroazobenzene. J. Agr. Food Chem. 19:50-51.
- Sadler, L., S. A. Taylor, L. A. Willardson and J. Keller. 1965. Miscible Displacement of Soluble Salts in Reclaiming a Salted Soil. Soil Sci. 100:348-355.

- Schwab, G. W. and G. G. Patchett. 1967. Ordram Residue Method for Rice and Sweet Potatoes by Gas Chromatography. Stauffer Chemical Co. RR-67-13A.
- Shamir, U. Y. and D. R. F. Harleman. 1967. Numerical Solutions for Dispersion in a Porous Medium. Water Resour. Res. 3:557-581.
- Skogerboe, G. V. and J. P. Law. 1971. Research Needs for Irrigation Return Flow Quality Control, EPA 13030---11/71. U.S. Environmental Protection Agency, Robert S. Kerr Water Research Center, Ada, Oklahoma. 97 pp.
- Skopp, J. and A. W. Warrick. 1974. A Two-Phase Model for the Miscible Displacement of Reactive Solutes in Soils. Soil Sci. Soc. Amer. Proc. 38:545-550.
- Sleight, B. H. 1972. Acute Toxicity of Ordram to Blue-gill, Rainbow trout, and Fathead minnows. (personal communication). Bionomics Inc., 790 Main St., Wareham, Massachusetts.
- Smajstrla, A. G., D. L. Reddell and E. A. Hiler. 1974. Simulation of Miscible Displacement in Soils. Amer. Soc. of Ag. Engrs. Paper No. 74-2015:19.
- Smith, S. J. 1972. Relative Rate of Chloride Movement in Leaching of Surface Soils. Soil Sci. 114:259-263.
- Smith, R. J. 1965. Propanil and Mixtures with Propanil for Weed Control in Rice. Weeds 13:236-238.
- Soileau, L. M. 1969. Effects of Fertilizers on Water Quality. Spec. Publ. Tenn. Valley Auth. TVA, Muscle Shoals, Alabama. 107 p.
- Statham, C. N. and J. J. Lech. 1975. Potentiation of the Acute Toxicity of Several Pesticides and Herbicides in Trout by Carbaryl. Toxicol. Appl. Pharmacol. 34:83.
- Statham, C. N. 1975. Biliary Excretion Products of 1-(1-¹⁴C) Naphthyl-N-Methylcarbamate (Carbaryl) in Rainbow Trout (Salmo Gairdneri). Drug Metabolism and Distribution. 3:400.
- Steel, R. G. D. and J. H. Torrie. 1960. Principles and Procedures of Statistics. McGraw Hill Book Co., Inc., New York. 110 pp.
- Stewart, N. W., R. W. Millemann, and W. P. Breese. 1967. Acute Toxicity of the Insecticide Sevin and its Hydrolytic Product, 1-Naphthol, to some Marine Organisms. Trans. Amer. Fish. Soc. 96:25-30.
- Stone, H. L. and P. L. T. Brian. 1963. Numerical Solution of Connective Transport Problems. J. Amer. Inst. of Chem. Engr. 9:681-688.
- Swoboda, A. R. and G. W. Kunze. 1968. Reactivity of Montmorillonite Surfaces with Weak Organic Bases. Soil Sci. Soc. Amer. Proc. 32:806-811.

- Sylvester, R. O. and R. W. Seabloom. 1963. Quality and Significance of Irrigation Return Flow. J. Irrig. Drain. Div. ASCE 89(IR3):1-27.
- Tanji, K. K., J. W. Biggar, M. Mehran, M. W. Cheung, and D. W. Henderson. 1974. Herbicide Persistence and Movement Studies with Molinate in Rice Irrigation Management. Calif. Agric. May:10-12.
- Tarzwel, C. M. 1968. The Determination Use and Value of Water Quality Requirements. Presentation to the 29th Annual International Water Conference of the Engineers Society of Western Pennsylvania, Chatham Center, Pittsburgh, Pennsylvania.
- Texas Water Development Board. 1971. Ground Water Resources of Chambers and Jefferson Counties, Texas. Report 133.
- Thomas, G. W. and A. R. Swoboda. 1970. Anion Exclusion Effects on Chloride Movement in Soils. Soil Sci. 110:163-166.
- Thorne, W. and H. B. Peterson. 1967. Salinity in United States Waters. In: Agriculture and the Quality of Our Environment, N. C. Brady (ed.). Amer. Assoc. Advan. Sci. Symp. 85, Washington, D. C. pp. 221-239.
- Toor, H. S. and K. Kaur, 1974. Toxicity of Pesticides to the Fish Cyprinus carpio. Indian Jour. of Exp. Biology. 12:334.
- Uchijima. 1969. Radiation Balance of a Paddy Field. J. of Agric. Meteor. Tokyo. 22:1-6.
- U. S. Geological Survey. 1968. Water Resources Data for Texas. Geological Survey - Water Resources Division. Part 1. Surface Water Records, 591 pp. Part 2. Water Quality Records. 748 pp.
- U. S. Salinity Laboratory Staff. 1954. Diagnosis and Improvement of Saline and Alkali Soils. U. S. Department of Agriculture Handbook 60. 160 pp.
- Utah State University Foundation. 1969. Characteristics and Pollution Problems of Irrigation Return Flow. Report No. 13030---05/69. U.S. Federal Water Pollution Control Administration, Robert S. Kerr Water Research Center, Ada, Oklahoma. 237 pp.
- Valentine, J. P. and S. W. Bingham. 1974. Influence of Several Algae on 2, 4-D Residues in Water. Weed Sci. 22:358-363.
- van Bavel, C. H. M. 1966. Potential Evaporation: The Combination Concept and Its Experimental Verification. Water Resources Res., in press.
- Viets, F. G., Jr. 1971. Fertilizer Use in Relation to Surface and Ground Water Pollution. In: Fertilizer Technology and Use. Madison, Wis. USA. Soil Sci. Soc. Amer. J. 2:517-532.

- Viets, F. G., Jr. and R. H. Hageman. 1971. Factors Affecting the Accumulation of Nitrate in Soil, Water, and Plants. Agri. Handbook. No. 413. USDA, ARS, 63 p.
- Warrick, A. W., J. W. Biggar and D. R. Nielsen. 1971. Simultaneous Solute and Water Transfer for an Unsaturated Soil. Water Resources Res. 7:1216-1225.
- Wauchope, R. D. and R. Haque. 1973. Effects of pH, Light, and Temperature on Carbaryl in Aqueous Media. Bulletin of Env. Cont. and Tox. 9(5):257-260.
- Weber, J. B. 1972. Interaction of Organic Pesticides with Particulate Matter in Aquatic and Soil Systems. Fate of Organic Pesticides in the Aquatic Environment. American Chemical Soc. Washington, D. C. p. 55-120.
- Weisburger, J. H. and E. K. Weisburger. 1966. Chemicals as Causes of Cancer. Chem. Eng. News 44:124-142.
- Westfall, D. G. 1972. Efficiency of Nitrogen in the Texas Gulf Coast. Nitrogen Symposium. Texas Agric. Exp. Sta., College Station, Texas. 3 pp.
- Westfall, D. G., C. L. Godfrey, N. S. Evatt and J. Crout. 1971. Soils of the Texas A&M University Agr. Res. and Extension Center at Beaumont. MP-1003. Texas Agric. Exp. Sta. Beaumont, Texas. 23 pp.
- Whitney, R. A. and R. Gardner. 1943. The Effect of Carbon Dioxide on Soil Reaction. Soil Sci. 55:127-141.
- Wilcox, L. V. 1962. Salinity Caused by Irrigation. J. Amer. Water Works Assoc. 54:217-222.
- Williams, G. B. 1972. Flooded Rice Soils of Northern Australia. I. Changes in Salinity. Aust. J. Soil Res. 10:43-51.

APPENDIX A

Logs of Rainfall and Cultural Practices During the 1973, 1974 and 1975 Growing Seasons

TABLE A-1. LOG OF RAINFALL AND CULTURAL PRACTICES FOR 1973

Date	Rain at plots (cm)	Event
April 30	0	Preplant fertilizer; rice planted
May 9	0	Rice emergence
May 23	0	Applied 3.4 kg/ha propanil to all plots
May 24	0	Flooded plots
May 25	0.76	Drained plots
May 31	0.13	
June 1	0.13	
June 4	0	Applied propanil treatments
June 5	0	Applied tillering nitrogen and permanent flood
June 6	6.22	
June 7	0.81	
June 8	0.38	
June 9	1.91	
June 11	5.59	
June 12	2.03	
June 13	0.56	
June 15	0	Applied carbofuran and molinate
June 24	0.89	
June 26	0	Panicle differentiation nitrogen applied
July 2	0.25	
July 3	0.13	
July 4	1.02	
July 5	0.25	
July 6	7.87	
July 8	0.13	
July 10	0.15	
July 25	0.81	
July 26	1.27	
July 27	1.27	
July 30	0	Applied carbaryl treatment
August 1	7.75	
August 5	0.13	
August 6	0.13	
August 7	2.03	
August 8	0.13	
August 13	0.64	
August 16	0.89	
August 21	0	Plots drained
August 24	44.26	Plots harvested

TABLE A-2. LOG OF RAINFALL AND CULTURAL PRACTICES FOR 1974

Date	Rain at plots (cm)	Event
April 29	0	
April 30	0	Preplant fertilizer; rice planted
May 1	1.55	
May 3	T	Plots flushed for first time
May 4	0	Plots drained
May 5	0.91	
May 9	1.65	Rice emergence
May 10	1.96	
May 20	5.31	
May 21	T	
May 25	0.48	
May 26	0.64	
May 27	0	Applied 3.4 kg/ha propanil to all plots
May 28	0	Flooded plots
May 29	0	Drained plots
May 30	1.27	
May 31	0.89	
June 1	1.14	
June 5	0	Applied propanil treatments
June 6	0.10	Applied tillering N-permanent flood
June 10	T	
June 14	0.64	
June 20	1.79	
June 21	0.69	
June 24		Applied carbofuran and molinate
June 26		Panicle differentiation, nitrogen application
July 1	1.24	
July 6	0.23	
July 14	1.14	
July 15	0.15	
July 16	0.15	
July 17	0.84	
July 30	0	Applied carbaryl treatments
July 31	8.26	
August 2	0.46	
August 3	2.67	
August 7	2.69	
August 12	0.69	
August 13	0.23	
August 14	0.30	
August 15	0.25	
August 18	5.08	
August 21	0	Plots drained
August 22	T	

(continued)

TABLE A-2. (Continued)

Date	Rain at plots (cm)	Event
August 25	0.84	
August 26	3.51	
August 28	0.99	Recommended rate plots harvested
August 29	1.17	
August 30	0.03	
August 31	1.12	
September 1	0.25	
September 3	0.28	
September 4	0.51	
September 8	0.51	
September 9	1.42	
September 10	T	
September 12	T	
September 13	1.60	
September 14	3.68	
September 15	T	
September 16	0	Excessive rate plots harvested: 3W, 5W, 6W, 1E, 2E, 4E

TABLE A-3. LOG OF RAINFALL AND CULTURAL PRACTICES FOR 1975

Date	Rainfall at plots (cm)	Event
April 29		Preplant fertilizer
April 30	2.26	Rice planted and flooded
May 2	0.05	
May 6		Rice emergence
May 7	0.30	
May 8	0.46	
May 11	4.39	
May 13	0.46	
May 15	0.46	
May 21		Applied 3.4 kg/ha propanil to all plots
May 22		Flood applied
May 23		Flood drained
May 24	0.58	
May 28	10.26	
May 29	3.56	
May 30	5.26	
June 1	5.26	
June 5		Applied propanil treatments 3.4 kg/ha and 6.7 kg/ha
June 6		Applied tillering N and permanent flood
June 9	21.59	
June 10	0.76	
June 15	0.64	
June 19		Panicle differentiation nitrogen application
June 21	0.23	
June 23	T	Applied carbofuran and molinate
June 24	0.53	
June 25	0.36	
June 26	0.43	
June 28	0.79	
June 30	0.15	
July 2	0.51	
July 3	0.38	
July 10	0.20	
July 11	1.73	
July 13	0.25	
July 14	0.51	
July 28	3.56	Applied carbaryl treatments
July 29	0.53	
July 30	0.41	
July 31	3.78	
August 1	3.51	
August 3	0.43	
August 4	4.06	
August 5	1.50	
August 7	0.25	
August 8	1.27	
August 17	.05	Harvest

Appendix B
Climatological Data
during the
1973, 1974 and 1975
Growing Seasons

TABLE B-1. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1973 (APRIL)

Month <u>APRIL</u>									
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	51	78	30	98	.14	.25	0	59.9	C.
2	52	78	28	100	.11	.22	0	44.6	C.
3	50	78	30	98	.11	.15	Trace	74.8	C.
4	43	70	48	96	.22	.28	0	130.8	C.
5	40	63	38	90	.16	.22	0	73.1	P.C.
6	45	66	30	98	.12	.13	.03	43.6	P.C.
7	49	58	78	98	.07	.09	.96	146.9	Cl.
8	45	67	56	98	.05	.04	0	34.2	Cl.
9	39	70	64	99	.22	.19	.11	136.9	P.C.
10	35	59	27	92	.16	.23	0	83.3	C.
11	39	65	22	98	.14	.19	0	46.1	C.
12	49	68	33	98	.12	.15	0	51.2	P.C.
13	54	75	36	100	.07	.18	0	44.7	C.
14	55	78	44	98	.08	.28	0	51.3	C.
15	64	78	33	98	overflow		1.10	100.5	Cl.
16	64	71	90	99	overflow		1.70	177.0	Cl.
17	60	70	85	99	overflow		1.73	60.0	Cl.
18	57	68	86	99	.16	overfl.	2.20	87.9	Cl.
19	71	75	60	99	.13	.19	Trace	117.6	Cl.
20	70	75	89	97	.02	.06	0.01	194.9	Cl.
21	70	76	90	95	.05	.10	0	239.3	Cl.
22	69	75	87	97	.05	.10	0	180.2	Cl.
23	70	78	77	98	.05	.12	0	101.1	Cl.
24	71	80	71	98	.06	.17	Trace	136.3	P.C.
25	68	81	72	98	.09	.17	0.03	87.8	P.C.
26	59	86	46	98	.11	.32	0.32	72.1	P.C.
27	53	75	52	92	.24	.33	0	151.0	P.C.
28	49	74	38	97	.21	.25	0.2	59.9	P.C.
29	59	75	34	97	.11	.24	0	31.7	C.
30	64	77	56	94	.11	.22	0	105.2	P.C.
31									
total	1664	2187	1630	2916	3.16	4.87	8.39	2923.9	
mean	55.5	72.9	54.3	97.2	0.105	0.162	0.280	97.46	

* H-haze, C-clear, P. C.-partially cloudy, Cl-cloudy

TABLE B-2. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL
EXPERIMENT STATION, BEAUMONT, TEXAS, 1973 (MAY)

Month <u>MAY</u>									
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	69	77	73	97	.09	.17	TRACE	168.9	P.C.
2	64	75	86	99	.02	.16	1.13	113.2	Cl.
3	56	78	84	99	overfl.	.23	1.01	102.9	Cl.
4	51	74	40	97	.21	.24	0	73.6	C.
5	54	75	34	98	.16	.27	0	56.7	C.
6	68	77	50	98	.16	.25	0	120.3	P.C.
7	63	76	86	99	overfl.	.17	0.96	136.4	Cl.
8	60	82	69	98	.08	.09	0.05	62.3	P.C.
9	62	87	32	98	.08	.25	0	21.6	C.
10	61	85	46	96	.16	.27	0	29.0	C.
11	67	85	48	96	.11	.24	0	60.0	C.
12	63	86	54	96	.11	.27	TRACE	61.0	C.
13	58	74	80	97	.11	.18	0.92	124.0	--
14	55	78	30	92	.18	.28	0	78.7	C.
15	57	79	34	70	.14	.26	0	56.9	P.C.
16	51	78	30	92	.18	.27	0	47.4	C.
17	58	80	26	98	.17	.28	0	44.9	C.
18	61	85	42	98	.14	.27	0	73.9	P.C.
19	67	85	42	95	.17	.25	0	79.2	C.
20	71	84	59	93	.15	.29	0	118.9	P.C.
21	67	85	58	97	.14	.18	0	42.6	P.C.
22	67	85	52	95	.15	.35	0	102.0	P.C.
23	73	87	56	95	.14	.25	0	80.9	P.C.
24	71	87	55	94	.14	.28	0	80.0	P.C.
25	71	89	47	94	.13	.24	0	63.4	P.C.
26	69	88	56	95	.17	.28	0.27	75.2	P.C.
27	69	88	66	95	.13	.22	0	132.1	Cl.
28	61	93	26	96	.19	.28	0	61.7	P.C.
29	60	83	39	98	.20	.31	0	70.0	C.
30	60	87	34	98	.12	.20	0	17.6	P.C.
31	66	89	32	98	.19	.20	0.04	49.9	C.
total	1950	2561	1566	2961	4.12	7.48	4.38	2405	
mean	62.9	82.6	50.5	95.5	0.13	0.24	0.14	77.6	

* H-haze, C-clear, P. C.-partially cloudy, Cl- cloudy

TABLE B-3. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1973 (JUNE)

Month <u>JUNE</u>									
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	70	87	66	99	.09	.17	0.05	64.3	P.C.
2	75	88	58	96	.16	.29	0.03	111.6	P.C.
3	74	88	58	94	.19	.35	0	144.4	P.C.
4	75	88	62	94	.14	.25	0	104.1	P.C.
5	66	89	58	96	.15	.29	0	94.8	P.C.
6	64	88	62	99	.30	overflow	1.40	110.6	Cl.
7	64	81	58	96	.11	.21	0	52.2	P.C.
8	66	87	35	90	.17	.31	0	49.3	C.
9	68	83	67	99	.18	.15	0.56	53.5	P.C.
10	69	85	70	99	.24	-	0.57	48.5	Cl.
11	69	87	60	98	.09	.19	0.08	41.2	Cl.
12	67	84	76	99	overflow		2.06	82.5	Cl.
13	74	82	77	99	.05	.22	0.86	56.3	Cl.
14	75	82	80	99	.04	.05	0.18	71.5	Cl.
15	73	88	66	96	.09	.19	0	61.9	P.C.
16	75	89	63	96	.13	.27	0	70.4	P.C.
17	74	89	57	95	.15	.25	0	67.8	P.C.
18	73	90	62	95	.15	.26	0	35.1	P.C.
19	73	90	60	96	.16	.27	0	89.4	P.C.
20	72	90	60	96	.14	.27	0	60.6	P.C.
21	70	90	53	99	.15	.30	0.94	54.9	P.C.
22	71	84	54	96	.10	.08	0	76.5	--
23	70	87	46	96	.17	.25	0	48.1	Cl.
24	71	89	52	98	.08	.22	0	18.6	Cl.
25	73	90	52	98	.12	.16	0.11	32.8	Cl.
26	70	87	62	97	.10	.16	0	28.3	P.C.
27	70	91	45	96	.15	.30	0	40.1	P.C.
28	73	91	44	96	.18	.33	0	70.0	P.C.
29	74	92	52	96	.15	.31	0	86.3	P.C.
30	73	90	48	96	.16	.32	0	53.2	C.
31									
total	2131	2626	1763	2899	4.09	6.42	5.84	1988.8	
mean	71.0	87.5	58.8	96.6	0.14	0.214	0.19	66.3	

* H-haze, C-clear, P. C.-partially cloudy, Cl-cloudy

TABLE B-4. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL
EXPERIMENT STATION, BEAUMONT, TEXAS, 1973 (JULY)

Month JULY

Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	73	91	44	97	.18	.34	0	49.0	C.
2	75	92	47	96	.17	.34	TRACE	46.6	C.
3	74	91	57	97	.16	.29	0.02	50.0	P.C.
4	74	92	57	97	.13	.28	0.05	41.3	--
5	72	92	52	98	.13	.20	0.05	30.9	Cl.
6	71	92	56	98	.14	.17	0.49	50.5	Cl.
7	69	81	80	96	overflow		1.67	47.7	Cl.
8	73	81	70	99	.11	.17	1.40	49.6	Cl.
9	73	89	65	97	.14	.26	0	50.2	C.
10	72	92	43	94	.23	.35	0	46.1	P.C.
11	74	92	44	92	.18	.32	0	58.7	P.C.
12	75	92	46	94	.19	.44	0.01	51.5	P.C.
13	74	90	50	92	.14	.15	TRACE	37.0	Cl.
14	71	91	47	92	.18	.30	0	45.7	P.C.
15	73	91	46	92	.20	.31	0	64.2	P.C.
16	75	92	54	92	.21	.33	0	65.7	P.C.
17	75	91	66	96	.09	.18	0.10	44.5	P.C.
18	73	91	54	95	.12	.23	0	33.3	P.C.
19	73	93	45	94	.19	.32	0	29.3	P.C.
20	75	94	44	94	.19	.33	0	37.4	C.
21	74	93	48	95	.19	.32	0	42.2	P.C.
22	76	94	40	94	.19	.31	0	39.5	P.C.
23	74	91	52	96	.14	.22	0.02	32.6	P.C.
24	73	92	54	96	.20	.22	0	48.0	C.
25	74	96	39	95	.17	.33	0	28.5	C.
26	72	91	57	99	.18	.26	0.48	36.8	P.C.
27	71	94	54	99	.25	overflow	0.94	66.7	P.C.
28	74	93	47	95	.16	.26	0	31.5	P.C.
29	76	92	54	96	.14	.26	0	31.7	P.C.
30	75	94	52	97	.19	.32	0	45.8	P.C.
31	75	94	50	94	.22	.33	0	62.7	P.C.
total	2278	2834	1614	2958	5.11	8.14	5.23	1395.2	
mean	73.5	91.4	52.1	95.4	0.16	0.26	0.17	45.0	

* H-haze, C-clear, P. C.-partially cloudy, Cl-cloudy

TABLE B-5. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1973 (AUGUST)

Month <u>AUGUST</u>									
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo- sphere
	min	max	min	max	2	4			
1	72	91	58	96	overflow		3.82	51.2	P.C.
2	72	84	80	97	.06	.07	0.09	52.8	Cl.
3	70	88	53	95	.11	.19	0	35.4	P.C.
4	66	87	50	96	.22	.33	0	75.4	P.C.
5	69	87	48	95	.17	.23	0	30.0	Cl.
6	74	85	64	96	.11	.23	0.58	31.4	P.C.
7	74	88	60	96	.10	.18	0	47.0	P.C.
8	71	89	68	98	.07	.20	0.75	31.7	Cl.
9	71	85	72	98	.05	.09	0.08	11.4	P.C.
10	70	90	58	96	.12	.16	0	19.8	P.C.
11	70	92	44	98	.15	.28	0.04	20.8	P.C.
12	74	92	49	98	.15	.23	TRACE	26.9	Cl.
13	73	88	62	98	.08	.11	0.04	9.3	P.C.
14	70	90	54	98	.13	.20	0	21.7	P.C.
15	70	87	72	99	.09	.10	0.32	14.6	Cl.
16	72	84	64	98	.07	.07	0.03	11.4	Cl.
17	72	82	78	97	.06	.08	0.04	9.9	Cl.
18	74	83	86	99	.04	.04	0.22	35.6	Cl.
19	73	89	58	98	.08	.16	0	31.1	Cl.
20	73	92	46	98	.16	.25	0	18.7	P.C.
21	71	91	46	96	.17	.30	0	39.8	C.
22	70	93	46	95	.19	.31	0	39.0	P.C.
23	65	91	32	96	.21	.31	0	31.4	C.
24	69	94	39	95	.19	.28	0	24.6	C.
25	69	91	44	96	.19	.24	0	27.0	C.
26	70	90	42	97	.18	.33	0	32.6	C.
27	68	91	44	99	.31	overflow	1.11	45.4	Cl.
28	70	88	54	96	.17	.20	0	38.9	P.C.
29	71	94	60	98	.17	.23	0.20	41.1	P.C.
30	70	94	54	97	.15	.19	0.02	30.5	C.
31	72	94	48	98	.13	.24	0	33.9	P.C.
total	2195	2764	1733	3007	4.08	5.83	7.34	970.3	
mean	70.8	89.2	55.9	97	0.13	0.19	0.24	31.3	

* H-haze, C-clear, P. C.-partially cloudy, Cl-cloudy

TABLE B-6. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL
EXPERIMENT STATION, BEAUMONT, TEXAS, 1974 (APRIL)

Month APRIL

Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo- * sphere
	min	max	min	max	2	4			
1	68	83	60	96	.11	.21	0	75.2	P.C.
2	56	82	70	98	.06	.12	0.01	126.2	P.C.
3	69	82	45	98	.14	.25	0	149.9	P.C.
4	58	87	26	98	.15	.28	0	66.1	C
5	43	72	26	82	.23	.26	0	97.5	P.C.
6	43	70	20	96	.23	.31	0	70.9	C
7	63	75	22	90	.20	.32	0	135.3	P.C.
8	57	77	60	98	.05	.14	0	92.0	Cl
9	45	78	27	73	.22	.37	0	106.1	C
10	51	73	30	98	.14	.25	0	55.3	C
11	68	76	57	90	.11	.14	0	207.1	Cl
12	70	76	76	98	.02	.07	0.03	209.7	--
13	72	83	70	98	.06	.15	0	100.0	P.C.
14	65	85	58	97	.12	.27	0.02	78.1	P.C.
15	54	74	40	78	.18	.25	0.13	98.6	Cl
16	46	60	70	99	.10	.05	0.46	18.1	P.C.
17	50	77	32	98	.11	.18	0	38.6	C
18	52	75	44	97	.14	.25	0	59.4	--
19	56	78	49	98	.16	.28	0	62.9	C
20	48	96	48	96	.18	.30	0	165.7	P.C.
21	71	79	66	97	.07	.14	0	184.4	--
22	63	81	74	96	.09	.15	0	139.7	P.C.
23	62	85	64	99	overflow		1.81	103.9	--
24	58	76	74	98	.08	.17	0	70.4	Cl
25	53	81	34	98	.16	.28	0	53.7	C
26	55	77	42	98	.14	.24	0	46.7	C
27	60	77	50	97	.16	.25	0	74.6	--
28	60	80	58	98	.12	.22	0	113.0	P.C.
29	65	82	59	98	.13	.21	0	98.1	P.C.
30	65	82	64	98	.11	.21	0	89.4	P.C.
31									
total	1746	2359	1515	2853	4.03	6.32	2.46	2986.6	
mean	58.2	78.6	50.5	95.1	0.13	0.21	0.08	99.6	

* H-haze, C-clear, P. C.-partially cloudy, Cl-cloudy

TABLE B-7. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1974 (MAY)

Month <u> MAY </u>									
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	66	82	64	98	.10	.19	0	61.9	P.C.
2	64	73	97	100	.06	.02	0.61	40.7	P.C.
3	66	84	64	100	.07	.22	0	61.6	P.C.
4	66	87	60	98	.12	.22	TRACE	79.6	Cl
5	63	84	62	98	.10	.16	0	48.7	Cl
6	60	79	56	99	.08	.13	0.36	61.1	Cl
7	55	79	47	98	.12	.18	0	49.2	P.C.
8	60	81	43	100	.12	.23	0	47.5	P.C.
9	62	85	54	100	.12	.20	0	23.6	P.C.
10	62	85	60	99	overflow		0.65	99.4	P.C.
11	63	75	72	99	overflow		0.77	71.7	Cl
12	67	81	70	98	.09	.11	0	44.0	C
13	62	88	50	98	.16	.29	0	35.9	C
14	74	85	54	98	.22	.38	0	154.3	C
15	75	85	72	98	.12	.22	0	125.9	P.C.
16	73	84	80	98	.10	.14	0	132.2	Cl
17	72	85	78	98	.12	.23	0	127.7	P.C.
18	69	87	67	98	.18	.31	0	110.0	P.C.
19	68	88	62	98	.20	.29	0	63.0	P.C.
20	69	88	57	98	.20	.32	0	65.7	P.C.
21	70	78	94	99	overfl	.22	2.09	90.8	Cl
22	70	83	86	99	.11	.19	TRACE	76.1	Cl
23	65	85	68	98	.13	.22	0	65.5	P.C.
24	67	87	58	100	.16	.26	0	45.5	P.C.
25	69	88	58	98	.15	.24	0	54.7	P.C.
26	71	88	58	99	.14	.26	0.19	78.5	C
27	65	88	50	96	.19	.34	0	70.4	P.C.
28	66	86	44	97	.17	.28	0	47.7	P.C.
29	72	87	49	98	.20	.32	0	86.1	P.C.
30	74	90	56	98	.18	.30	0	87.5	P.C.
31	71	88	59	98	.24	.38	0.50	138.6	P.C.
total	2076	2613	1929	3051	4.67	6.85	5.17	2345.1	
mean	67.0	84.3	62.2	98.4	0.15	0.22	0.17	75.6	

* H-haze, C-clear, P. C.-partially cloudy, Cl-cloudy

TABLE B-8. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1974 (JUNE)

Month JUNE

Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	66	83	79	99	.17	.17	0.66	98.5	P.C.
2	68	87	55	97	.20	.22	0	51.0	C
3	66	86	50	98	.18	.27	0	39.5	P.C.
4	69	87	48	98	.15	.27	0	38.4	C
5	72	89	56	98	.15	.29	0	79.2	--
6	76	88	62	98	.24	.32	0.04	171.2	P.C.
7	77	87	66	97	.18	.29	0	183.1	P.C.
8	78	88	74	97	.18	.23	TRACE	184.7	P.C.
9	77	88	78	97	.19	.32	0	168.8	C
10	71	90	72	98	.18	.27	0.01	100.1	C1
11	65	83	82	98	.26	.39	TRACE	48.8	C1
12	69	90	47	97	.17	.27	0	39.9	C
13	69	90	54	98	.17	.31	0	43.6	C1
14	68	89	51	99	.24	.35	0.13	82.3	P.C.
15	69	91	46	98	.09	.32	0	47.4	P.C.
16	70	92	44	96	.11	.34	0	60.1	P.C.
17	72	93	39	97	.20	.30	0	60.1	C
18	73	92	35	97	.21	.34	0	66.4	C
19	73	91	46	97	.21	.31	0	55.1	C
20	71	91	50	98	.20	.29	0	66.1	C
21	71	92	49	97	.21	.32	0	40.7	C
22	70	91	52	98	.21	.33	0.08	63.6	P.C.
23	71	93	45	96	.23	--	0	75.8	P.C.
24	68	95	40	96	.31	--	0	115.7	P.C.
25	59	85	36	73	.41	.46	0	131.0	P.C.
26	58	83	33	97	.33	.40	0	98.7	H.
27	58	85	28	98	.27	.36	0	70.5	C
28	60	85	23	84	.24	.33	0	38.1	C
29	62	88	26	80	.37	.54	0	67.9	C
30	64	87	28	92	.12	.16	0	29.0	C
31									
total	2060	2659	1494	2863	6.38	8.77	0.92	2414.7	
mean	68.7	88.6	49.8	95.4	0.21	0.29	0.03	80.5	

* H-haze, C-clear, P. C.-partially cloudy, C1-cloudy

TABLE B-9. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL
EXPERIMENT STATION, BEAUMONT, TEXAS, 1974 (JULY)

		Month <u>JULY</u>							
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	71	90	54	96	.17	.24	0	54.0	P.C.
2	70	90	52	99	.15	.18	0.35	51.4	P.C.
3	71	90	54	95	.19	.31	0	74.5	P.C.
4	72	92	43	94	.29	.35	0	74.4	P.C.
5	74	95	42	95	.19	.33	0	93.7	P.C.
6	72	93	37	92	.26	.40	0	41.8	P.C.
7	70	93	43	99	.19	.25	0.06	36.1	--
8	70	90	44	98	.18	.22	0.02	54.9	Cl
9	69	85	64	97	.15	.24	0.46	39.2	P.C.
10	69	91	50	97	.19	.29	0	44.8	P.C.
11	70	92	24	97	.21	.33	0	27.6	C
12	69	89	55	96	.14	.21	TRACE	66.0	C
13	71	93	42	97	.27	.33	0	47.5	P.C.
14	71	96	39	99	.21	.34	0.09	57.2	P.C.
15	70	95	42	99	.22	.28	0.34	38.4	Cl
16	69	84	83	99	.10	.11	0.04	50.8	Cl
17	70	90	52	99	.14	.23	0.07	51.3	Cl
18	68	89	56	99	.13	.21	0.29	46.3	Cl
19	70	91	45	98	.19	.27	0	34.7	C
20	71	93	40	98	.16	.28	0	46.2	C
21	73	94	52	98	.28	.30	0	46.1	P.C.
22	75	96	41	98	.19	.31	0	32.6	C
23	73	96	44	98	.22	.34	0	57.4	C
24	73	95	43	98	.23	.32	0	55.2	C
25	76	94	42	97	.21	.28	0	43.7	P.C.
26	76	92	52	99	.20	.29	0	81.6	Cl
27	75	93	52	99	.33	.41	0	145.0	P.C.
28	74	97	42	99	.34	.25	0	49.8	P.C.
29	72	96	40	98	.26	.33	0.12	27.1	Cl
30	73	95	35	98	.30	.31	0	60.2	P.C.
31	69	95	36	96	.32	.40	0	83.9	P.C.
total	2216	2864	1470	3021	6.44	8.94	1.84	1713.4	
mean	71.5	92.4	47.4	97.4	0.21	0.29	0.06	55.3	

* H-haze, C-clear, P. C.-partially cloudy, 'Cl-cloudy

TABLE B-10. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1974 (AUGUST)

		Month <u>AUGUST</u>							
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo- * sphere
	min	max	min	max	2	4			
1	67	90	54	99	overflow		3.40	59.0	P.C.
2	69	88	61	99	.25	.25	0.04	27.1	Cl
3	68	85	58	99	.10	.12	0.22	40.3	P.C.
4	70	92	42	99	.18	overflow	1.07	37.0	P.C.
5	67	87	50	99	.14	.21	0	32.7	P.C.
6	67	88	32	98	.20	.29	0	47.6	P.C.
7	71	84	55	99	.09	.12	0.03	27.4	Cl
8	73	82	82	99	overflow		1.22	40.5	Cl
9	75	89	67	98	.18	.18	0	50.2	P.C.
10	74	90	62	98	.20	.31	0.09	94.2	Cl
11	72	91	60	98	.16	.21	0	45.4	P.C.
12	71	93	--	97	.23	.28	0	23.5	P.C.
13	71	92	50	99	.17	.26	0.49	14.9	P.C.
14	69	92	50	99	.27	.29	0.06	56.0	P.C.
15	70	91	52	99	.21	.27	0.31	34.7	P.C.
16	72	90	56	99	.18	.20	0.15	19.2	P.C.
17	72	93	50	98	.18	.24	0	21.2	P.C.
18	72	93	54	98	.19	.26	0	35.5	P.C.
19	72	93	50	98	.18	.27	0	25.0	P.C.
20	72	95	36	98	.20	.29	0	34.8	C
21	70	93	46	96	.18	.28	0	34.9	P.C.
22	70	95	46	98	.18	.23	TRACE	35.0	C
23	72	95	30	98	.20	.28	0	41.6	C
24	71	91	50	98	.17	.23	0	37.8	--
25	72	91	52	99	.20	.30	0.33	63.3	Cl
26	73	80	93	99	overflow	1.22	1.38	152.2	Cl
27	71	88	60	98	.12	.23	0	43.7	P.C.
28	74	92	62	99	.13	.22	0.39	31.5	P.C.
29	73	87	78	99	.12	.21	0.46	49.1	P.C.
30	73	89	60	98	.16	.23	0.01	70.2	Cl
31	73	88	67	99	.11	.44	0.44	44.9	Cl
total	2206	2787	1665	3051	4.88	6.92	10.09	1370.4	
mean	71.2	89.9	53.7	98.4	0.16	0.22	0.32	44.2	

* H-haze, C-clear, P. C.-partially cloudy, Cl-cloudy

TABLE B-11. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1975 (APRIL)

Month <u>April</u>								
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day
	min	max	min	max	2	4		
1	51	78	64	96	.02	.02	Trace	54.0
2	46	78	28	48	.18	.26	.02	151.0
3	36	64	22	70	.13	.23	.00	66.0
4	40	64	34	89	.15	.24	.00	87.0
5	45	69	34	84	.05	.17	.00	68.0
6	57	75	33	95	.10	.20	.00	64.0
7	55	75	64	94	.05	.19	.89	121.0
8	60	74	73	97	-	.07	.45	76.0
9	65	77	62	94	.08	.13	.02	74.0
10	59	73	80	97	.09	.14	.66	110.0
11	55	73	39	89	.16	.23	.00	87.0
12	49	68	38	84	.12	.18	.00	55.0
13	53	67	80	98	Overflow		1.76	125.0
14	52	65	78	98	.08	.06	.03	38.0
15	47	73	42	99	.10	.17	.00	32.0
16	50	75	50	92	.12	.24	.00	176.0
17	61	77	74	93	.02	.08	.00	150.0
18	68	81	64	93	.09	.21	.01	109.0
19	56	75	28	88	.15	.23	.00	77.0
20	56	70	29	73	.13	.18	.00	98.0
21	59	64	80	99	.01	.05	.62	78.0
22	61	77	76	96	.03	.07	.00	100.0
23	67	80	64	96	.06	.17	.00	118.0
24	70	82	61	95	.09	.22	.00	104.0
25	72	85	50	94	.14	.25	.00	96.0
26	73	83	63	92	.10	.19	.00	136.0
27	72	83	63	94	.15	.25	.00	129.0
28	71	82	64	96	.07	.14	.01	65.0
29	64	84	60	100	.06 overflow		.65	70.0
30	63	80	67	99	.16	.31	.89	62.0
31								
total								
mean								

* H= haze, C= clear, P.C.= partially cloudy, Cl.= cloudy

TABLE B-12. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL
EXPERIMENT STATION, BEAUMONT, TEXAS, 1975 (MAY)

Month <u>May</u>									
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	62	85	44	94	.12	.14	.00	29.0	Cl.
2	65	83	56	91	.13	.19	.02	117.0	P.C.
3	74	84	57	94	.12	.23	.00	87.0	Cl.
4	65	84	51	94	.13	.20	.00	77.0	Cl.
5	67	83	62	94	.09	.17	.00	112.0	P.C.
6	75	84	68	96	.08	.15	.00	100.0	Cl.
7	68	86	62	96	.17	.24	.12	97.0	P.C.
8	66	85	54	94	.13	.21	.18	98.0	P.C.
9	69	87	42	94	.16	.33	.00	60.0	CL.
10	66	82	54	95	.08	.05	.00	32.0	P.C.
11	65	84	52	98	overflow		1.73	60.0	P.C.
12	64	87	44	95	.15	.22	.00	33.0	P.C.
13	67	84	55	96	.17	.23	.18	61.0	P.C.
14	64	82	46	84	.13	.23	.00	58.0	P.C.
15	63	76	56	99	.14	.17	.18	88.0	P.C.
16	62	79	54	98	.11	.18	.00	59.0	P.C.
17	60	85	33	97	.13	.25	.00	21.0	P.C.
18	63	84	46	97	.18	.24	.00	37.0	C.
19	69	84	60	98	.15	.23	.00	68.0	P.C.
20	72	85	67	98	.11	.16	.00	114.0	P.C.
21	75	88	57	98	.16	.13	.00	78.0	Cl.
22	70	86	50	97	.18	.29	.00	81.0	P.C.
23	71	87	50	97	.15	.24	.00	69.0	P.C.
24	69	85	60	99	.17	.20	.23	75.0	P.C.
25	68	88	54	97	.16	.27	.00	71.0	P.C.
26	69	89	48	99	.25	.30	.00	47.0	P.C.
27	68	89	46	97	.14	.31	.00	49.0	P.C.
28	66	84	62	99	overflow		4.04	71.0	P.C.
29	67	87	62	99	overflow		1.40	74.0	Cl.
30	65	80	80	99	Overflow		2.07	76.0	P.C.
31	64	79	34	96	.30	.33	.00	66.0	P.C.
total									
mean									

* H= haze, C= clear, P.C.= partially cloudy, Cl.= cloudy

TABLE B-13. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1975 (JUNE)

Month <u>June</u>									
Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	58	83	39	98	.21	.35	2.07	33.0	C
2	64	86	44	99	.16	.34	.00	36.0	C
3	66	87	45	98	.17	.27	.00	49.0	C
4	72	89	57	98	.18	.33	.00	101.0	C
5	76	89	58	98	.17	.28	.00	82.0	P.C.
6	75	92	52	98	.20	.34	.00	107.0	P.C.
7	73	90	60	98	.14	.26	.00	19.0	P.C.
8	73	89	54	96	.15	.16	Trace	63.0	P.C.
9	78	86	78	100	overflow		8.50	82.0	Cl
10	70	81	70	97	overflow		.53	52.0	Cl
11	71	81	75	99	.08	.06	.02	40.0	Cl
12	71	92	48	97	.19	.24	.00	26.0	Cl
13	72	90	50	96	.20	.30	.00	36.0	C
14	75	89	52	93	.26	.38	.00	111.0	P.C.
15	77	86	60	98	.18	.25	.17	91.0	C
16	76	89	65	98	.17	.34	.00	129.0	P.C.
17	78	89	53	98	.20	.37	.00	149.0	P.C.
18	76	89	62	97	.21	.31	.00	113.0	P.C.
19	76	89	60	99	.17	.23	.00	85.0	P.C.
20	74	92	43	96	.19	.13	.00	57.0	P.C.
21	71	92	46	99	.19	.26	.09	22.0	P.C.
22	72	90	48	99	.14	.27	.00	46.0	P.C.
23	69	90	50	99	.20	.28	.12	102.0	P.C.
24	71	86	58	99	.12	.20	.11	41.0	Cl
25	72	84	77	99	.12	.11	.27	25.0	Cl
26	71	83	70	99	.08	.10	.04	33.0	Cl
27	72	89	52	98	.11	.21	.01	33.0	Cl
28	69	88	49	99	.22	.20	.13	35.0	P.C.
29	69	88	58	98	.12	.15	Trace	39.0	P.C.
30	70	92	50	99	.12	.21	.15	36.0	P.C.
31									
total									
mean									

* H= haze, C= clear, P.C.= partially cloudy, Cl.= cloudy

TABLE B-14. SUMMARY OF CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1975 (JULY)

Month July

Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	68	86	56	99	.15	.22	.12	60	P.C.
2	72	89	46	98	.02	.23	.00	50	P.C.
3	74	82	61	98	.19	.07	.18	31	P.C.
4	70	90	46	95	.14	.24	.00	34	C
5	72	91	46	96	.17	.30	.00	56	P.C.
6	73	90	44	95	.25	.32	.00	62	P.C.
7	73	92	40	96	.21	.34	.00	76	C
8	73	92	42	95	.19	.26	.00	82	P.C.
9	75	93	39	99	.19	.26	.00	54	P.C.
10	76	91	55	99	.21	.34	.18	83.8	C
11	72	86	70	99	.15	.19	.55	60.3	P.C.
12	70	91	51	99	.13	.25	.00	40.3	Cl
13	71	91	40	99	.17	.30	.15	62.8	P.C.
14	69	87	68	99	.14	.16	.07	58.6	P.C.
15	72	83	64	99	.08	.13	.03	46.7	Cl
16	70	87	57	99	.12	.18	.00	39.9	P.C.
17	72	88	62	99	.10	.18	Trace	52	P.C.
18	73	90	61	99	.20	.28	.00	45	P.C.
19	74	90	50	99	.18	.36	.00	63.2	P.C.
20	73	94	50	99	.17	.27	.00	40.3	P.C.
21	73	95	48	99	.17	.28	Trace	46.7	Cl
22	76	87	69	99	.09	.13	0.1	34.4	C
23	75	91	65	99	.10	.14	0.6	40.6	P.C.
24	72	89	60	99	.11	.11	.00	42.8	P.C.
25	72	91	58	99	.11	.24	.00	38.1	C
26	72	92	60	99	.14	.22	.05	41.3	P.C.
27	72	97	48	99	.16	.33	.00	49.2	P.C.
28	74	95	56	99	.18	.29	.35	63.1	P.C.
29	73	91	63	99	.21	.28	.40	60.9	P.C.
30	71	91	64	99	.15	.16	.11	51.5	Cl
31	73	89	75	99	overflow		.35	53.8	P.C.
total									
mean									

* H= haze, C= clear, P.C.= partially cloudy, Cl.= cloudy

TABLE B-15. SUMMARY CLIMATOLOGICAL OBSERVATION AT THE TEXAS AGRICULTURAL EXPERIMENT STATION, BEAUMONT, TEXAS, 1975 (AUGUST)

Month August

Day	Air Temperature		Relative Humidity		Pan Evaporation		Precipitation inches	Wind miles/day	Atmo-* sphere
	min	max	min	max	2	4			
1	71	90	63	99	overflow		1.49	73.3	P.C.
2	71	86	71	99	.14	.09	Trace	54.8	P.C.
3	73	84	71	99	.13	.37	.26	50.2	P.C.
4	72	87	72	99	overflow		2.16	58.1	P.C.
5	71	87	65	99	.12	-	1.10	39.9	Cl
6	71	89	60	99	.12	.06	.00	27.6	P.C.
7	73	91	56	99	.21	.27	.13	45.4	P.C.
8	68	89	58	99	.21	.42	.40	49.5	Cl
9	69	86	68	99	.18	.36	.02	57.8	P.C.
10	72	85	69	99	.10	.15	.00	31.4	P.C.
11	73	91	54	99	.14	.24	.00	28.9	P.C.
12	73	91	57	99	.13	.21	.00	25.1	P.C.
13	72	93	54	99	.13	.25	.00	29.8	P.C.
14	73	93	51	99	.16	.25	.00	34.2	P.C.
15	73	94	53	99	.20	.28	.00	35.1	P.C.
16	74	90	60	99	.09	.18	.00	25.5	P.C.
17	73	92	56	99	.17	.21	.05	26.2	P.C.
18	73	92	59	99	.17	.27	.00	31.2	P.C.
19	73	92	58	99	.15	.18	.00	23.4	P.C.
20	73	95	50	98	.14	.22	.00	23.3	P.C.
21	74	92	63	98	.11	.19	.00	28.3	P.C.
22	74	90	60	99	.18	.28	.57	63.8	P.C.
23	74	86	64	99	.21	.23	.38	44.5	P.C.
24	70	86	86	99	overflow		1.13	47.5	P.C.
25	72	89	75	99	.10	.17	.26	46.8	Cl
26	73	87	75	99	.12	.25	.31	66.5	P.C.
27	71	90	65	98	.15	.27	.00	73.4	Cl
28	71	91	57	98	.16	.25	.00	44.8	P.C.
29	73	90	66	98	.14	.19	.00	35.9	P.C.
30	72	86	68	98	.08	.04	.00	43.7	Cl
31									
total									
mean									

*H= haze, C= clear, P.C.= partially cloudy, Cl.= cloudy

APPENDIX C

DETAILED CHEMICAL ANALYSIS METHODS FOR SOIL, SOIL SOLUTIONS AND WATER SAMPLES TAKEN FROM RICE PADDIES DURING THE 1973, 1974 AND 1975 GROWING SEASONS

Methods

Chemical analysis methods for soils, soil solutions, and water samples were those found in Methods of Soil Analysis, Monograph No. 9, ASA, Diagnosis and Improvement of Saline and Alkali Soils, USDA Handbook 60, and Standard Methods for Examination of Water and Wastewater, American Public Health Association, Inc. Nutrient ion analysis was performed by either autoanalyzer, atomic absorption, or flame emission.

Soil Extractions

The following extraction procedures were used in the determination of NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , and Cl^- . All extracts were analyzed using a Technicon Autoanalyzer.*

NO_4^+ , NO_2^- , and NO_3^-

An equilibrium extraction using 1N KCl was used to extract all soil samples for NH_4^+ , NO_2^- , and NO_3^- . Ten grams of soil were placed in a 250 ml centrifuge tube and 100 ml of 1N KCl was added. The tubes were stoppered and placed on a reciprocating shaker (150 cycles/min.) for exactly 5 minutes. The suspension was then centrifuged for 4 minutes at 1200 RPM and the supernatant was poured off through a Whatman No. 1 filter. Corrections for soil moisture were made and results were reported on an oven dry basis.

Example:

$$\frac{\text{amt. H}_2\text{O lost}}{(\text{amt. of sample}) - (\text{amt. of H}_2\text{O})} \times 100 = \% \text{ moisture}$$

$$10 - (10 \times \% \text{ H}_2\text{O as decimal}) = \text{dry wt.}$$

$$100 \times \text{ppm} = \text{dry ppm}$$

*Mention does not constitute endorsement.

PO₄⁻³

An extract using 1.4N NH₄OAc was used to determine P in soil samples. Ten grams of soil were placed in a 250 ml centrifuge tube and 50 ml of 1.4N NH₄OAc was added. The centrifuge tubes were placed on a reciprocating shaker (150 cycles/min.) for 15 minutes. The suspension was centrifuged at 1200 RPM for 4 minutes and the supernatant filtered with Whatman No. 1 filter paper. Samples were analyzed within 2 days after extraction. Appropriate moisture corrections were made and final data were reported on an oven dry basis.

Example: 10 - (10 X % H₂O as a decimal) = dry wt.

$$\frac{50}{\text{dry wt.}} \times \text{ppm} = \text{dry ppm}$$

SO₄⁻² and Cl⁻

Ten grams of soil were weighted out into a 250 ml polyethelene bottle and 100 ml of de-ionized water were added to each bottle. The bottles were then placed on a reciprocating shaker for 5 minutes at 150 cycles/min. The suspension was centrifuged at 3,000 RPM for 30 minutes and the supernatant was filtered through 2 thicknesses of Baroid Low Pressure filter paper. No suction was used in the filtering process. The filtrate was analyzed within 2 days after extraction. Corrections were made for moisture and final data reported on an oven dry basis.

Example: 10 - (10 x % H₂O as decimal) = dry wt.

$$\frac{100}{\text{dry wt.}} \times \text{ppm} = \text{dry ppm}$$

pH and E.C.

Conductivity was measured using a wheatstone bridge, and pH by a pH meter. The suspension from the water extract procedure used in the determination of SO₄⁻² and Cl⁻ was also used to determine pH and E.C.

Ca⁺², Mg⁺²

Calcium and Magnesium analysis was made using atomic absorption. The 1.4N NH₄OAc extracts used in PO₄⁻³ analysis were also used for the analysis of these two cations. Moisture corrections were made and results reported on an oven dry basis.

K⁺, Na⁺

Potassium and Sodium analysis was made using flame emission. The 1.4N NH₄OAc extract was also used in this analysis. Results were reported on an oven dry basis.

Water Samples and Soil Solution Analysis

All water and soil solution samples were analyzed for nutrient ions using the autoanalyzer, atomic absorption, or flame emission. The auto-analyzer was used to determine NH_4^+ , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , and Cl^- using Technicon Methods. Results were reported in ppm.

Documented procedures for the analyses were:

Nitrate and Nitrite	Industrial Method No. 100-70W June, 1973 Preliminary
Ortho Phosphate	Industrial Method No. AAIL 94-70W June, 1971
Chloride	Industrial Method No. AAIL 99-70W June, 1971
Sulfate	Industrial Method No. 118-71W December, 1972 Preliminary
Ammonia	Industrial Method No. AAIL 98-70W June, 1971

Appendix D

Daily Water Depths During
1974 and 1975 in Each Plot

TABLE D-1. WATER DEPTH AT THE END OF EACH DAY DURING PERMANENT FLOOD IN 1974
(JUNE 6 - JULY 4)

Date	Plots											
	1E	2E	3E	4E	5E	6E	1W	2W	3W	4W	5W	6W
June 6	9.6	7.8	9.8	7.2	10.8	1.8	9.5	7.2	8.2	2.2	11.5	3.1
June 7	10.0	9.9	8.3	9.5	9.1	1.8	12.4	6.8	8.6	2.2	11.1	6.3
June 8	10.7	11.8	9.1	9.8	8.1	3.0	12.1	8.5	11.8	2.2	13.9	8.4
June 9	11.9	11.7	11.3	10.5	8.7	4.3	11.8	8.5	12.1	2.2	14.7	8.7
June 10	10.3	9.1	10.1	10.9	9.8	2.2	12.0	8.8	13.1	2.1	15.5	9.0
June 11	9.3	8.4	9.1	9.6	9.0	3.8	12.2	8.8	13.2	2.2	15.8	8.6
June 12	8.9	8.0	8.6	9.1	8.7	5.9	12.4	9.0	13.3	2.1	15.7	8.4
June 13	8.6	8.1	8.3	9.2	8.9	7.0	12.7	9.3	13.2	2.2	15.7	8.1
June 14	8.6	6.8	8.3	8.4	9.7	6.3	11.7	9.3	13.3	1.2	15.4	6.7
June 15	6.8	4.9	6.6	6.5	8.3	4.4	10.3	7.7	11.9	0.0	12.7	4.9
June 16	5.3	3.4	4.9	5.1	6.8	3.1	9.3	6.3	10.3	0.0	12.4	3.5
June 17	3.8	2.1	3.0	4.0	5.5	1.6	7.9	2.7	9.0	0.0	9.9	2.2
June 18	2.6	1.1	1.4	3.6	4.2	1.2	7.3	0.0	8.2	0.0	9.1	1.7
June 19	0.8	0.1	0.2	3.6	2.6	1.6	7.1	0.0	7.0	0.0	7.9	1.3
June 20	9.8	5.7	11.2	9.8	9.5	7.5	9.5	6.2	13.0	0.5	6.9	0.5
June 21	9.6	5.8	10.9	13.2	9.3	9.0	10.6	5.2	13.0	3.1	6.9	1.3
June 22	8.6	5.1	9.8	13.2	8.5	8.6	10.5	3.3	12.1	3.8	6.0	1.4
June 23	7.5	4.2	8.8	13.1	7.7	8.4	10.3	1.8	11.2	4.1	5.1	1.4
June 24	9.5	3.9	11.9	10.8	9.8	9.2	9.9	6.8	13.8	4.1	11.0	1.3
June 25	8.4	2.8	10.5	8.3	8.7	8.7	9.8	5.3	12.8	2.9	9.5	1.9
June 26	7.2	1.7	9.4	7.3	7.7	8.1	9.9	3.9	11.9	2.1	8.6	2.6
June 27	6.0	1.9	8.3	7.1	6.7	7.5	10.5	2.6	11.0	2.9	7.4	3.8
June 28	11.0	4.9	11.7	7.0	12.4	7.4	10.8	8.1	14.1	3.2	11.6	4.5
June 29	10.1	4.9	10.6	6.6	11.2	7.2	10.6	7.2	13.3	3.4	10.5	5.0
June 30	9.3	4.8	9.7	6.3	10.3	7.1	10.7	6.5	13.5	3.7	9.6	5.7
July 1	10.1	6.2	10.6	8.0	11.2	8.3	12.2	7.2	13.4	4.3	10.1	7.6
July 2	9.3	6.3	9.6	8.1	10.1	8.5	11.6	6.5	12.7	2.8	9.0	7.4
July 3	8.4	6.2	8.6	7.8	9.2	8.3	11.2	5.5	11.9	3.1	8.0	7.3
July 4	7.6	6.3	7.4	7.8	8.6	8.0	11.1	4.7	11.2	4.9	7.7	7.1

TABLE D-2. WATER DEPTH AT THE END OF EACH DAY DURING PERMANENT FLOOD IN 1974
(JULY 5 - AUGUST 2)

Date	Plots											
	1E	2E	3E	4E	5E	6E	1W	2W	3W	4W	5W	6W
July 5	6.6	6.8	6.5	8.0	7.7	8.2	11.3	3.8	10.3	4.9	6.7	7.4
July 6	6.1	7.7	5.9	8.7	7.4	8.5	11.5	3.0	9.9	4.4	6.3	7.0
July 7	5.6	8.2	5.2	9.2	6.8	8.7	11.4	2.5	9.4	4.3	5.7	6.9
July 8	7.2	10.6	6.7	10.7	8.6	10.8	16.3	8.5	13.4	5.7	6.6	8.3
July 9	6.5	10.5	6.0	9.3	8.2	9.9	12.5	8.6	12.7	4.1	5.9	7.0
July 10	5.8	10.1	5.1	8.7	7.5	9.8	11.7	7.8	12.0	3.3	5.2	6.4
July 11	5.3	9.9	4.5	8.7	6.9	9.8	11.5	6.8	11.6	2.9	4.7	6.3
July 12	9.9	10.9	6.6	9.0	10.4	9.7	13.9	8.2	12.5	2.4	8.8	6.1
July 13	9.3	10.6	6.1	9.5	9.7	9.6	12.6	7.3	11.9	2.3	8.2	5.9
July 14	9.9	11.6	6.6	10.7	8.7	10.2	12.3	7.7	12.6	3.3	8.7	6.5
July 15	9.8	10.7	6.6	10.1	7.8	10.0	12.6	7.6	12.3	3.3	8.8	6.7
July 16	9.5	10.2	6.3	9.6	6.9	9.9	12.7	7.3	12.1	3.1	8.5	7.3
July 17	9.8	10.6	6.7	9.8	6.7	10.3	13.4	7.7	12.6	3.9	9.0	8.2
July 18	9.1	9.8	6.0	9.1	4.7	10.2	12.9	7.2	11.9	3.8	8.3	7.5
July 19	8.5	9.8	5.3	8.9	3.2	9.9	12.4	6.5	11.4	3.9	7.5	6.7
July 20	7.8	9.6	4.5	8.5	1.6	9.5	12.1	5.7	10.7	4.2	6.6	6.3
July 21	7.1	9.4	3.6	8.1	0.0	9.4	11.8	4.8	9.8	4.4	6.4	5.9
July 22	15.4	9.2	3.1	8.0	13.0	9.4	13.9	9.7	14.1	4.2	5.1	2.2
July 23	14.8	9.2	2.1	8.1	14.1	9.3	12.4	11.2	13.3	4.0	4.0	0.8
July 24	14.1	9.1	6.2	8.2	13.4	9.1	12.0	10.5	12.6	3.8	9.8	3.8
July 25	13.3	9.3	5.6	8.3	12.5	9.2	12.0	9.7	12.0	3.9	10.8	4.8
July 26	12.3	9.4	4.6	8.4	11.5	9.0	12.0	8.6	11.3	4.5	11.3	5.4
July 27	11.4	9.5	3.7	8.3	10.6	8.8	12.2	7.4	10.5	5.4	11.6	5.7
July 28	10.7	9.8	2.9	8.4	9.8	8.7	12.2	6.4	9.8	5.4	12.3	6.3
July 29	14.1	9.8	8.2	8.4	11.1	8.6	11.9	9.4	13.5	5.8	13.6	8.2
July 30	13.2	9.8	7.2	8.5	12.1	8.4	12.0	7.9	12.7	5.9	13.2	8.0
July 31	7.0	10.0	9.0	11.1	16.0	14.1	12.0	7.8	11.0	3.0	9.1	4.3
August 1	6.1	10.1	8.2	9.8	13.4	8.4	12.5	6.7	10.6	5.5	9.9	4.7
August 2	6.3	10.8	8.4	10.1	12.9	7.3	13.4	6.4	10.9	6.2	11.8	7.1

TABLE D-3. WATER DEPTH AT THE END OF EACH DAY DURING PERMANENT FLOOD IN 1974
(AUGUST 3 - AUGUST 23)

Date	Plots											
	1E	2E	3E	4E	5E	6E	1W	2W	3W	4W	5W	6W
August 3	9.3	13.5	11.4	12.4	14.6	9.5	16.6	9.1	13.8	7.3	16.1	10.1
August 4	8.9	11.5	10.8	10.1	13.9	7.6	14.7	7.9	13.4	6.4	14.5	9.8
August 5	8.3	10.7	10.1	8.9	12.6	6.6	13.3	6.6	12.6	6.3	13.5	8.9
August 6	7.9	10.6	9.7	8.8	12.0	6.4	13.1	5.9	12.2	6.5	13.6	8.9
August 7	9.3	13.0	11.1	11.1	14.1	9.2	14.9	8.7	13.1	6.9	13.8	9.2
August 8	7.4	11.3	10.6	10.1	12.5	7.5	13.5	8.0	10.9	6.7	11.5	6.8
August 9	6.5	10.7	10.2	9.5	11.8	6.7	13.1	7.2	10.6	6.4	10.7	6.0
August 10	5.8	10.3	9.6	9.1	11.1	6.2	12.9	6.3	10.0	6.3	10.1	5.4
August 11	5.2	10.2	8.9	9.4	10.6	5.9	12.6	5.3	9.4	6.4	9.8	5.2
August 12	5.5	10.7	9.0	10.1	11.1	6.5	12.1	5.2	9.7	6.9	10.5	6.1
August 13	4.8	10.4	8.5	9.7	10.7	6.2	11.3	4.1	9.2	6.6	10.2	5.7
August 14	4.9	10.4	8.7	9.8	10.9	6.6	11.4	3.8	9.4	6.8	10.6	6.1
August 15	4.8	10.4	8.6	10.1	10.8	6.3	11.4	3.3	9.4	7.1	10.6	6.0
August 16	4.2	10.1	7.8	9.7	10.1	5.8	11.5	2.5	8.6	7.2	9.7	4.9
August 17	3.5	9.8	7.1	9.4	9.3	5.5	11.3	1.5	7.8	7.2	9.3	4.5
August 18	2.8	9.7	6.5	9.1	8.7	5.3	11.1	0.4	7.2	7.2	9.1	4.3
August 19	2.1	9.5	5.9	9.1	8.1	5.1	11.3	0.0	6.4	7.1	8.7	4.0
August 20	1.3	0.0	5.2	9.3	7.4	5.0	11.1	0.0	5.9	7.2	8.8	4.1
August 21	1.0	0.0	0.0	0.0	6.4	0.0	10.5	0.0	5.4	0.0	0.0	0.0
August 22	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
August 23	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE D-4. WATER DEPTH AT THE END OF EACH DAY DURING PERMANENT FLOOD IN 1975
(JUNE 5 - JULY 3)

Date	Plots											
	1E	2E	3E	4E	5E	6E	1W	2W	3W	4W	5W	6W
June 5	12.0	14.6	12.0	15.9	7.4	18.4	13.2	29.1	10.2	14.3	9.7	14.4
June 6	9.6	16.5	10.8	15.5	6.4	19.0	15.3	26.9	9.2	16.3	10.4	12.1
June 7	7.8	15.8	9.6	13.2	5.4	17.4	14.6	25.7	8.3	14.7	9.5	8.9
June 8	6.2	15.1	8.7	12.4	4.6	16.9	14.5	24.7	7.7	14.3	8.7	7.4
June 9	20.8	21.7	25.8	22.3	20.2	23.7	18.8	22.1	19.0	19.8	20.6	20.1
June 10	15.3	17.8	22.2	15.9	14.7	19.0	17.4	19.0	13.7	16.7	14.6	13.2
June 11	13.1	15.9	16.8	14.2	11.7	17.7	15.5	16.8	11.4	15.2	12.2	8.4
June 12	11.8	15.1	14.3	13.3	9.5	17.0	14.1	15.6	10.0	14.6	10.8	6.0
June 13	10.5	14.8	13.0	13.1	8.3	16.7	13.2	14.7	9.0	14.3	9.7	5.3
June 14	9.4	14.7	11.7	13.4	7.1	16.5	12.2	13.5	8.0	14.1	8.7	4.3
June 15	9.0	15.4	11.3	14.4	6.8	16.7	12.1	13.2	7.9	14.9	8.5	4.1
June 16	8.0	15.3	10.3	13.4	5.8	16.2	11.4	12.4	7.3	14.6	7.7	3.2
June 17	6.9	15.1	8.9	12.5	4.5	15.5	10.4	11.3	6.3	14.0	6.6	2.0
June 18	5.4	14.6	7.5	12.0	3.4	15.1	9.7	10.2	5.3	13.8	5.6	11.6
June 19	12.3	14.2	12.4	11.8	7.2	15.6	12.1	13.4	8.8	13.5	9.2	12.2
June 20	10.9	14.5	11.1	12.0	6.0	15.7	12.5	12.5	7.9	13.5	8.4	12.6
June 21	10.0	14.8	10.0	12.8	5.0	16.0	12.8	11.7	7.3	13.8	8.0	13.1
June 22	9.3	15.3	8.9	13.4	4.3	16.2	12.8	11.0	6.7	13.9	7.5	13.3
June 23	13.1	15.1	11.1	12.5	7.3	16.0	13.0	13.9	8.3	13.3	10.2	13.2
June 24	13.0	14.6	10.7	12.0	7.1	15.6	13.1	13.8	8.3	13.1	10.1	11.6
June 25	13.1	14.6	10.6	12.4	7.3	16.4	13.5	13.9	8.6	13.5	10.4	10.6
June 26	13.3	15.3	10.6	12.9	7.5	17.4	14.2	14.2	8.9	14.3	10.6	10.7
June 27	12.9	15.5	10.1	12.5	7.0	17.2	14.3	13.6	8.4	14.3	10.1	10.6
June 28	13.2	16.2	10.3	14.7	7.2	17.6	15.3	13.8	8.7	15.0	10.4	11.6
June 29	12.9	16.5	9.9	15.3	7.0	17.0	15.1	13.4	8.3	14.8	10.0	12.3
June 30	12.6	17.0	9.7	13.8	6.7	16.6	15.4	13.1	8.1	14.4	9.8	12.7
July 1	12.0	17.1	9.0	12.4	6.2	16.9	15.2	12.5	7.6	13.4	9.2	13.4
July 2	12.1	16.3	9.0	11.9	6.2	18.0	15.0	12.5	7.9	13.7	9.2	14.1
July 3	12.3	16.2	9.3	13.2	6.5	18.1	15.4	12.6	7.7	14.3	9.5	14.6

TABLE D-5. WATER DEPTH AT THE END OF EACH DAY DURING PERMANENT FLOOD IN 1975
(JULY 4 - AUGUST 1)

Date	Plots											
	1E	2E	3E	4E	5E	6E	1W	2W	3W	4W	5W	6W
July 4	11.8	16.0	8.6	14.9	6.0	17.5	15.6	12.0	7.2	13.6	8.9	14.4
July 5	10.9	15.8	7.8	15.2	5.1	17.1	15.5	11.1	6.3	13.0	8.1	14.4
July 6	10.1	15.8	6.7	15.4	4.3	16.9	15.2	10.1	5.3	12.5	7.1	14.6
July 7	13.2	15.4	11.2	14.0	9.0	16.4	15.4	14.8	11.6	12.6	12.0	14.5
July 8	12.4	14.9	10.4	12.7	8.1	16.3	15.4	13.7	9.9	13.3	10.7	13.7
July 9	11.2	14.9	9.3	11.8	7.2	16.3	14.0	12.7	8.6	13.3	9.5	12.8
July 10	10.4	14.8	8.4	11.2	6.4	16.0	13.4	11.7	7.6	13.2	8.6	12.6
July 11	12.6	16.6	10.4	12.8	8.3	17.8	14.6	13.5	9.4	14.8	10.4	13.9
July 12	12.0	16.3	9.8	11.9	7.7	17.6	13.6	12.9	8.6	13.7	9.7	12.9
July 13	11.6	15.8	9.3	11.3	7.3	17.3	12.8	12.5	8.1	13.3	9.3	12.5
July 14	11.9	15.4	9.7	11.5	7.5	16.9	13.1	12.6	8.3	13.7	9.6	12.5
July 15	11.7	14.5	9.4	10.8	7.4	16.0	12.8	12.4	8.2	13.8	9.3	11.7
July 16	11.2	13.6	8.9	10.3	6.9	15.7	12.4	11.9	7.7	13.4	8.8	11.0
July 17	11.9	13.5	10.9	10.6	9.4	15.4	12.1	15.1	11.2	13.0	11.1	10.7
July 18	11.3	12.9	10.2	11.1	8.5	15.3	11.8	14.3	9.9	12.2	10.2	11.9
July 19	10.4	12.3	9.2	11.1	7.6	14.9	11.0	13.3	8.7	11.4	9.2	10.1
July 20	9.8	11.9	8.5	11.8	6.9	14.3	10.3	12.4	7.9	10.5	8.5	9.6
July 21	8.9	13.2	7.7	11.7	6.0	14.6	13.7	11.3	7.1	12.1	7.7	10.1
July 22	10.9	13.1	10.5	11.9	8.1	15.0	13.5	15.4	11.6	12.2	12.0	8.8
July 23	10.7	13.0	10.3	11.9	7.8	15.4	13.6	14.6	10.7	12.6	11.2	7.7
July 24	10.3	12.9	9.9	11.8	7.4	15.4	13.7	13.3	9.8	12.5	10.4	8.7
July 25	9.8	12.6	9.2	11.6	6.8	15.3	13.4	12.3	9.1	12.4	9.7	12.2
July 26	9.2	12.2	8.6	11.5	6.2	15.1	12.6	11.1	8.3	12.2	9.1	11.2
July 27	8.3	11.6	7.9	10.7	5.4	14.7	12.2	9.9	7.5	11.5	8.4	10.1
July 28	12.8	13.2	12.7	11.5	8.3	15.1	13.3	14.6	11.1	14.0	11.5	10.8
July 29	12.9	13.3	12.7	11.8	8.3	15.5	13.7	14.2	11.0	14.1	11.8	11.3
July 30	13.3	13.7	13.1	11.8	8.7	16.2	14.0	14.2	11.0	14.4	12.0	11.3
July 31	15.7	16.8	16.4	14.8	12.5	18.9	17.3	17.6	15.1	17.1	15.4	13.6
August 1	18.1	19.0	18.9	16.4	15.5	20.8	18.7	20.4	18.1	18.9	18.1	15.4

TABLE D-6. WATER DEPTH AT THE END OF EACH DAY DURING PERMANENT FLOOD IN 1975
(AUGUST 2 - AUGUST 16)

Date	Plots											
	1E	2E	3E	4E	5E	6E	1W	2W	3W	4W	5W	6W
August 2	14.9	16.0	15.5	13.1	12.9	17.2	15.1	17.4	15.6	15.5	14.9	11.6
August 3	14.2	15.5	14.9	12.4	12.1	16.1	14.7	16.6	15.4	14.7	14.9	10.7
August 4	16.6	18.2	16.5	17.2	13.5	19.7	18.0	17.8	17.1	17.8	14.8	14.9
August 5	16.6	17.9	16.5	15.5	12.4	19.1	17.5	18.1	14.3	17.3	14.8	14.3
August 6	14.9	15.9	14.6	13.9	11.3	17.4	15.7	16.1	11.6	15.1	12.2	12.5
August 7	7.6	15.3	5.4	13.6	2.2	17.1	15.0	9.3	3.7	14.4	5.7	11.9
August 8	8.6	16.1	5.1	14.6	3.3	17.9	15.7	9.9	4.3	14.8	6.6	12.4
August 9	8.3	15.3	4.9	14.0	3.1	17.0	14.9	8.9	3.9	14.1	6.4	11.8
August 10	7.9	14.8	4.5	13.8	2.7	16.7	14.4	7.8	3.5	13.7	6.0	11.5
August 11	7.5	14.5	4.0	13.8	2.1	16.5	14.3	6.7	3.0	13.5	5.4	11.4
August 12	7.1	13.8	3.4	13.3	1.7	16.7	14.3	5.7	2.3	13.8	4.9	11.3
August 13	6.7	13.3	2.8	13.5	1.2	16.9	14.2	4.6	1.7	13.8	4.3	11.0
August 14	6.2	13.1	2.1	13.7	0.4	17.0	14.2	3.5	1.2	13.9	3.8	10.5
August 15	5.6	12.9	1.3	13.2	0.0	17.1	14.0	2.3	0.5	13.8	3.2	10.0
August 16	5.3	12.8	0.7	12.9	0.0	17.3	13.9	0.7	0.0	13.8	2.8	9.8

Appendix E

Minimum and Maximum Soil and Water Temperatures in the Rice Paddies

TABLE E-1. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (JUNE 1 - JUNE 30, 1973)

June 1 - June 30, 1973

June of 1973	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
14						
15	27.78	31.94	30.17	27.22	33.89	30.28
16	27.78	32.22	29.06	26.67	33.61	29.39
17	26.67	32.22	29.22	26.39	34.17	29.44
18	26.67	32.78	29.11	26.11	34.17	29.39
19	26.67	31.67	29.06	26.39	33.06	30.06
20	26.61	31.39	28.72	25.72	34.44	30.33
21	26.39	28.78	27.06	25.28	28.28	26.39
22	24.44	30.00	27.28	25.89	30.94	27.22
23	25.89	30.00	28.00	25.00	30.72	28.06
24	26.67	32.22	29.00	26.39	33.89	29.22
25	27.22	30.00	28.72	26.94	31.39	28.89
26	26.67	32.78	29.56	26.11	36.11	30.44
27	27.50	32.50	30.00	27.22	34.39	30.33
28	27.67	32.11	29.83	27.22	34.33	30.28
29	27.67	31.67	29.61	27.22	33.17	29.61
30	27.22	32.22	29.50	26.78	34.22	29.67
A	29.61	31.56	29.00	26.33	33.17	29.33

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A. = Monthly Average.

TABLE E-2. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (JULY 1 - JULY 31, 1973)

July 1 - July 31, 1973

July of 1973	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
1	27.67	33.33	30.28	27.22	35.56	30.61
2	28.33	32.50	30.50	28.22	33.33	30.89
3	30.56	32.67	30.72	30.44	33.89	31.78
4	28.33	32.67	30.72	28.33	34.61	31.44
5	27.78	31.33	29.44	27.50	32.22	29.44
6	26.11	29.33	27.44	26.00	28.89	27.28
7	25.56	27.50	26.44	24.61	27.67	26.00
8	24.56	30.00	26.11	24.22	32.22	26.89
9	-	-	-	-	-	-
10	26.67	32.22	29.89	26.11	34.44	30.17
11	30.17	32.22	31.17	28.78	34.33	31.06
12	30.83	31.56	31.17	28.83	32.22	30.11
13	30.00	31.11	30.67	27.78	32.50	30.06
14	30.00	31.11	30.61	27.61	32.78	23.33
15	30.00	31.11	30.56	27.78	32.78	29.72
16	-	-	-	-	-	-
17	29.44	30.56	30.00	26.67	31.11	29.44
18	29.44	31.39	30.56	27.78	34.44	30.61
19	30.00	31.39	30.89	28.17	34.44	31.61
20	30.11	31.28	30.89	28.56	34.44	31.50
21	30.00	31.11	30.72	28.44	33.33	31.06
22	30.00	31.11	30.56	28.72	33.22	30.33
23	29.44	30.44	30.17	27.67	32.27	29.78
24	29.94	31.11	30.50	26.67	33.33	30.22
25	30.00	31.11	30.33	29.67	31.39	29.72
26	29.56	30.22	30.00	27.22	31.11	29.06
27	30.00	30.56	30.22	26.94	33.17	29.83
28	30.00	31.00	30.50	28.89	32.33	30.72
29	30.00	30.83	30.56	28.61	32.78	31.39
30	-	-	-	-	-	-
31	-	-	-	-	-	-
A	29.06	29.28	30.06	27.78	32.56	29.78

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A. = Monthly Average.

TABLE E-3. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (JUNE 15 - JUNE 30, 1974)

June 15 - June 30, 1974

June of 1974	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
15	27.78	31.94	30.11	27.22	33.89	30.28
16	27.78	32.22	29.06	26.67	33.61	29.39
17	26.67	32.22	29.22	26.39	34.17	29.44
18	26.67	32.78	29.11	26.11	34.17	29.39
19	26.67	31.67	29.06	26.39	33.06	30.00
20	26.61	31.39	28.72	25.72	34.44	30.33
21	26.39	28.78	27.06	25.28	28.28	26.39
22	24.44	30.00	27.28	24.44	30.94	27.22
23	25.89	30.00	28.00	25.00	30.72	28.06
24	26.67	32.22	29.00	26.39	33.89	29.22
25	27.22	30.00	28.72	26.94	31.39	28.89
26	26.67	32.78	29.56	26.11	36.11	30.44
27	27.50	32.50	30.00	27.22	34.39	30.33
28	27.67	32.11	29.83	27.22	34.33	30.28
29	27.67	31.67	29.61	27.22	33.17	29.61
30	27.22	32.22	29.50	26.78	34.22	29.67
A.	26.85	31.53	28.99	26.32	33.17	29.31

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A = Monthly Average.

TABLE E-4. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (JULY 1 - JULY 31, 1974)

July 1 - July 31, 1974

July of 1974	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
1	27.67	33.33	30.28	26.72	35.56	30.61
2	28.33	32.50	30.50	28.22	33.33	30.89
3	30.56	32.67	30.72	30.44	33.89	31.78
4	28.33	32.67	30.72	28.33	34.61	31.44
5	27.78	31.33	29.44	27.50	32.22	29.44
6	26.11	29.33	27.44	26.00	28.89	27.28
7	25.56	27.50	26.44	24.61	27.67	26.00
8	24.56	30.00	26.11	24.22	32.22	26.83
9	-	-	-	-	-	-
10	26.67	32.22	29.89	26.11	34.44	30.17
11	30.17	31.56	31.17	28.78	34.33	31.06
12	30.83	32.22	31.17	28.83	32.22	30.11
13	30.00	31.11	30.67	27.78	32.50	30.06
14	30.00	31.11	30.61	27.61	32.78	23.33
15	30.00	31.11	30.56	27.78	32.78	29.72
16	-	-	-	-	-	-
17	29.44	30.56	30.00	26.67	31.11	29.44
18	29.44	31.39	30.56	27.78	34.44	30.61
19	30.00	31.39	30.89	28.17	34.44	31.61
20	30.11	31.28	30.89	28.56	34.44	31.50
21	30.00	31.11	30.72	28.44	33.33	31.06
22	30.00	31.11	30.56	28.72	33.22	30.33
23	29.44	30.44	30.17	27.67	32.22	29.78
24	29.94	31.11	30.56	26.67	33.33	30.22
25	30.00	31.11	30.33	29.67	31.39	29.72
26	29.56	30.22	30.00	27.22	31.11	29.06
27	30.00	30.56	30.22	26.94	33.17	29.83
28	30.00	31.00	30.50	28.89	32.33	30.72
29	30.00	30.83	30.56	28.61	32.78	31.39
30	-	-	-	-	-	-
31	-	-	-	-	-	-
A.	29.06	31.14	30.06	27.66	32.77	29.78

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A. = Monthly Average.

TABLE E-5. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (AUGUST 1 - AUGUST 19, 1974)

August 1 -August 19, 1974

Aug. of 1974	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
1	28.89	30.56	29.83	26.67	30.28	28.28
2	28.67	29.44	28.67	26.11	29.67	27.17
3	28.78	29.78	29.33	26.67	30.00	28.61
4	28.33	29.83	29.17	25.39	30.00	28.00
5	28.33	29.44	28.88	25.61	29.44	27.50
6	-	-	-	-	-	-
7	-	-	-	-	-	-
8	-	-	-	-	-	-
9	27.78	28.89	28.56	25.44	28.33	26.00
10	28.33	29.06	28.89	25.67	30.00	27.22
11	28.78	29.89	29.28	26.67	31.67	29.22
12	28.94	30.00	29.44	27.83	31.39	29.24
13	28.72	29.17	28.94	26.67	30.00	28.06
14	-	-	-	-	-	-
15	28.33	29.33	28.72	25.56	27.50	26.44
16	28.33	28.89	28.67	26.11	26.67	26.39
17	28.06	28.61	28.33	25.56	26.67	26.06
18	28.06	28.89	28.17	25.56	28.33	26.22
19	28.33	29.44	28.83	26.39	31.11	28.28
A.	28.44	29.41	28.91	26.13	29.40	27.51

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A. = Monthly Average.

TABLE E-6. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (JUNE 1 - JUNE 30, 1975)

June 1 - June 30, 1975

June of 1975	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	-	-	-	-	-	-
8	-	-	-	-	-	-
9	-	-	-	-	-	-
10	-	-	-	-	-	-
11	25.67	26.11	25.89	26.11	26.22	26.11
12	25.28	27.50	26.22	24.72	28.33	26.56
13	26.67	28.89	27.67	26.39	30.56	28.56
14	27.50	29.28	28.44	27.39	30.89	29.22
15	26.67	28.78	27.56	26.11	28.44	27.44
16	26.67	28.33	27.44	26.67	29.33	28.06
17	27.22	28.39	28.06	27.22	29.89	28.56
18	27.78	28.61	28.11	26.61	29.00	28.00
19	27.78	28.89	28.33	27.17	29.39	28.39
20	28.00	29.44	28.78	27.67	29.78	28.67
21	27.72	29.00	28.50	26.67	29.50	28.22
22	27.17	28.39	28.11	25.83	28.44	27.44
23	26.94	28.22	27.67	25.72	28.06	26.89
24	26.94	27.50	27.33	25.83	27.22	26.67
25	25.56	26.39	26.00	24.61	25.78	25.39
26	25.50	26.11	25.83	24.44	25.67	25.17
27	-	-	-	-	-	-
28	-	-	-	-	-	-
29	-	-	-	-	-	-
30	-	-	-	-	-	-
A	26.78	28.17	27.50	26.11	28.56	27.44

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A. = Monthly Average.

TABLE E-7. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (JULY 1 - JULY 31, 1975)

July 1 - July 31, 1975

July of 1975	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	-	-	-	-	-	-
8	-	-	-	-	-	-
9	-	-	-	-	-	-
10	27.50	27.78	27.67	27.22	27.72	27.44
11	26.94	27.78	27.33	26.17	27.72	27.00
12	26.22	26.89	26.67	25.22	26.78	26.11
13	26.33	27.00	26.72	25.56	27.33	26.39
14	26.11	27.00	26.44	25.22	26.94	25.94
15	26.06	26.39	26.17	25.28	26.11	25.67
16	25.83	26.17	26.06	25.00	26.00	25.33
17	26.06	26.22	26.17	25.06	26.39	25.72
18	26.11	26.67	26.33	25.00	26.89	25.94
19	26.33	27.22	26.67	25.33	27.78	26.56
20	26.67	27.22	27.06	26.00	27.78	26.95
21	-	-	-	26.11	27.78	26.94
22	-	-	-	-	-	-
23	-	-	-	-	-	-
24	25.89	26.67	26.22	24.44	26.11	25.17
25	26.33	26.83	26.61	25.00	26.44	25.78
26	26.39	26.94	26.67	25.11	26.67	26.00
27	26.33	27.22	26.78	25.22	26.89	26.11
28	-	-	-	26.11	26.83	26.56
29	-	-	-	-	-	-
30	-	-	-	-	-	-
31	-	-	-	25.17	26.00	25.67
A	26.33	26.94	26.61	25.44	26.89	26.17

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A. = Monthly Average.

TABLE E-8. SOIL AND WATER TEMPERATURE IN RICE PADDY,
BEAUMONT, TEXAS (AUGUST 1 - AUGUST 31, 1975)

August 1 - August 31, 1975

August of 1975	Soil (°C)			Water (°C)		
	MIN.	MAX.	MEAN	MIN.	MAX.	MEAN
1	-	-	-	25.00	26.11	25.61
2	-	-	-	24.89	25.89	25.33
3	-	-	-	25.00	25.56	25.39
4	-	-	-	-	-	-
5	-	-	-	-	-	-
6	-	-	-	-	-	-
7	-	-	-	-	-	-
8	-	-	-	-	-	-
9	-	-	-	-	-	-
10	-	-	-	-	-	-
11	-	-	-	-	-	-
12	-	-	-	-	-	-
13	-	-	-	-	-	-
14	-	-	-	-	-	-
15	-	-	-	-	-	-
16	-	-	-	-	-	-
17	-	-	-	-	-	-
18	-	-	-	-	-	-
19	-	-	-	-	-	-
20	-	-	-	-	-	-
21	-	-	-	-	-	-
22	-	-	-	-	-	-
23	-	-	-	-	-	-
24	-	-	-	-	-	-
25	-	-	-	-	-	-
26	-	-	-	-	-	-
27	-	-	-	-	-	-
28	-	-	-	-	-	-
29	-	-	-	-	-	-
30	-	-	-	-	-	-
31	-	-	-	-	-	-
A	-	-	-	24.94	25.83	25.44

MAX. = Daily Maximum; MIN. = Daily Minimum; The table means were computed from six daily interval chart readings of continuous recordings; A. = Monthly Average.

Appendix F. Average daily water balance in the
six rice paddies for each irrigation treatment for 1974 and 1975 growing seasons.

TABLE F-1. DAILY WATER BALANCE FOR RICE PADDIES WITH CONTINUOUS IRRIGATION FOR MAY 1974,
GIVEN IN CM

Date	Inflow	Irrigation	Total Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
May 1				1.55	1.55				
May 5				0.91	0.91				
May 9				1.65	1.65				
May 10				1.96	1.96				
May 11						0.50			
May 20				5.31	5.31				
May 21						2.10			
May 22		13.00	13.00		13.00				
May 23						9.50			
May 25				0.48	0.48				
May 26				0.64	0.64				
May 30				1.27	1.27				
May 31				0.89	0.89				
<hr/>									
MAY TOTALS		13.00	13.00	14.66	27.66	12.10			
<hr/>									
June 1				1.14	1.14		0.00	0.00	
June 2							0.00	0.00	
June 3							0.00	0.00	
June 4							0.00	0.00	
June 5							0.00	0.00	
June 6		14.00	14.00	0.10	14.10	0.02	0.60	0.00	0.62
June 7						0.21	0.60	0.00	0.81
June 8	0.90		0.90		0.90	0.41	0.58	0.66	1.65
June 9	0.90		0.90		0.90	0.59	0.53		1.12
June 10	0.90	0.48	1.38		1.38	0.45	0.47		0.92
June 11	0.90		0.90		0.90	0.38	0.44	0.60	1.42
June 12	0.90		0.90		0.90	0.32	0.42	0.53	1.27
June 13	0.90		0.90		0.90	0.31	0.39	0.70	1.40
June 14	0.90		0.90	0.64	1.54	0.51	0.36	0.54	1.41
June 15	0.90		0.90		0.90	0.08	0.34	0.78	1.20
June 16	0.90		0.90		0.90	0.02	0.33	1.05	1.40
June 17	0.90		0.90		0.90	0.00	0.30	0.95	1.25
June 18	0.90		0.90		0.90	0.00	0.27	0.86	1.13

(continued)

TABLE F-1. (Continued)

Date	Inflow	Irrigation	Total Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
June 19	0.90		0.90		0.90	0.00	0.27	0.86	1.13
June 20	0.90	4.48	5.38	1.79	7.17	0.05	0.25		0.30
June 21	0.90		0.90	0.69	1.59	0.42	0.24		0.66
June 22	0.90		0.90		0.90	0.47	0.22	0.92	1.61
June 23	0.90		0.90		0.90	0.47	0.20	0.82	1.49
June 24	0.90		0.90		0.90	0.52	0.19	1.01	1.72
June 25	0.90		0.90		0.90	0.21	0.18	1.00	1.39
June 26	0.90		0.90		0.90	0.09	0.16	0.80	1.05
June 27	0.90		0.90		0.90	0.09	0.15	0.86	1.10
June 28	0.90	0.66	1.56		1.56	0.14	0.14	0.71	0.99
June 29	0.90		0.90		0.90	0.12	0.13	0.66	0.91
June 30	0.90		0.90		0.90	0.13	0.12	0.65	0.99
JUNE TOTALS	27.00	19.62	40.32	4.36	44.68	6.01	7.88	14.96	28.94
July 1	0.90		0.90	1.24	2.14	0.23	0.13	0.49	0.85
July 2	0.90		0.90		0.90	0.28	0.12	0.74	1.14
July 3	0.90		0.90		0.90	0.23	0.12	0.84	1.19
July 4	0.90		0.90		0.90	0.25	0.12	0.78	1.15
July 5	0.90		0.90		0.90	0.33	0.11	0.82	1.26
July 6	0.90		0.90	0.23	1.13	0.33	0.11	0.62	1.06
July 7	0.90		0.90		0.90	0.32	0.11	0.60	1.03
July 8	0.90		0.90		0.90	1.19	0.10	0.25	1.54
July 9	0.90		0.90		0.90	0.65	0.10	0.76	1.51
July 10	0.90		0.90		0.90	0.42	0.10	0.70	1.22
July 11	0.90		0.90		0.90	0.35	0.10	0.51	0.96
July 12	0.90	0.58	1.48		1.48	0.69	0.10	0.70	1.49
July 13	0.90		0.90		0.90	0.45	0.09	0.54	1.08
July 14	0.90		0.90	1.14	2.04	0.55	0.09	0.57	1.21
July 15	0.90		0.90	0.15	1.05	0.52	0.09	0.18	0.79
July 16	0.90		0.90	0.15	1.05	0.57	0.09	0.33	0.99
July 17	0.90		0.90	0.84	1.74	0.60	0.09	0.33	1.02
July 18	0.90		0.90		0.90	0.54	0.09	0.70	1.33

(continued)

TABLE F-1. (Continued)

Date	Inflow	Irrigation	Total Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
July 19	0.90		0.90		0.90	0.44	0.09	0.57	1.10
July 20	0.90		0.90		0.90	0.38	0.08	0.67	1.13
July 21	0.90		0.90		0.90	0.34	0.08	0.65	1.07
July 22	0.90	0.68	1.58		1.58	0.49	0.08	0.81	1.38
July 23	0.90	0.15	1.05		1.05	0.42	0.08	0.89	1.39
July 24	0.90	0.58	1.48		1.48	0.32	0.08	0.68	1.08
July 25	0.90		0.90		0.90	0.27	0.08	0.65	1.00
July 26	0.90		0.90		0.90	0.29	0.08	0.76	1.13
July 27	0.90		0.90		0.90	0.36	0.08	0.94	1.38
July 28	0.90		0.90		0.90	0.38	0.08	0.62	1.08
July 29	0.90		0.90		0.90	0.56	0.08	0.70	1.34
July 30	0.90		0.90		0.90	0.48	0.08	1.00	1.56
July 31	0.90		0.90	8.26	9.16	1.03	0.08	0.20	1.31
TOTALS	27.90	1.99	29.89	12.01	41.90	14.26	2.91	19.60	36.77
August 1	0.90		0.90		0.90	0.80	0.08	0.53	1.41
August 2	0.90		0.90	0.46	1.36	0.50	0.08	0.18	0.76
August 3	0.90		0.90	2.67	3.57	1.17	0.08	0.30	1.55
August 4	0.90		0.90		0.90	0.99	0.08	0.62	1.69
August 5	0.90		0.90		0.90	0.82	0.08	0.64	1.54
August 6	0.90		0.90		0.90	0.56	0.07	0.27	0.90
August 7	0.90		0.90	2.69	3.59	1.28	0.07	0.40	1.75
August 8	0.90		0.90		0.90	0.75	0.07	0.67	1.49
August 9	0.90		0.90		0.90	0.54	0.07	0.50	1.11
August 10	0.90		0.90		0.90	0.45	0.07	0.83	1.35
August 11	0.90		0.90		0.90	0.42	0.07	0.56	1.05
August 12	0.90		0.90	0.69	1.59	0.49	0.07	0.48	1.04
August 13	0.90		0.90	0.23	1.13	0.44	0.07	0.50	1.01
August 14	0.90		0.90	0.30	1.20	0.59	0.07	0.47	1.13
August 15	0.90		0.90	0.25	1.15	0.44	0.07	0.28	0.79
August 16	0.90		0.90		0.90	0.44	0.07	0.52	1.03

(continued)

TABLE F-1. (Continued)

Date	Inflow	Irrigation	Total Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
August 17	0.90		0.90		0.90	0.40	0.07	0.64	1.11
August 18	0.90		0.90	5.08	5.98	0.37	0.07	0.63	1.07
August 19	0.90		0.90		0.90	0.34	0.07	0.69	1.10
August 20	0.90		0.90		0.90	0.29	0.07	0.59	0.95
August 21	0.90		0.90		0.90	0.19	0.07	0.52	0.78
August 22	0.90		0.90		0.90	1.77	0.07	0.41	2.25
TOTALS	19.80		19.80	12.37	32.17	14.04	1.59	11.23	26.86

TABLE F-2. DAILY WATER BALANCE FOR RICE PADDIES WITH IMPOUNDED IRRIGATION FOR 1974 GIVEN IN CM

Date	Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
May 1		1.55	1.55				
May 5		0.91	0.91				
May 9		1.65	1.65				
May 10		1.96	1.96				
May 11				0.5			
May 20		5.31	5.31				
May 21				2.1			
May 22	9.27		9.27				
May 23				6.2			
May 25		0.48	0.48				
May 26		0.64	0.64				
May 30		1.27	1.27				
May 31		0.89	0.89				
MAY TOTALS	9.27	14.66	23.93	8.8			
June 1		1.14					
June 6	10.3	0.10	10.40	0.04	0.60	0.13	0.77
June 7				0.97	0.60		0.67
June 8				0.24	0.58	0.66	1.48
June 9				0.55	0.53		1.08
June 10				0.58	0.47		1.04
June 11				0.60	0.44	0.60	1.64
June 12				0.59	0.42	0.53	1.53
June 13				0.59	0.39	0.70	1.68
June 14		0.64	0.64	1.04	0.36	0.57	1.97
June 15				0.41	0.34	0.78	1.53
June 16				0.19	0.33	1.05	1.57
June 17				0.70	0.30	0.95	1.32
June 18				0.02	0.29	0.85	1.17
June 19				0.01	0.27	0.86	1.14
June 20	7.74	1.79	9.53	0.34	0.25		0.59

(continued)

TABLE F-2. (Continued)

Date	Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
June 21		0.69	0.69	0.49	0.24		0.73
June 22				0.31	0.22	0.92	1.45
June 23				0.21	0.20	0.82	1.23
June 24	4.70		4.70	0.35	0.19	1.01	1.55
June 25				0.20	0.18	1.00	1.38
June 26				0.28	0.15	0.80	1.24
June 27				0.18	0.15	0.86	1.18
June 28	4.71		4.71	0.57	0.14	0.71	1.42
June 29				0.53	0.13	0.66	1.32
June 30				0.35	0.13	0.65	1.13
JUNE TOTALS	27.45	4.36	30.67	10.34	7.90	15.11	31.81
July 1		1.24	1.24	0.36	0.13	0.49	0.98
July 2				0.36	0.12	0.74	1.22
July 3				0.25	0.12	0.84	1.21
July 4				0.17	0.12	0.78	1.07
July 5				0.11	0.11	0.82	1.04
July 6		0.23	0.23	0.08	0.11	0.62	0.81
July 7				0.06	0.11	0.60	0.77
July 8				0.26	0.10	0.25	0.61
July 9				0.33	0.10	0.76	1.19
July 10	0.0		0.0	0.25	0.10	0.69	1.04
July 11				0.18	0.10	0.51	0.79
July 12	4.65		4.65	0.48	0.10	0.70	1.28
July 13	0.22		0.22	0.25	0.09	0.54	0.88
July 14	0.0	1.14	1.14	0.26	0.09	0.57	0.92
July 15		0.15	0.15	0.24	0.09	0.18	0.51
July 16		0.15	0.15	0.27	0.09	0.33	0.69
July 17		0.84	0.84	0.25	0.09	0.33	0.67
July 18				0.22	0.09	0.70	1.01
July 19				0.17	0.09	0.57	0.83
July 20				0.13	0.08	0.67	0.88
July 21				0.08	0.08	0.65	0.81
July 22	5.87		5.87	0.82	0.08	0.81	1.71

(continued)

TABLE F-2. (Continued)

Date	Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
July 23				1.65	0.08	0.89	2.63
July 24	0.58		0.58	1.19	0.08	0.68	1.95
July 25	1.57		1.57	0.70	0.08	0.65	1.43
July 26				0.48	0.08	0.76	1.32
July 27				0.29	0.08	0.94	1.31
July 28				0.16	0.08	0.62	0.86
July 29	3.26		3.26	0.48	0.08	0.70	1.26
July 30				0.75	0.08	1.00	1.83
July 31		8.26	8.26	0.83	0.08	0.20	1.11
JULY TOTALS	16.15	12.01	28.16	12.11	2.91	19.59	34.62
August 1				0.35	0.08	0.53	0.96
August 2		0.46	0.46	0.22	0.08	0.18	0.48
August 3		2.67	2.67	0.62	0.08	0.30	0.99
August 4				0.77	0.08	0.62	1.47
August 5				0.54	0.08	0.64	1.26
August 6				0.40	0.07	0.27	0.74
August 7		2.69	2.69	0.87	0.07	0.40	1.34
August 8				0.42	0.07	0.67	1.16
August 9				0.27	0.07	0.50	0.84
August 10				0.19	0.07	0.83	1.09
August 11				0.12	0.07	0.56	0.75
August 12		0.69	0.69	0.10	0.07	0.48	0.65
August 13		0.23	0.23	0.10	0.07	0.49	0.66
August 14		0.30	0.30	0.12	0.07	0.47	0.66
August 15		0.25	0.25	0.09	0.07	0.28	0.44
August 16				0.06	0.07	0.52	0.66
August 17				0.02	0.07	0.64	0.73
August 18		5.08	5.08	0.00	0.07	0.63	0.70
August 19				0.00	0.07	0.69	0.76
August 20				0.00	0.07	0.59	0.66
August 21					0.07	0.52	0.59
August 22				2.13	0.07	0.41	2.61
AUGUST TOTALS		12.37	12.37	7.39	1.59	11.22	20.20

TABLE F-3. DAILY WATER BALANCE FOR RICE PADDIES WITH CONTINUOUS IRRIGATION FOR 1975 GIVEN IN CM

Date	Rate of Inflow	Intermittent Irrigation	Total Irrigation	Rainfall	Total H ₂ O	Runoff	Leaching	Evts	Total Loss
May 1									
May 2				.05	.05	.05			
May 3		9.4	9.4		9.4				
May 4									
May 5									
May 6				.05	.05				
May 7				.30	.30				
May 8				.46	.46				
May 9									
May 10									
May 11				4.39	4.39	1.2			
May 12									
May 13				.46	.46				
May 14									
May 15				.46	.46				
May 16									
May 17									
May 18									
May 19									
May 20									
May 21									
May 22									
May 23									
May 24				.58	.58				
May 25									
May 26									
May 27									
May 28		8.43	17.83	10.26	18.69				
May 29				3.56	3.56				
May 30				5.26	5.26				
May 31									
MAY TOTALS		9.37	18.77	25.83	43.66	1.7			(continued)

TABLE F-3. (Continued)

Date	Rate of Inflow	Intermittent Irrigation	Total Irrigation	Rainfall	Total H ₂ O	Runoff	Leaching	Evts	Total Loss
June 1				5.26	5.26				
June 2									
June 3									
June 4									
June 5	.94	7.43	.94		8.37	.13		.14	.27
June 6	.94		.94		.94	2.06	.60	.60	3.26
June 7	.94		.94		.94	.42	.60	.55	1.57
June 8	.94		.94		.94	.50	.58	.48	1.56
June 9	.94		.94	21.59	22.53	19.98	.53	.14*	20.65
June 10	.94		.94	.79	1.7	4.99	.47	.32*	5.78
June 11	.94		.94		.94	1.85	.44	.27	2.56
June 12	.94		.94		.94	.57	.42	.56	1.55
June 13	.94		.94		.94	.43	.39	.72	1.54
June 14	.94		.94		.94	.37	.36	.87	1.60
June 15	.94		.94	.64	1.58	.44	.34	.75	1.53
June 16	.94		.94		.94	.43	.33	.85	1.61
June 17	.94		.94		.94	.31	.30	.95	1.56
June 18	.94	1.35	2.29		2.29	.22	.29	1.01	1.52
June 19	.94	1.07	2.01		2.01	.19	.27	.93	1.39
June 20	.94	.47	1.41		1.41	.21	.25	.80	1.26
June 21	.94		.94	.23	1.17	.24	.24	.77	1.25
June 22	.94		.94		.94	.34	.22	.54	1.10
June 23	.94		.94		.94	.31	.20	.48	0.99
June 24	.94		.94	.53	1.47	.25	.19	.50	0.94
June 25	.94		.94	.36	1.30	.40	.18	.11	0.69
June 26	.94		.94	.43	1.37	.43	.16	.23	0.82
June 27	.94		.94		.94	.49	.15	.36	1.00
June 28	.94		.94	.79	1.73	.52	.14	.59	1.25
June 29	.94		.94		.94	.76	.13	.26	1.15
June 30	.94		.94	.15	1.09	.72	.13	.36	1.21
JUNE TOTALS	24.44	10.32	27.33	30.77	65.50	37.56	7.91	14.14	59.61

(continued)

TABLE F-3. (Continued)

Date	Rate of Inflow	Intermittent Irrigation	Total Irrigation	Rainfall	Total H ₂ O	Runoff	Leaching	Evts	Total Loss
July 1	.94		.94		.94	.88	.13	.47	1.48
July 2	.94		.94	.51	1.45	.66	.12	.52	
July 3	.94		.94	.38	1.32	.62	.12	.14	
July 4	.94		.94		.94	.72	.12	.56	
July 5	.94		.94		.94	.73	.11	.81	
July 6	.94		.94		.94	.80	.11	.79	
July 7	.94	.22	1.16		1.16	.60	.11	.75	
July 8	.94		.94		.94	.49	.10	.77	
July 9	.94		.94		.94	.36	.10	.88	
July 10	.94		.94	.20	1.14	.28	.10	.81	
July 11	.94		.94	1.73	2.67	.52	.10	.32	
July 12	.94		.94		.94	.56	.10	.50	
July 13	.94		.94	.25	1.19	.41	.09	.59	
July 14	.94		.94	.51	1.45	.34	.09	.21	
July 15	.94		.94		.94	.26	.09	.14	
July 16	.94		.94		.94	.18	.09	.40	
July 17	.94	.45	1.39		1.39	.12	.09	.36	
July 18	.94		.94		.94	.10	.09	.60	
July 19	.94		.94		.94	.07	.09	.73	
July 20	.94		.94		.94	.04	.08	.56	
July 21	.94	2.13	3.07		3.07	.07	.08	.71	
July 22	.94	1.42	3.30		3.30	.13	.08	.30	
July 23	.94		.94		.94	.15	.08	.15	
July 24	.94		.94		.94	.16	.08	.33	
July 25	.94	.79	1.73		1.73	.14	.08	.42	
July 26	.94		.94		.94	.10	.08	.50	
July 27	.94		.94		.94	.06	.08	.68	
July 28	.94	.44	1.38	3.56	4.94	.07	.08	.98	
July 29	.94		.94	.53	1.47	.16	.08	.46	
July 30	.94		.94	.41	1.35	.28	.08	.39	
July 31	.94		.94	3.78	4.72	.89	.08	.84	
JULY TOTALS	29.14	5.45	35.53	11.86	47.39	10.95	2.91	16.67	1.48

(continued)

TABLE F-3. (Continued)

Date	Rate of Inflow	Intermittent Irrigation	Total Irrigation	Rainfall	Total H ₂ O	Runoff	Leaching	EVTs	Total Loss
August 1	.94		.94	3.5	4.44	1.10	.08		1.18
August 2	.94		.94		.94	1.08	.08	1.04	2.20
August 3	.94		.94	.40	1.34	.50	.08	.34	.92
August 4	.94		.94	4.1	5.04	1.59	.08	.55	2.22
August 5	.94		.94	1.5	2.44	1.49	.08	.71	2.28
August 6	.94		.94		.94	.97	.07	.67	1.71
August 7	.94		.94	.25	1.19	.59	.07	.85	1.51
August 8	.94		.94	1.27	2.21	.69	.07	.62	1.38
August 9	.94		.94		.94	.65	.07	.34	1.06
August 10	.94		.94		.94	.49	.07	.37	.93
August 11	.94		.94		.94	.47	.07	.52	1.06
August 12	.94		.94		.94	.39	.07	.38	.84
August 13	.94		.94		.94	.41	.07	.48	.96
August 14	.94		.94		.94	.39	.07	.64	1.10
August 15	.94		.94		.94	.40	.07	.66	1.13
August 16	.94		.94		.94	.35	.07	.30	.72
August 17	.94		.94	.05	.99	3.4	.07	.51	.92
TOTALS	15.98		15.98	11.07	27.05	14.96	1.24	8.98	35.54

* estimated from climatological data

TABLE F-4. DAILY WATER BALANCE FOR RICE PADDIES WITH IMPOUNDED IRRIGATION FOR 1975 GIVEN IN CM

Date	Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
April 30		2.26					
APRIL TOTALS		2.26					
May 2		0.05	2.26				
May 3	12.4		12.4				
May 4				9.4			
May 6			0.05				
May 7		0.30	0.30				
May 8		0.46	0.46				
May 11		4.39	4.39				
May 12				2.1			
May 13		0.46	0.46				
May 15		0.46	0.46				
May 24		0.58	0.58				
May 28	11.4	10.26	21.66	11.3			11.3
May 29		3.56	3.56	7.2			7.2
May 30		5.26	5.26	2.1			2.1
MAY TOTALS	23.8	25.78	51.84	32.1			20.6
June 1		5.26					
June 5	10.40		10.40	0.37		0.14	0.51
June 6				0.97	0.60	0.60	2.17
June 7				0.58	0.60	0.55	1.73
June 8				0.48	0.58	0.48	1.54
June 9		21.59	21.59	16.7	0.53	0.13*	17.36
June 10		0.76	0.76	4.20	0.47	0.32*	4.99
June 11				0.73	0.44	0.28	1.45
June 12				0.20	0.42	0.56	1.18
June 13				0.07	0.39	0.72	1.18
June 14				0.02	0.36	0.87	1.29
June 15		0.64	0.64	0.00	0.34	0.75	1.09
June 16				0.00	0.33	0.85	1.18
June 17				0.00	0.30	0.95	1.25

(continued)

TABLE F-4. (Continued)

Date	Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
June 18				0.00	0.29	0.01	0.30
June 19	4.33		4.33	0.01	0.27	0.93	1.21
June 20				0.01	0.25	0.80	1.06
June 21		0.23	0.23	0.00	0.24	0.77	1.01
June 22				0.00	0.22	0.54	0.76
June 23	2.57		2.57	0.02	0.20	0.48	0.70
June 24		0.53	0.53	0.01	0.19	0.50	0.70
June 25		0.36	0.36	0.00	0.18	0.11	0.29
June 26				0.01	0.16	0.23	0.40
June 27				0.01	0.15	0.36	0.52
June 28		0.79	0.79	0.00	0.14	0.58	0.72
June 29				0.00	0.13	0.26	0.39
June 30		0.15	0.15	0.00	0.13	0.36	0.49
JUNE TOTALS	17.30	30.31	45.47	24.39	7.91	13.13	45.47
July 1				0.00	0.13	0.47	0.60
July 2		0.51	0.51	0.00	0.12	0.52	0.74
July 3		0.38	0.38	0.00	0.12	0.14	0.26
July 4				0.00	0.12	0.56	0.68
July 5				0.00	0.11	0.81	0.92
July 6				0.00	0.11	0.79	0.90
July 7	5.71		5.71	0.06	0.11	0.75	0.92
July 8				0.05	0.10	0.77	0.93
July 9				0.01	0.10	0.88	0.99
July 10		0.20	0.20	0.00	0.10	0.81	0.91
July 11		1.73	1.73	0.01	0.10	0.32	0.43
July 12				0.01	0.10	0.50	0.61
July 13		0.25	0.25	0.00	0.09	0.59	0.68
July 14		0.51	0.51	0.00	0.09	0.21	0.30
July 15				0.00	0.90	0.13	0.22
July 16				0.00	0.09	0.40	0.49
July 17	3.09		3.09	0.04	0.09	0.36	0.49
July 18				0.04	0.09	0.60	0.73
July 19				0.01	0.09	0.73	0.83
July 20				0.00	0.08	0.56	0.64
July 21				0.00	0.08	0.71	0.79
July 22	3.72		3.72	0.05	0.08	0.30	0.43

(continued)

TABLE F-4. (Continued)

Date	Irrigation	Rain	Total Water	Runoff	Leachate	Evapo- transpiration	Total Loss
July 23				0.04	0.08	0.15	0.27
July 24				0.02	0.08	0.33	0.43
July 25				0.00	0.08	0.42	0.50
July 26				0.00	0.08	0.50	0.58
July 27				0.00	0.08	0.68	0.66
July 28	4.02	3.56	7.58	0.02	0.08	0.98	1.08
July 29		0.53	0.53	0.06	0.08	0.46	0.60
July 30		0.41	0.41	0.09	0.08	0.39	0.56
July 31		3.78	3.78	0.47	0.08	0.84	1.39
JULY TOTALS	16.54	11.86	28.40	0.98	3.72	16.66	20.56
August 1		3.51	3.51	0.88	0.08	----	0.08
August 2				1.06	0.08	1.04	1.12
August 3		0.43	0.43	0.60	0.08	0.34	0.42
August 4		4.06	4.06	1.20	0.08	----	0.08
August 5		1.50	1.50	0.75	0.08	1.27	1.35
August 6	1.22		1.22	0.47	0.07	0.67	0.74
August 7		0.25	0.25	0.09	0.07	0.85	0.92
August 8		1.27	1.27	0.00	0.07	0.62	0.69
August 9				0.00	0.07	0.34	0.41
August 10				0.00	0.07	0.37	0.44
August 11				0.00	0.07	0.52	0.59
August 12				0.00	0.07	0.37	0.44
August 13				0.00	0.07	0.48	0.55
August 14				0.00	0.07	0.64	0.71
August 15				0.00	0.07	0.66	0.73
August 16				0.00	0.07	0.30	0.37
August 17		0.05	0.05	1.22	0.07	0.51	0.58
AUGUST TOTALS	1.22	11.07	12.29	6.27	1.24	8.98	10.22

* estimated from climatological data

Appendix G. Analysis of variance for various ions
and the electrical conductivity of the rice
paddy water for the 1974 and 1975 growing
seasons.

TABLE G-1. ANALYSIS OF VARIANCE FOR E.C. IN RICE PADDY WATER SAMPLED IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	.038	2	.0190	2.13
Times	4.637	20	.2320	25.42**
Irrigation Treatment	0.245	1	.2450	26.86**
Application Rate	.119	1	.1190	13.15**
Times x Irrigation	.684	20	.0340	3.75**
Times x Rate	.195	20	.0100	1.07
Irrigation x Rate	.008	1	.0080	0.88
Times x Irri- gation x Rate	.231	20	.0120	1.26
ERROR	7.885	189	.0090	
TOTAL		274		

**Significant at the 1% level.

TABLE G-2. ANALYSIS OF VARIANCE FOR E.C. IN RICE PADDY WATER SAMPLED IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.033	2	.0170	1.63
Times	9.403	21	.4480	44.74**
Irrigation Treatment	0.142	1	.1420	14.19**
Application Rate	0.165	1	.1650	16.54**
Times x Irrigation	0.259	21	.0120	1.23
Times x Rate	0.335	21	.0160	1.59
Irrigation x Rate	0.0029	1	.0029	0.29
Times x Irri- gation x Rate	0.201	21	.0096	0.96
ERROR	1.861	186	0.010	
TOTAL	12.404	275		

** Significant at the 1% level.

TABLE G-3. ANALYSIS OF VARIANCE FOR E.C. IN RICE PADDY WATER SAMPLED IN 1973

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.047	2	.0235	1.45
Times	6.992	8	.8740	53.00**
Irrigation Treatment	0.008	1	.0080	0.49
Application Rate	0.048	1	.0480	2.94
Times x Irrigation	0.141	8	.0176	1.07
Times x Rate	0.076	8	.0095	0.57
Irrigation x Rate	0.002	1	.0020	0.12
Times x Irri- gation x Rate	0.104	8	.0130	0.79
ERROR	1.154	70	.0160	
TOTAL	8.576	107		

**Significant at the 1% level.

TABLE G-4. ANALYSIS OF VARIANCE FOR pH IN RICE PADDY WATER SAMPLED IN 1973

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.493	2	0.247	5.57**
Times	7.969	8	0.996	22.51**
Irrigation Treatment	0.002	1	0.002	.05
Application Rate	0.458	1	0.458	10.34**
Times x Irrigation	0.509	8	0.063	1.43
Times x rate	0.296	8	0.037	0.83
Irrigation x Rate	0.285	1	0.285	6.44**
Times x Irri- gation x Rate	0.314	8	0.039	0.88
ERROR	3.097	70	0.044	
TOTAL	13.424	107		

**Significant at the 1% level.

TABLE G-5. ANALYSIS OF VARIANCE FOR pH IN RICE PADDY WATER SAMPLED IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.252	2	0.126	2.20
Times	36.660	20	1.833	37.83**
Irrigation Treatment	.345	1	0.345	7.36**
Application Rate	.088	1	0.088	2.76
Times x Irrigation	1.027	20	0.051	1.05
Times x Rate	0.693	20	0.350	0.69
Irrigation x Rate	0.050	1	0.050	0.32
Times x Irri- gation x Rate	0.797	20	0.039	0.82
ERROR	9.127	188	0.048	
TOTAL	49.041	273		

** Significant at the 1% level.

TABLE G-6. ANALYSIS OF VARIANCE FOR pH IN RICE PADDY WATER SAMPLED IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.304	2	0.152	3.43*
Times	30.522	21	1.453	32.87**
Irrigation Treatment	0.000	1	0.000	0.00
Application Rate	0.000	1	0.000	0.01
Times x Irrigation	1.391	21	0.066	1.49
Times x Rate	1.033	21	0.049	1.11
Irrigation x Rate	0.054	1	0.054	1.23
Times x Irri- gation x Rate	0.591	21	0.028	0.64
ERROR	8.224	186	0.044	
TOTAL	42.122	275		

**Significant at the 1% level.

TABLE G-7. ANALYSIS OF VARIANCE FOR NH_3 IN RICE PADDY WATER SAMPLED IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	10.548	2	5.274	1.00
Times	1957.795	18	108.766	20.62**
Irrigation Treatment	49.057	1	49.057	9.29**
Application Rate	34.866	1	34.866	6.61**
Times x Irrigation	152.960	18	8.497	1.61
Times x Rate	154.909	18	8.606	1.63
Irrigation x Rate	0.979	1	0.979	0.02
Times x Irri- gation x Rate	72.547	18	4.030	0.76
ERROR	791.354	150	5.276	
TOTAL	3225.017	227		

**Significant at the 1% level.

TABLE G-8. ANALYSIS OF VARIANCE FOR NH_3 IN RICE PADDY WATER SAMPLED IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	30.577	2	15.288	2.23
Times	3492.074	17	205.416	29.97**
Irrigation Treatment	2.622	1	2.622	0.38
Application Rate	67.737	1	67.737	9.88**
Times x Irrigation	243.014	17	14.295	2.09*
Times x Rate	287.798	17	16.929	2.47**
Irrigation x Rate	0.007	1	0.007	0.00
Times x Irri- gation x Rate	177.671	17	10.451	1.52
ERROR	973.140	142	6.853	
TOTAL	5274.640	215		

**Significant at the 1% level.

TABLE G-9. ANALYSIS OF VARIANCE FOR Ca^{++} IN RICE PADDY WATER SAMPLED IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	58.639	2	29.319	0.84
Times	2159.029	17	127.001	3.67**
Irrigation Treatment	356.674	1	356.674	10.31**
Application Rate	110.752	1	110.750	3.20
Times x Irrigation	368.948	17	21.702	0.62
Times x Rate	497.503	17	29.264	0.84
Irrigation x Rate	242.011	1	242.014	7.00**
Times x Irri- gation x Rate	557.373	17	32.786	0.94
ERROR	4839.623	140	34.568	
TOTAL	9190.555	213		

**Significant at the 1% level.

TABLE G-10. ANALYSIS OF VARIANCE FOR Ca^{++} IN RICE PADDY WATER SAMPLED
IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	48.834	2	24.417	0.73
Times	8621.322	17	507.137	15.24**
Irrigation Treatment	264.218	1	264.218	7.94**
Application Rate	268.523	1	268.523	8.07**
Times x Irrigation	860.927	17	50.643	1.52
Times x Rate	392.687	17	23.099	0.69
Irrigation x Rate	0.096	1	0.096	0.00
Times x Irri- gation x Rate	693.093	17	40.770	1.22
ERROR	4992.327	150	33.282	
TOTAL	16142.028	223		

TABLE G-11. ANALYSIS OF VARIANCE FOR Mg^{++} IN RICE PADDY WATER SAMPLED
IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	4367.308	2	2183.654	0.92
Times	59069.807	18	3281.656	1.38
Irrigation Treatment	523.106	1	523.106	0.22
Application Rate	907.059	1	907.059	0.38
Times x Irrigation	35278.452	18	1959.914	0.82
Times x Rate	42826.360	18	2379.242	1.00
Irrigation x Rate	3993.058	1	3993.058	1.68
Times x Irri- gation x Rate	44192.420	18	2455.134	1.03
ERROR	346357.889	146	2372.314	
TOTAL	537515.459	223		

TABLE G-12. ANALYSIS OF VARIANCE FOR Mg^{++} IN RICE PADDY WATER SAMPLED IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.187	2	0.094	0.16
Times	173.372	15	11.558	20.50**
Irrigation Treatment	8.250	1	8.250	14.63**
Application Rate	1.952	1	1.952	3.46
Times x Irrigation	11.531	15	0.769	1.36
Times x Rate	2.603	15	0.174	0.31
Irrigation x Rate	0.000	1	0.000	0.00
Times x Irri- gation x Rate	1.510	15	0.101	0.17
ERROR	76.660	136	0.563	
TOTAL	276.067	201		

TABLE G-13. ANALYSIS OF VARIANCE FOR Na⁺ IN RICE PADDY WATER SAMPLED
IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	7910.780	2	3955.390	1.24
Times	139436.298	19	7338.752	2.31**
Irrigation Treatment	132729.969	1	132729.969	41.86**
Application Rate	12603.507	1	12603.507	3.97**
Times x Irrigation	149598.794	19	7873.621	2.48**
Times x Rate	23396.803	19	1231.411	0.38
Irrigation x Rate	22112.470	1	22112.470	6.97**
Times x Irri- gation x Rate	38837.172	19	2044.062	0.64
ERROR	485084.014	153	3170.483	
TOTAL	11011709.813	234		

TABLE G-14. ANALYSIS OF VARIANCE FOR Na⁺ IN RICE PADDY WATER SAMPLED
IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	9.162	2	4.580	0.28
Times	6617.023	14	472.645	29.58**
Irrigation Treatment	192.518	1	192.518	12.05**
Application Rate	179.084	1	179.084	11.21**
Times x Irrigation	532.172	14	38.012	2.37**
Times x Rate	221.337	14	15.810	0.98
Irrigation x Rate	18.191	1	18.191	1.13
Times x Irri- gation x Rate	68.242	14	4.874	0.30
ERROR	2045.158	128	15.977	
TOTAL	9882.890	189		

TABLE G-15. ANALYSIS OF VARIANCE FOR $\text{SO}_4^{=}$ IN RICE PADDY WATER SAMPLED
IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	1296.353	2	648.177	2.40
Times	65210.916	18	3622.829	13.42**
Irrigation Treatment	18146.730	1	18146.730	67.22**
Application Rate	4941.365	1	4941.365	18.30**
Times x Irrigation	16191.520	18	899.529	3.33**
Times x Rate	6314.462	18	350.803	1.29
Irrigation x Rate	2683.289	1	2683.289	9.94**
Times x Irri- gation x Rate	2326.252	18	129.236	0.47
ERROR	41031.287	152		
TOTAL	158142.176	229		

TABLE G-16. ANALYSIS OF VARIANCE FOR $\text{SO}_4^{=}$ IN RICE PADDY WATER SAMPLED
IN 1975

Source	Sum of Squares	D f	Mean Square	F-Value Exp.
Reps	2134.479	2	1067.240	3.16*
Times	48979.978	13	3767.691	11.17**
Irrigation Treatment	28.361	1	28.361	0.08
Application Rate	2365.755	1	2365.755	7.02**
Times x Irrigation	4326.011	13	332.770	0.98
Times x Rate	2500.639	13	192.357	0.57
Irrigation x Rate	1147.517	1	1147.517	3.40
Times x Irri- gation x Rate	4065.745	13	312.750	0.93
ERROR	40445.400	120	337.045	
TOTAL	105993.889	177		

TABLE G-17. ANALYSIS OF VARIANCE FOR Cl^- IN RICE PADDY WATER SAMPLED IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	260.445	2		0.87
Times	14327.552	19		5.07**
Irrigation Treatment	4693.635	1		31.55**
Application Rate	1801.951	1		12.11**
Times x Irrigation	5252.609	19		1.86*
Times x Rate	3131.578	19		1.10
Irrigation x Rate	1133.952	1		7.62**
Times x Irri- gation x Rate	1782.309	19		0.63
ERROR	14392.266	164	148.733	
TOTAL	56776.198	245		

TABLE G-18. ANALYSIS OF VARIANCE FOR Cl^- IN RICE PADDY WATER SAMPLED IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	138.941	2	69.471	0.59
Times	32411.395	13	2493.184	21.41**
Irrigation Treatment	2654.925	1	1654.925	22.80**
Application Rate	537.074	1	537.074	4.61*
Times x Irrigation	5796.739	13	445.903	3.83**
Times x Rate	862.619	13	66.355	0.56
Irrigation x Rate	292.664	1	292.664	2.51
Times x Irri- gation x Rate	1066.162	13	158.936	1.36
ERROR	13969.717	120	116.44	
TOTAL	58730.239	177		

TABLE G-19. ANALYSIS OF VARIANCE FOR NO_3^- IN RICE PADDY WATER SAMPLED IN 1974

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.007	2	0.004	0.67
Times	2.821	19	0.149	25.88**
Irrigation Treatment	0.299	1	0.299	52.16**
Application Rate	0.018	1	0.018	3.22
Times x Irrigation	1.249	19	0.066	11.46**
Times x Rate	0.150	19	0.008	1.37
Irrigation x Rate	0.007	1	0.007	1.36
Times x Irri- gation x Rate	0.035	19	0.001	0.31
ERROR	0.952	166	0.005	
TOTAL	5.540	247		

TABLE G-20. ANALYSIS OF VARIANCE FOR NO_3^- IN RICE PADDY WATER SAMPLED
IN 1975

Source	Sum of Squares	Df	Mean Square	F-Value Exp.
Reps	0.049	2	0.025	4.05*
Times	1.530	10	0.153	25.27**
Irrigation Treatment	0.017	1	0.017	2.78
Application Rate	0.016	1	0.016	2.65
Times x Irrigation	0.146	10	0.015	2.41*
Times x Rate	0.030	10	0.003	0.51
Irrigation x Rate	0.000	1	0.000	0.02
Times x Irri- gation x Rate	0.053	10	0.005	0.87
ERROR	0.581	96	0.006	
TOTAL	2.424	141		

APPENDIX H

CONCENTRATIONS OF INDIVIDUAL IONS IN

PADDY WATER DURING 1973, 1974 AND 1975 GROWING SEASONS

TABLE H-1. ANALYSIS FOR NITRATE (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	<u>Canal</u> Water
May 1	0.9	+0.3	0.4	+0.3	0.7	+0.1	0.7	+0.2	---
May 3	0.7	+0.1	0.7	+0.1	0.8	+0.2	0.7	+0.1	---
May 7	1.4	+0.9	0.9	+0.3	1.1	+0.5	1.1	+0.2	---
May 12	---	---	2.5	+3.0	---	---	3.2	+1.5	---
May 18	1.5	+0.7	1.3	+0.7	1.6	+0.1	2.0	+0.7	0.1
May 28	0.2	+0.1	0.3	+0.3	0.2	+0.2	0.0	+0.0	0.2
June 5	0.3	+0.4	0.3	+0.4	0.3	+0.3	0.3	+0.4	0.1
June 6	0.5	+0.3	0.5	+0.2	0.3	+0.1	0.4	+0.1	0.9
June 8	0.3	+0.1	0.3	+0.1	0.2	+0.0	0.2	+0.0	0.1
June 12	0.1	+0.0	0.0	+0.0	0.1	+0.0	---	---	0.1
June 15	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 15	0.1	+0.0	0.1	+0.0	---	---	0.1	+0.0	0.0
June 26	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 27	0.0	+0.0	0.1	+0.1	0.0	+0.0	0.0	+0.0	0.0
June 28	0.1	+0.0	0.2	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 30	0.1	+0.0	0.1	+0.1	0.2	+0.1	0.2	+0.1	---
July 4	0.1	+0.1	0.1	+0.0	0.0	+0.0	0.0	+0.0	---
July 12	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 27	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 13	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.1
August 20	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---

TABLE H-2. ANALYSIS FOR NITRATE (PPM) FOR 1974

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 3	4.4	+4.0	1.5	+0.7	1.0	+0.3	0.8	+0.3	0.1
May 3	2.0	+0.9	3.4	+2.2	1.7	+0.7	1.4	+0.3	1.0
May 21	2.0	+0.8	2.0	+0.5	2.3	+0.4	1.8	+0.8	0.1
May 29	---	---	0.2	+0.0	---	---	0.3	+0.2	---
June 6	0.1	+0.1	0.1	+0.1	0.1	+0.0	0.1	+0.1	0.0
June 7	0.4	+0.3	0.3	+0.2	0.1	+0.0	0.2	+0.1	0.1
June 8	0.2	+0.1	0.4	+0.3	0.1	+0.0	0.1	+0.0	0.1
June 8	0.6	+0.1	0.6	+0.1	0.2	+0.1	0.2	+0.0	---
June 10	0.5	+0.1	0.5	+0.1	0.1	+0.0	0.1	+0.1	0.0
June 10	0.3	+0.2	0.1	+0.1	0.0	+0.0	0.0	+0.0	---
June 14	0.0	+0.0	0.1	+0.1	0.0	+0.0	0.0	+0.0	---
June 17	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.1
June 24	0.0	+0.0	0.0	+0.0	---	---	0.0	+0.0	---
June 24	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 26	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 27	---	---	---	---	0.0	+0.1	0.1	+0.0	---
June 27	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 28	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
June 28	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 29	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.0	+0.0	0.0
July 1	---	---	0.0	+0.0	---	---	0.0	+0.0	---
July 3	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 3	0.0	+0.0	0.0	+0.0	---	---	0.1	+0.0	---
July 5	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 8	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 8	0.0	+0.0	---	---	---	---	0.0	+0.0	---
July 11	---	---	---	---	---	---	---	---	---
July 15	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 17	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 22	---	---	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 24	---	---	---	---	0.0	+0.0	0.0	+0.0	---
July 26	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 29	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0

(Continued)

TABLE H-2. (Continued)

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
August 2	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 5	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 12	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 15	0.0	+0.0	---	---	0.0	+0.0	0.0	+0.0	---
August 16	0.0	+0.0	0.0	+0.0	---	---	0.0	+0.0	---
August 19	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 21	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0

TABLE H-3. ANALYSIS FOR NITRATE (PPM) FOR 1975

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
April 30	0.4	+0.1	0.4	+0.1	0.3	+0.1	0.4	+0.1	0.2
May 1	0.6	+0.0	0.6	+0.1	0.6	+0.1	0.6	+0.1	0.2
May 12	0.7	+0.2	1.2	+0.5	1.1	+0.6	0.7	+0.2	---
May 21	0.3	+0.2	0.2	+0.2	0.2	+0.1	0.3	+0.2	0.0
May 28	0.5	+0.0	0.4	+0.0	0.3	+0.1	0.3	+0.1	0.1
June 5	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.1	0.1
June 6	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.1	0.0
June 7	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.0
June 9	0.0	+0.0	---	---	0.0	+0.0	0.0	+0.0	0.0
June 9	---	---	0.1	+0.1	0.1	+0.0	0.1	+0.0	---
June 10	0.3	+0.1	0.2	+0.1	0.1	+0.1	0.2	+0.2	0.1
June 12	---	---	0.2	+0.1	0.0	+0.0	0.1	+0.1	0.0
June 13	0.1	+0.1	0.0	+0.0	0.0	+0.1	0.0	+0.0	0.0
June 16	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 19	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 23	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 26	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 30	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 7	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0

TABLE H-4. ANALYSIS FOR ELECTRICAL CONDUCTIVITY (MICROMHOS) FOR 1973

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 2, 1973	180.0	+57.0	172.3	+17.5	164.3	+37.7	219.7	+50.6	----
May 3	192.0	+66.5	190.0	+20.0	186.7	+51.6	239.7	+46.2	----
May 7	191.3	+53.3	212.3	+23.2	204.3	+31.7	234.3	+37.0	----
May 12	356.7	+125.8	423.3	+32.1	383.3	+90.7	403.3	+40.4	----
June 15	153.3	+ 5.8	163.3	+15.3	183.3	+66.6	140.0	+ 0.0	140.0
July 12	121.3	+ 8.1	145.7	+33.0	131.7	+10.7	123.0	+ 6.2	112.0
July 27	143.7	+ 7.8	166.3	+38.6	121.0	+ 8.5	114.7	+ 5.5	187.0
August 8	144.7	+31.4	143.7	+24.0	119.3	+10.0	119.0	+ 3.5	110.0
August 13	124.7	+22.3	136.3	+23.1	89.0	+5.6	85.0	+ 7.5	81.0

TABLE H-5. ANALYSIS FOR ELECTRICAL CONDUCTIVITY (MICROMHOS) FOR 1974

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 3, 1974	214.0	+21.4	219.7	+47.1	249.3	+67.9	216.7	+35.8	118.0
May 3	225.3	+22.4	308.3	+95.8	199.3	+24.6	227.3	+25.0	150.0
May 21	113.3	+ 5.5	148.3	+30.0	124.0	+23.5	133.0	+ 8.7	115.0
May 29	137.3	+11.0	131.3	+ 4.2	153.0	+10.1	146.3	+18.8	132.0
June 6	212.7	+17.5	220.3	+ 8.7	228.3	+46.8	263.7	+17.9	159.0
June 7	285.0	+17.4	309.7	+25.9	194.3	+47.9	260.7	+77.5	125.0
June 8	189.0	+48.7	223.0	+19.1	128.7	+ 2.1	121.7	+13.6	-----
June 8	211.0	+68.4	223.3	+41.4	137.0	+ 9.6	134.0	+ 6.1	130.0
June 17	181.0	+38.7	182.3	+34.7	130.0	+ 4.6	132.3	+ 7.8	135.0
June 24	122.7	+ 5.0	141.3	+32.7	116.3	+ 6.5	112.0	+ 1.7	116.0
June 26	273.0	+67.1	215.0	+20.0	195.3	+30.6	243.0	+21.4	133.0
June 27	255.7	+28.1	280.7	+29.0	227.7	+36.8	327.7	+41.3	130.0
June 28	191.7	+14.4	216.3	+41.2	216.0	+ 6.9	226.0	+96.2	130.0
June 29	201.0	+33.0	181.3	+27.2	202.7	+10.8	238.7	+19.0	135.0
July 1	186.3	+20.6	219.3	+21.0	193.0	+24.9	241.0	+45.9	139.0
July 8	198.3	+20.2	214.3	+17.2	151.7	+ 2.9	163.3	+15.3	135.0
July 15	163.7	+ 4.5	173.0	+12.1	157.3	+ 4.7	154.3	+ 5.9	142.0
July 22	-----	-----	173.3	+15.3	153.0	+ 2.6	154.7	+ 4.2	125.0
July 29	181.3	+ 2.9	190.3	+ 7.6	152.7	+ 6.8	160.0	+ 0.0	130.0
August 5	136.7	+10.7	136.3	+ 5.8	131.7	+ 3.5	131.7	+ 1.5	141.0
August 12	167.0	+ 7.8	161.0	+ 8.7	156.0	+ 0.0	159.7	+ 0.6	139.0
August 19	205.7	+ 4.7	189.0	+ 0.0	151.3	+ 8.0	153.7	+ 7.6	135.0
August 21	192.3	+31.6	184.3	+26.3	156.3	+ 9.5	184.7	+26.4	143.0

TABLE H-6. ANALYSIS FOR ELECTRICAL CONDUCTIVITY (MICROMHOS) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30, 1975	230.0	+70.0	306.7	+76.4	215.3	+28.6	242.0	+25.2	122.0
May 1	207.0	+19.0	258.0	+18.4	210.7	+ 9.0	252.0	+27.1	160.0
May 12	193.7	+30.4	224.7	+15.6	184.3	+26.6	244.3	+14.4	-----
May 21	213.3	+19.0	291.3	+102.7	216.3	+38.1	275.3	+75.7	88.0
May 28	60.7	+ 5.0	58.7	+ 9.0	32.0	+ 8.7	53.0	+20.0	100.0
June 5	168.3	+27.5	141.0	+16.5	121.7	+10.4	213.3	+59.2	90.0
June 6	180.0	+17.4	151.0	+45.0	140.3	+45.0	108.0	+23.6	82.0
June 7	225.7	+ 3.3	237.3	+15.7	142.7	+32.9	175.0	+34.0	100.0
June 9	227.7	+19.1	217.7	+50.0	178.3	+58.0	165.3	+58.6	115.0
June 10	71.7	+ 5.8	73.3	+ 7.6	61.7	+ 5.8	76.7	+12.6	65.0
June 12	76.7	+ 5.8	76.7	+ 5.8	70.0	+ 0.0	73.3	+ 5.8	100.0
June 16	110.0	+13.2	98.3	+12.6	101.7	+16.1	87.7	+10.8	50.0
June 19	81.7	+14.4	73.3	+ 5.8	71.7	+10.4	70.0	+10.0	60.0
June 19	91.7	+10.4	110.0	+26.5	96.7	+ 5.8	83.3	+ 2.9	70.0
June 20	203.3	+ 5.8	253.3	+61.1	236.7	+70.9	216.7	+58.6	80.0
June 22	181.7	+12.6	213.3	+25.2	180.0	+60.8	196.7	+55.1	85.0
June 23	164.3	+25.0	203.0	+34.6	151.3	+24.9	155.3	+69.3	101.0
June 26	126.0	+ 8.5	151.0	+20.1	124.7	+28.6	128.3	+30.6	118.0
July 7	138.0	+10.4	148.3	+ 7.6	142.7	+16.2	144.3	+16.0	120.0
July 14	131.0	+ 4.6	150.0	+26.5	123.0	+ 1.0	140.7	+16.3	120.0
July 21	170.7	+10.1	173.3	+23.6	158.7	+25.5	162.0	+20.7	140.0
August 4	110.0	+13.9	140.7	+34.1	118.3	+ 5.5	119.3	+ 9.1	101.0
August 15	106.7	+ 7.6	122.3	+ 7.5	108.3	+10.1	113.3	+ 8.5	78.0

TABLE H-7. ANALYSIS FOR pH FOR 1973

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 2	6.0	+0.1	5.8	+0.0	6.0	+0.1	5.7	+0.3	---
May 3	6.1	+0.2	5.9	+0.3	6.3	+0.1	5.8	+0.5	---
May 7	6.3	+0.2	6.3	+0.5	6.6	+0.2	6.2	+0.1	---
May 12	6.7	+0.2	6.8	+0.5	7.2	+0.5	6.7	+0.4	---
June 15	6.4	+0.2	6.3	+0.2	6.6	+0.1	6.5	+0.0	7.2
July 12	6.4	+0.0	6.4	+0.1	6.4	+0.1	6.3	+0.1	6.5
July 27	6.7	+0.1	6.6	+0.1	6.5	+0.2	6.4	+0.1	6.8
August 8	6.3	+0.1	6.3	+0.2	6.2	+0.1	6.2	+0.1	6.5
August 13	6.2	+0.2	6.3	+0.1	6.1	+0.1	6.1	+0.0	6.3

TABLE H-8. ANALYSIS FOR pH FOR 1974

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 3	6.6	+0.2	7.5	+1.1	---	----	6.8	+0.2	7.0
May 3	7.2	+0.2	7.1	+0.2	7.1	+0.2	7.2	+0.1	7.5
May 21	5.9	+0.3	6.1	+0.2	6.0	+0.3	5.9	+0.2	6.0
May 29	6.2	+0.1	6.3	+0.0	6.2	+0.1	6.3	+0.0	6.3
June 6	6.4	+0.1	6.4	+0.2	6.6	+0.2	6.5	+0.2	6.8
June 7	6.2	+0.1	6.2	+0.1	6.2	+0.1	6.3	+0.1	6.3
June 8	6.0	+0.0	6.0	+0.0	6.1	+0.0	6.1	+0.1	---
June 8	6.0	+0.1	6.0	+0.1	6.1	+0.1	6.1	+0.1	6.4
June 17	6.0	+0.1	6.0	+0.1	6.1	+0.1	6.0	+0.0	6.3
June 24	6.1	+0.2	6.1	+0.1	6.1	+0.3	6.2	+0.0	6.3
June 26	6.2	+0.1	6.2	+0.1	6.3	+0.1	6.2	+0.0	6.6
June 27	6.3	+0.1	6.2	+0.1	6.5	+0.1	6.6	+0.3	6.7
June 29	5.8	+0.3	5.4	+0.7	5.9	+0.2	5.8	+0.5	6.6
June 28	6.3	+0.1	6.4	+0.1	6.4	+0.3	6.4	+0.1	6.8
July 1	5.9	+0.3	5.8	+0.2	5.9	+0.2	5.6	+0.6	7.0
July 8	5.9	+0.2	5.7	+0.2	6.3	+0.1	6.3	+0.0	7.0
July 15	6.5	+0.1	6.3	+0.1	6.5	+0.1	6.4	+0.1	6.8
July 22	---	----	6.6	+0.1	6.7	+0.0	6.6	+0.1	7.2
July 29	6.7	+0.0	6.7	+0.1	6.8	+0.1	6.7	+0.1	6.9
August 5	6.6	+0.0	6.5	+0.0	6.6	+0.1	6.6	+0.0	6.8
August 12	6.7	+0.1	6.7	+0.1	6.8	+0.1	6.7	+0.0	6.9
August 19	6.7	+0.0	6.7	+0.0	6.8	+0.0	6.8	+0.0	7.0
August 21	6.7	+0.1	6.7	+0.1	6.6	+0.1	6.7	+0.0	6.9

TABLE H-9. ANALYSIS FOR pH FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	6.5	+0.2	6.4	+0.1	6.4	+0.1	6.4	+0.2	6.6
May 1	6.2	+0.1	6.2	+0.1	6.2	+0.0	6.2	+0.1	6.4
May 12	5.4	+0.1	5.3	+0.1	5.4	+0.1	5.3	+0.1	---
May 21	5.9	+0.1	5.7	+0.1	5.9	+0.1	5.8	+0.1	6.3
May 28	6.2	+0.8	6.1	+0.2	5.6	+0.3	6.1	+0.3	6.3
June 5	6.2	+0.1	6.2	+0.1	6.3	+0.1	6.1	+0.2	6.5
June 6	6.2	+0.1	5.9	+0.1	6.1	+0.3	6.0	+0.3	6.3
June 7	5.8	+0.0	5.7	+0.1	5.9	+0.1	6.0	+0.1	6.5
June 9	5.7	+0.1	5.8	+0.2	5.9	+0.0	6.0	+0.1	6.5
June 10	6.4	+0.1	6.4	+0.0	6.5	+0.0	6.5	+0.2	6.6
June 12	6.0	+0.1	6.0	+0.1	6.2	+0.1	6.1	+0.1	6.6
June 16	6.0	+0.1	5.9	+0.1	6.2	+0.0	6.2	+0.1	6.6
June 19	6.5	+0.0	6.4	+0.1	6.4	+0.1	6.5	+0.1	6.9
June 19	6.4	+0.1	6.5	+0.2	6.4	+0.0	6.5	+0.0	6.7
June 20	6.1	+0.2	6.0	+0.3	6.0	+0.2	6.0	+0.3	6.5
June 22	5.7	+0.2	5.7	+0.2	5.3	+0.4	5.5	+0.4	6.4
June 23	5.8	+0.4	5.5	+0.3	5.4	+0.6	5.4	+0.8	6.5
June 26	6.1	+0.2	5.9	+0.3	6.0	+0.1	6.0	+0.2	6.7
July 7	6.4	+0.1	6.3	+0.0	6.3	+0.1	6.3	+0.1	6.3
July 14	6.3	+0.2	6.2	+0.0	6.1	+0.1	6.1	+0.1	6.2
July 21	6.3	+0.2	6.7	+0.2	6.6	+0.1	6.6	+0.2	6.9
August 4	6.1	+0.3	6.3	+0.1	6.3	+0.1	6.3	+0.1	6.9
August 15	6.6	+0.1	7.0	+0.2	6.5	+0.0	6.8	+0.4	6.8

TABLE H-10. ANALYSIS FOR NITRITE (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
May 1	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	+0.1	----
May 3	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	----
May 7	0.1	±0.1	0.0	±0.0	0.0	±0.0	0.1	+0.1	----
May 12	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	----
May 18	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
May 28	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	----
June 5	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 6	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 8	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 12	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 15	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 15	0.0	±0.0	0.1	±0.0	0.1	±0.0	0.1	±0.0	0.0
June 26	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 27	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 28	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
June 30	0.0	±0.0	0.0	±0.0	0.1	±0.0	0.0	±0.0	----
July 4	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
July 12	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	----
July 27	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0
August 13	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0	±0.0	0.0

TABLE H-11. ANALYSIS FOR NITRITE (PPM) FOR 1974

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 3	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
May 3	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
May 21	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
May 29	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 6	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 7	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 8	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.1
June 8	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
June 10	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 10	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 14	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
June 17	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
June 20	---	---	0.0	+0.0	---	---	0.0	+0.0	0.0
June 24	0.0	+0.0	0.0	+0.0	---	---	---	---	---
June 24	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
June 26	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 27	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 27	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
June 28	0.0	+0.0	0.0	+0.0	0.1	+0.0	0.0	+0.0	0.0
June 28	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
June 29	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 1	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 3	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 3	0.0	+0.0	0.0	+0.0	---	---	0.0	+0.0	0.0
July 5	0.0	+0.0	0.0	+0.0	---	---	0.0	+0.0	---
July 8	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
July 8	0.0	+0.0	0.0	+0.0	---	---	0.0	+0.0	0.0
July 11	---	---	---	---	---	---	0.0	+0.0	---
July 15	0.0	+0.0	0.0	+0.0	0.0	+0.0	---	---	---
July 17	---	---	---	---	---	---	0.0	+0.0	0.0
July 22	---	---	---	---	---	---	---	---	---
July 24	---	---	---	---	0.0	+0.0	0.0	+0.0	0.0
July 26	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
July 29	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
July 29	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0

(Continued)

TABLE H-11. (Continued)

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
August 2	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 5	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
August 12	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 15	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
August 16	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
August 19	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 21	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 20	---	----	0.0	+0.0	---	----	---	----	---

TABLE H-12. ANALYSIS FOR NITRITE (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
May 1	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
May 12	0.1	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
May 21	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.1
May 28	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 5	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 6	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 7	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 9	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 10	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 12	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 16	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 19	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 19	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 20	0.3	+0.1	0.4	+0.2	0.2	+0.1	0.3	+0.1	0.1
June 22	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 23	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 26	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
July 7	0.1	+0.0	---	----	0.1	+0.1	0.2	+0.1	0.4
July 14	---	----	---	----	---	----	---	----	---

TABLE H-13. ANALYSIS FOR AMMONIUM (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	<u>Canal</u> Water
May 1	0.1	+0.0	0.2	+0.2	0.1	+0.0	0.2	+0.2	---
May 3	0.1	+0.2	0.4	+0.1	0.3	+0.2	0.1	+0.1	---
May 7	0.3	+0.1	0.3	+0.1	0.2	+0.0	0.4	+0.1	---
May 12	0.1	+0.2	0.1	+0.1	0.0	+0.0	0.2	+0.3	---
May 18	0.0	+0.1	0.0	+0.1	0.0	+0.0	0.0	+0.0	---
May 28	0.1	+0.1	0.0	+0.0	0.1	+0.0	0.1	+0.0	0.2
June 5	5.2	+1.2	16.8	---	17.7	---	17.7	---	---
June 6	7.0	+1.0	9.7	+1.3	7.9	+1.4	9.3	+0.5	---
June 8	4.9	+1.2	8.7	+4.9	2.6	+0.6	4.0	+0.9	0.2
June 12	0.9	+0.6	0.8	+0.0	0.4	+0.3	0.2	+0.1	---
June 15	0.2	+0.1	0.6	+0.1	0.1	+0.1	0.1	+0.0	---
June 15	0.8	+0.5	1.1	+0.5	0.4	+0.1	0.2	+0.1	---
June 26	2.9	+0.8	3.1	+0.6	3.1	+1.3	2.0	+1.7	5.0
June 27	5.0	+3.0	---	---	4.0	+0.9	7.4	+1.5	2.1
June 28	2.6	+0.5	7.3	+1.0	1.7	+0.6	4.1	+1.1	0.2
June 30	0.3	+0.0	1.3	+1.0	1.1	+1.6	0.9	+0.3	---
July 4	0.1	+0.1	0.1	+0.1	0.1	+0.0	0.0	+0.0	0.1
July 12	0.2	+0.2	0.2	+0.0	0.1	+0.1	0.1	+0.0	---
July 27	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.1	+0.1	---
August 13	0.1	+0.0	0.1	+0.0	0.0	+0.0	0.0	+0.0	0.1
August 20	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.1	0.1

TABLE H-14. ANALYSIS FOR AMMONIUM (PPM) FOR 1974

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 3, 1974	2.0	+1.2	1.3	+0.3	0.9	+0.3	0.9	+0.3	0.1
May 3	1.7	+0.6	3.4	+1.8	1.8	+0.1	2.1	+0.5	0.3
May 21	0.5	+0.1	0.7	+0.1	0.7	+0.1	0.6	+0.2	0.0
May 29	0.1	+0.0	0.1	+0.0	0.2	+0.0	0.1	+0.1	0.0
June 6	2.2	+3.4	---	---	---	---	---	---	0.0
June 7	9.1	+1.4	10.5	+2.3	4.4	+3.4	8.6	+3.8	0.2
June 8	3.9	+1.1	6.9	+0.8	2.5	+1.2	3.5	+0.7	0.3
June 8	5.1	+2.5	6.9	+0.8	3.0	+0.4	2.6	+0.8	---
June 10	2.7	+2.1	2.6	+1.2	1.0	+0.6	0.6	+0.1	0.0
June 10	6.2	+2.1	7.9	+3.3	5.8	+1.0	8.6	+2.7	---
June 14	0.2	+0.2	0.1	+0.1	0.2	+0.3	0.1	+0.2	---
June 17	0.1	+0.1	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 20	---	---	2.2	+2.8	---	---	---	---	---
June 24	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 26	10.1	+4.7	4.6	+0.7	3.8	+1.9	8.5	+2.6	0.2
June 27	---	---	---	---	1.0	+0.8	1.1	+0.0	---
June 27	6.5	+2.2	9.0	+1.0	6.0	+2.5	12.9	+2.8	0.3
June 28	4.3	+2.1	6.2	+1.4	4.6	+3.5	8.1	+2.5	---
June 28	2.1	+0.9	2.3	+0.7	3.5	+1.5	5.3	+1.1	0.3
June 29	0.8	+0.2	2.1	+1.0	3.5	+1.5	4.1	+4.1	0.2
July 1	0.4	+0.2	0.4	+0.2	1.0	+1.2	1.0	+0.8	0.1
July 3	0.2	+0.1	0.4	+0.3	0.3	+0.2	0.3	+0.1	0.2
July 3	0.2	+0.1	1.2	+1.5	---	---	2.9	+2.7	---
July 5	0.1	+0.0	0.2	+0.1	0.4	+0.4	0.2	+0.1	---
July 8	0.1	+0.1	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
July 8	0.1	+0.1	---	---	---	---	0.1	+0.1	---
July 11	---	---	---	---	---	---	---	---	---
July 15	0.2	+0.0	0.2	+0.1	0.2	+0.1	0.1	+0.0	0.1
July 17	---	---	0.5	+0.3	---	---	---	---	---
July 22	---	---	0.2	+0.0	0.1	+0.0	0.1	+0.0	0.1
July 24	---	---	---	---	0.3	+0.2	0.2	+0.1	---
July 26	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	---
July 29	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
August 2	0.1	+0.0	0.1	+0.1	0.1	+0.0	0.1	+0.0	---
August 5	0.0	+0.0	0.1	+0.0	0.0	+0.1	0.0	+0.0	0.0

(Continued)

TABLE H-14. (Continued)

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
August 12	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 15	0.2	+0.0	---	---	0.3	+0.1	0.2	+0.1	---
August 16	0.0	+0.0	0.0	+0.0	---	---	0.0	+0.0	---
August 19	0.0	+0.0	0.1	+0.1	0.0	+0.0	0.0	+0.0	0.1
August 21	0.0	+0.0	0.1	+0.0	0.0	+0.0	0.0	+0.0	0.1

TABLE H-15. ANALYSIS FOR AMMONIUM (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
1975									
April 30	1.6	+1.0	3.0	+0.8	1.6	+0.1	2.8	+0.8	0.1
May 1	2.1	+0.5	3.3	+0.2	1.9	+0.1	3.3	+0.8	0.1
May 12	0.6	+0.1	1.5	+0.4	0.9	+0.4	0.9	+0.3	---
May 21	0.8	+0.4	1.7	+1.9	0.7	+0.2	2.0	+1.1	0.0
May 28	0.4	+0.1	0.2	+0.1	0.2	+0.0	0.3	+0.1	0.1
June 5	5.8	+1.1	4.2	+1.2	2.9	+0.9	---	---	0.1
June 6	4.0	+0.8	3.2	+2.3	3.3	+2.5	---	---	0.0
June 7	3.5	+0.7	6.5	+2.4	2.7	+1.7	3.6	+1.6	0.2
June 9	2.6	+0.0	3.2	+2.3	2.0	+1.0	1.1	+1.1	0.0
June 9	---	---	8.6	+1.3	4.9	+1.1	8.6	+3.1	---
June 10	1.0	+0.2	1.6	+0.4	0.6	+0.1	1.0	+0.3	0.1
June 12	---	---	1.8	+0.5	---	---	0.8	+0.3	0.1
June 13	2.2	+1.7	3.0	+0.4	3.4	+3.3	3.0	+2.8	---
June 16	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2
June 19	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 19	1.8	+0.9	2.8	+1.6	3.1	+0.2	1.9	+0.6	0.1
June 20	3.3	+0.8	3.8	+0.8	3.0	+1.0	4.0	+1.6	0.1
June 20	10.9	+7.2	10.8	+3.7	---	---	16.9	+5.8	---
June 22	2.0	+0.4	2.5	+0.8	2.5	+1.1	2.3	+0.8	0.1
June 23	0.7	+0.3	1.0	+0.3	0.1	+0.1	0.6	+0.8	0.0
June 26	0.3	+0.2	0.3	+0.1	0.2	+0.0	0.2	+0.1	0.0
June 30	0.1	+0.0	0.3	+0.3	0.1	+0.0	0.1	+0.0	---
July 7	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2	+0.1	0.3
July 10	0.2	+0.0	0.1	+0.1	---	---	0.2	+0.0	---
July 14	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.0
July 21	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 25	0.2	+0.0	0.2	+0.0	0.1	+0.0	0.3	+0.2	---
August 4	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.3

TABLE H-16. ANALYSIS FOR SULFATE (PPM) FOR 1973

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 1	35.7	---	27.3	---	30.3	---	39.5	----	---
May 3	39.2	---	33.3	+8.1	36.8	---	50.3	+9.7	---
May 7	47.3	---	49.2	+2.8	45.1	+8.4	57.8	+8.3	---
May 12	81.8	---	86.7	+8.1	63.6	+9.9	89.3	+4.0	---
May 18	43.8	---	38.5	---	27.8	+2.4	35.3	----	7.3
May 28	20.3	+6.7	22.7	+4.6	42.2	---	25.3	----	8.0
June 5	35.7	---	50.5	---	48.2	---	60.8	----	35.0
June 6	39.0	+8.5	44.3	---	50.7	+7.7	36.7	----	3.0
June 8	35.7	---	60.8	---	27.5	+4.3	27.7	+4.0	14.0
June 12	8.7	+4.4	5.5	+0.5	4.7	+1.0	1.7	+0.8	5.0
June 15	3.7	+0.3	8.8	+3.8	3.3	+1.5	4.3	+0.6	4.0
June 15	22.3	---	26.9	---	25.7	---	16.7	+2.9	4.0
June 26	15.0	+3.1	34.7	---	9.3	+1.9	12.2	+2.4	3.0
June 27	25.3	---	---	---	12.5	+6.9	29.3	----	4.5
June 28	56.6	+1.9	77.1	---	19.6	+1.0	36.8	+0.4	7.5
June 30	50.1	+4.8	47.6	---	34.4	---	23.3	+9.0	---
July 4	28.8	---	20.2	---	22.3	---	15.0	----	2.0
July 12	29.8	---	47.8	---	23.0	+0.0	12.8	+6.3	24.0
July 27	6.0	+0.5	5.7	+0.6	5.9	+0.4	4.7	+0.8	8.5
August 13	4.7	+0.6	4.5	+1.5	3.8	+0.3	3.6	+0.3	3.5
August 20	5.3	+0.6	5.5	+0.9	7.5	+2.1	6.5	+0.5	8.0

TABLE H-17. ANALYSIS FOR SULFATE (PPM) FOR 1974

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 3	58.0	----	51.3	----	44.3	----	83.7	----	18.0
May 3	42.0	----	86.0	----	----	----	63.3	+3.1	12.0
May 21	26.7	+6.7	31.0	+7.0	24.7	+3.8	23.7	+4.0	8.0
May 29	17.0	+3.6	21.7	+7.8	15.3	+2.5	21.7	+5.5	8.0
June 6	26.3	+6.5	36.7	+1.2	32.0	+8.5	38.0	+5.6	8.0
June 7	50.0	----	57.0	+7.0	36.3	----	43.3	----	5.0
June 8	47.3	----	67.7	+4.2	20.0	+6.0	28.3	+5.5	12.0
June 8	56.0	----	71.3	----	23.3	+4.2	21.0	+9.5	----
June 10	41.3	----	51.0	----	12.7	+4.0	12.7	+2.9	10.0
June 10	----	----	----	----	----	----	----	----	----
June 14	----	----	55.0	----	21.3	+5.5	25.7	+2.1	----
June 17	44.3	----	51.7	----	16.7	+0.6	19.7	+5.7	16.0
June 20	----	----	----	----	----	----	----	----	----
June 24	----	----	----	----	----	----	----	----	----
June 24	----	----	33.0	----	----	----	----	----	----
June 26	58.3	+0.6	53.3	+7.0	39.0	----	79.7	----	16.0
June 27	----	----	----	----	----	----	----	----	----
June 27	81.7	----	----	----	57.0	----	----	----	13.0
June 28	----	----	----	----	----	----	----	----	----
June 28	45.3	----	33.7	----	44.0	+4.4	61.0	----	13.0
June 29	43.3	----	55.3	----	30.7	----	----	----	13.0
July 1	65.7	----	75.7	----	50.7	----	89.3	----	16.0
July 3	52.3	+2.5	65.0	+1.0	----	----	51.0	+7.0	17.0
July 3	----	----	----	----	----	----	----	----	----
July 5	4.3	+1.5	4.0	+2.0	17.7	+1.5	14.7	+2.1	----
July 8	50.3	----	48.3	----	27.7	----	29.7	----	20.0
July 8	----	----	----	----	----	----	----	----	----
July 11	----	----	----	----	----	----	----	----	----
July 15	18.7	+5.8	25.0	+8.7	11.7	+1.5	12.7	+2.1	15.0
July 17	----	----	71.3	----	----	----	----	----	----
July 22	----	----	17.3	+4.6	12.3	+3.2	11.7	+0.6	16.0
July 24	----	----	----	----	87.3	----	82.7	----	----
July 26	0.0	+0.0	0.0	+0.0	1.7	+2.9	0.0	+0.0	0.0
July 29	7.0	+2.0	7.0	+1.7	10.7	+1.5	7.7	+2.1	13.0

(Continued)

TABLE H-17. (Continued)

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
August 2	7.0	+1.0	6.3	+0.6	6.7	+1.2	6.7	+0.6	----
August 5	6.0	+1.0	5.0	+1.7	9.3	+1.2	7.0	+1.0	12.0
August 12	3.3	+1.2	2.7	+1.2	9.3	+1.2	8.3	+0.6	13.0
August 15	----	----	----	----	----	----	----	----	----
August 16	----	----	----	----	----	----	----	----	----
August 19	----	----	----	----	----	----	----	----	----
August 21	7.3	+4.0	6.3	+4.2	21.7	----	7.3	+3.8	----

TABLE H-18. ANALYSIS FOR SULFATE (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	47.4	----	77.4	----	41.7	+7.1	63.1	----	9.9
May 1	52.8	----	65.7	+9.9	54.1	+4.4	69.5	----	10.5
May 12	26.3	+4.7	55.7	----	44.9	----	31.2	----	---
May 21	24.8	+9.1	40.2	----	34.5	----	42.3	----	4.5
May 28	14.1	+4.2	11.7	+1.6	10.9	+1.2	11.3	+0.8	14.3
June 5	13.8	+2.3	10.0	+5.3	11.8	+5.1	37.3	----	3.0
June 6	26.0	+4.9	28.3	----	25.3	----	15.1	+7.5	7.5
June 7	28.8	+5.0	44.0	----	22.8	----	26.0	----	9.0
June 9	28.5	+2.6	----	----	23.3	+3.9	20.0	+10.0	11.3
June 9	----	----	----	----	----	----	----	----	---
June 10	15.5	+2.2	18.5	+2.4	11.3	+0.8	14.5	+4.6	6.8
June 12	----	----	14.8	+1.2	7.5	+4.0	9.8	+3.3	3.0
June 13	74.5	----	83.8	+7.8	82.0	----	61.8	----	---
June 16	20.3	+1.3	13.0	+3.1	10.6	+3.6	10.5	+6.0	13.5
June 19	15.3	+3.8	14.5	+0.4	10.0	+2.3	10.8	+1.9	9.0
June 19	21.5	+2.4	29.5	----	22.9	+6.0	17.3	+4.2	7.5
June 20	48.5	+9.0	51.5	----	42.0	----	50.3	----	11.3
June 20	----	----	----	----	----	----	----	----	---
June 22	34.9	+4.2	44.5	----	26.3	+8.8	30.3	----	6.0
June 23	41.3	----	68.6	----	44.0	----	46.8	----	6.0
June 26	30.8	+7.2	37.3	----	32.5	----	28.0	----	16.5
June 30	----	----	----	----	----	----	----	----	---
July 7	17.7	+2.3	18.3	+5.4	13.5	+1.3	12.3	+0.4	10.5
July 10	----	----	----	----	----	----	----	----	---
July 14	11.8	+3.0	16.2	----	10.1	+0.1	10.2	+0.6	15.5
July 21	----	----	----	----	----	----	----	----	---

TABLE H-19. ANALYSIS FOR ORTHO-PHOSPHATE (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
May 1	1.9	+1.7	---	---	2.1	+0.1	2.5	+0.5	---
May 3	0.2	+0.1	0.2	+0.1	0.3	+0.2	0.1	+0.0	---
May 7	---	---	---	---	---	---	---	---	---
May 12	0.2	+0.2	0.1	+0.1	0.1	+0.1	0.1	+0.1	---
May 18	0.5	+0.3	0.5	+0.4	0.5	+0.2	0.4	+0.2	0.7
May 28	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 5	0.2	+0.1	0.1	+0.1	0.1	+0.1	0.2	+0.1	0.1
June 6	0.0	+0.0	0.0	+0.0	0.0	+0.0	---	---	---
June 8	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 12	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 15	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 15	0.0	+0.0	0.0	+0.1	0.0	+0.0	0.0	+0.0	0.0
June 26	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 27	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 28	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 30	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	---
July 4	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 12	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
July 27	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.1
August 13	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
August 20	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.1	0.0

TABLE H-20. ANALYSIS FOR ORTHO-PHOSPHATE (PPM) FOR 1974

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
May 3	1.7	+0.5	2.2	+0.5	1.1	+0.6	2.4	+0.5	1.1
May 3	1.6	+0.4	4.6	+4.7	1.3	+0.3	2.2	+0.7	1.1
May 21	0.0	+0.1	0.0	+0.1	0.0	+0.1	0.0	+0.0	0.0
May 29	0.0	+0.1	0.0	+0.1	0.1	+0.1	0.0	+0.1	0.0
June 6	0.0	+0.0	0.1	+0.1	0.1	+0.1	0.1	+0.1	0.0
June 7	0.6	+0.2	0.4	+0.1	0.4	+0.1	0.5	+0.1	0.4
June 8	---	---	---	---	---	---	---	---	---
June 8	0.3	+0.1	0.3	+0.0	0.4	+0.1	0.4	+0.1	---
June 10	---	---	---	---	---	---	---	---	---
June 10	0.2	+0.1	0.5	+0.4	0.5	+0.7	0.4	+0.3	---
June 14	0.2	+0.2	0.1	+0.1	0.1	+0.1	0.1	+0.1	---
June 17	0.2	+0.1	0.1	+0.2	0.2	+0.1	0.3	+0.1	0.5
June 20	---	---	2.2	+1.6	---	---	---	---	---
June 24	---	---	---	---	---	---	0.2	+0.3	---
June 24	0.3	+0.4	0.3	+0.2	0.3	+0.3	0.1	+0.1	2.7
June 26	0.1	+0.1	0.1	+0.1	0.0	+0.1	0.1	+0.0	0.1
June 27	---	---	---	---	0.2	+0.1	1.3	+1.7	---
June 27	0.1	+0.1	0.2	+0.1	0.1	+0.1	0.2	+0.1	0.1
June 28	0.1	+0.1	0.1	+0.0	0.1	+0.1	0.2	+0.3	---
June 28	0.2	+0.1	0.2	+0.0	0.2	+0.3	0.3	+0.4	0.2
June 29	0.1	+0.1	0.1	+0.1	0.2	+0.1	0.1	+0.1	0.2
July 1	3.9	+5.0	0.2	+0.2	0.1	+0.1	0.3	+0.4	0.2
July 3	0.1	+0.1	0.4	+0.4	0.1	+0.1	0.2	+0.1	0.2
July 3	1.1	+1.8	0.1	+0.1	---	---	0.1	+0.1	---
July 5	0.2	+0.1	0.3	+0.2	0.2	+0.1	0.2	+0.0	---
July 8	0.1	+0.0	0.1	+0.0	0.1	+0.1	0.1	+0.0	0.2
July 8	0.0	+0.0	0.0	+0.0	---	---	0.0	+0.0	0.0
July 11	---	---	---	---	---	---	---	---	---
July 15	0.1	+0.1	0.1	+0.0	0.2	+0.1	0.1	+0.0	0.1
July 17	---	---	0.2	+0.2	---	---	---	---	---
July 22	---	---	0.1	+0.1	0.1	+0.1	0.1	+0.0	0.2
July 24	---	---	---	---	0.2	+0.1	0.2	+0.1	---
July 26	0.0	+0.1	0.1	+0.1	0.2	+0.3	0.1	+0.1	---

(Continued)

TABLE H-20. (Continued)

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
July 29	0.0	+0.1	0.1	+0.1	2.2	+3.7	0.0	+0.1	0.1
August 2	0.2	+0.2	0.0	+0.1	0.1	+0.2	0.0	+0.0	---
August 5	0.3	+0.1	0.3	+0.2	0.2	+0.1	0.2	+0.1	0.2
August 12	0.3	+0.1	0.2	+0.1	0.2	+0.2	0.3	+0.2	0.3
August 15	0.2	+0.1	---	---	0.3	+0.1	0.3	+0.1	---
August 16	0.1	+0.1	0.1	+0.0	---	---	0.1	+0.0	---
August 19	0.2	+0.1	0.2	+0.1	0.4	+0.4	0.2	+0.1	0.4
August 21	0.2	+0.1	0.5	+0.5	0.2	+0.1	0.3	+0.2	1.0

TABLE H-21. ANALYSIS FOR ORTHO-PHOSPHATE (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	1.4	+0.6	0.7	+0.5	1.1	+0.1	0.5	+0.1	---
May 1	0.9	+0.4	0.5	+0.1	1.0	+0.2	0.4	+0.2	0.1
May 12	0.2	+0.0	0.2	+0.0	0.3	+0.2	0.4	+0.3	---
May 21	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
May 28	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 5	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2
June 6	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.3	+0.1	0.2
June 7	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.3	+0.3	0.1
June 9	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 9	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 10	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 12	0.1	+0.0	---	---	0.1	+0.0	0.3	+0.4	0.1
June 13	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0	+0.0	0.0
June 16	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2
June 19	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2
June 19	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 20	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1	+0.0	0.1
June 20	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2
June 22	0.3	+0.0	0.3	+0.0	0.3	+0.0	0.3	+0.0	0.3
June 23	---	---	---	---	---	---	---	---	---
June 26	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2	+0.0	0.2
June 30	0.2	+0.1	0.3	+0.2	0.3	+0.1	0.3	+0.1	0.2
July 7	0.3	+0.1	0.2	+0.0	0.2	+0.1	1.1	+1.5	0.3
July 10	---	---	---	---	---	---	---	---	---
July 14	---	---	---	---	---	---	---	---	---
July 21	---	---	---	---	---	---	---	---	---
July 25	---	---	---	---	---	---	---	---	---
August 4	---	---	---	---	---	---	---	---	---

TABLE H-22. ANALYSIS FOR POTASSIUM (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	<u>Canal</u> <u>Water</u>
May 1	2.0	+0.1	2.3	+0.4	2.0	+0.1	1.8	+0.3	---
May 3	1.6	+0.0	1.7	+0.3	1.6	+0.1	1.8	+0.3	---
May 7	1.6	+0.0	1.8	+0.5	1.5	+0.1	1.4	+0.3	---
May 12	2.2	+0.7	2.1	+0.4	1.4	+0.2	2.5	+0.3	---
May 18	2.5	+0.3	2.8	+0.3	2.7	+0.5	2.8	+0.1	---
May 28	1.4	+0.5	1.5	+0.5	2.0	+0.5	1.9	+0.7	---
June 5	2.1	+0.5	2.6	+0.3	2.7	+0.6	2.2	+1.6	---
June 6	1.0	+0.2	2.1	+0.3	1.1	+0.7	2.2	+0.8	---
June 8	2.3	+0.1	3.3	+0.4	2.9	+0.3	2.6	+0.5	---
June 12	1.3	+0.2	1.7	+0.5	2.1	+0.1	2.4	+0.1	---
June 15	1.4	+0.3	1.7	+0.5	2.1	+0.1	2.2	+0.2	---
June 15	1.4	+0.6	1.5	+0.9	2.0	+0.2	2.3	+0.1	---
June 26	0.3	+0.2	0.6	+0.2	0.8	+0.4	1.0	+0.2	---
June 27	0.6	+0.2	1.2	+0.8	1.2	+0.4	0.7	+0.2	---
June 28	0.7	+0.2	0.9	+0.5	1.1	+0.7	0.9	+0.7	---
June 30	0.5	+0.1	1.0	+0.3	1.1	+0.7	1.5	+0.6	---
July 4	0.4	+0.1	0.5	+0.1	0.7	+0.2	1.1	+0.2	---
July 12	0.4	+0.1	0.4	+0.1	1.5	+0.0	1.5	+0.3	---
July 27	2.2	+0.4	2.4	+0.3	3.5	+0.9	3.2	+0.3	---
August 13	2.2	+0.1	2.3	+0.5	1.8	+0.0	2.1	+0.5	---
August 20	3.1	+0.2	3.3	+0.2	2.6	+0.2	3.1	+0.3	---

TABLE H-23. ANALYSIS FOR POTASSIUM (PPM) FOR 1975

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
April 30	3.2	+0.5	4.6	+0.6	3.4	+0.3	4.0	+0.5	1.8
May 1	3.0	+0.4	4.1	+0.3	3.0	+0.1	3.8	+0.6	1.5
May 12	2.6	+0.3	3.3	+0.0	2.5	+0.3	3.4	+0.6	-
May 21	3.3	+0.3	5.0	+0.6	3.2	+0.4	4.6	+0.6	1.5
May 28	1.3	+0.2	1.5	+0.2	1.2	+0.2	1.3	+0.2	2.5
June 5	2.8	+0.5	2.4	+0.1	2.1	+0.2	3.1	+0.9	1.5
June 6	3.1	+0.8	2.8	+0.7	2.8	+0.8	2.2	+0.2	1.7
June 7	3.7	+0.4	4.2	+0.1	2.7	+0.3	3.3	+0.3	1.6
June 9	4.0	+0.5	3.5	+0.7	3.3	+0.8	2.8	+0.4	2.0
June 9	-	-	4.7	+0.3	3.6	+0.6	5.0	+0.8	-
June 10	1.5	+0.3	1.8	+0.1	1.3	+0.1	1.5	+0.1	1.0
June 12	-	-	1.6	+0.4	1.2	+0.1	1.4	+0.2	1.8
June 13	3.1	+1.3	4.4	+0.8	4.5	+0.7	3.8	+0.4	-
June 16	0.9	+0.2	1.2	+0.1	1.1	+0.1	1.3	+0.2	1.2
June 19	1.2	+0.1	1.1	+0.2	1.1	+0.4	0.9	+0.1	1.2
June 19	1.1	+0.1	1.0	+0.2	1.0	+0.3	1.1	+0.3	1.5
June 20	1.7	+0.3	1.5	+0.3	1.7	+0.4	1.6	+0.1	1.7
June 20	5.0	+2.1	5.3	+2.0	---	---	3.7	+2.7	---
June 22	1.7	+0.2	1.5	+0.1	1.4	+0.6	1.4	+0.6	1.6
June 23	1.1	+0.4	1.1	+0.2	0.8	+0.7	1.0	+0.7	1.5
June 26	1.0	+0.1	0.8	+0.3	1.1	+0.3	0.8	+0.5	2.4
June 30	1.6	+0.2	1.5	+0.3	1.6	+0.6	1.8	+0.5	---
July 7	1.5	+0.3	1.1	+0.3	1.6	+0.1	---	---	2.1
July 10	1.4	+0.2	1.9	+0.9	2.1	+0.5	---	---	---
July 14	1.6	+0.9	1.5	+0.8	1.3	+0.8	1.9	+0.8	2.6
July 21	0.5	+0.2	1.4	+0.5	1.4	+1.0	1.4	+1.2	2.3
July 25	1.3	+0.1	1.2	+0.2	0.9	+0.3	1.4	+0.6	---
August 4	2.9	+0.1	3.2	+0.5	4.2	+1.5	4.4	+0.8	2.0
August 15	2.4	+0.5	4.1	+0.4	2.7	+0.7	3.9	+1.5	3.9

TABLE H-24. ANALYSIS FOR MAGNESIUM (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	<u>Canal</u> Water
May 1	1.9	+0.7	3.4	+1.6	2.3	+1.0	2.7	+0.1	---
May 3	2.9	+0.7	2.4	+0.8	2.9	+0.4	2.9	+1.2	---
May 7	3.4	+0.7	3.5	+1.3	3.2	+0.6	3.0	+0.7	---
May 12	6.0	+1.9	7.0	+1.0	5.7	+1.6	7.0	+0.8	---
May 18	3.7	+1.4	3.6	+0.9	2.8	+0.2	3.6	+1.7	---
May 28	1.9	+0.6	1.8	+0.3	2.3	+0.5	2.2	+0.7	---
June 5	1.9	+0.4	2.3	+0.1	2.5	+0.7	2.2	+1.7	---
June 6	0.8	+0.2	1.5	+0.5	0.9	+0.5	1.8	+0.9	---
June 8	2.2	+0.1	2.9	+0.6	2.6	+0.4	2.2	+0.4	---
June 12	1.3	+0.2	1.4	+0.5	2.0	+0.2	2.1	+0.2	---
June 15	1.6	+0.3	1.7	+0.4	2.2	+0.1	2.1	+0.4	---
June 15	1.6	+0.4	1.3	+0.9	2.1	+0.1	1.3	+0.8	---
June 26	1.1	+0.8	1.8	+1.0	0.9	+0.4	1.1	+0.1	---
June 27	1.3	+0.4	2.2	+0.9	1.3	+0.3	0.8	+0.3	---
June 28	2.2	+0.6	2.2	+1.1	1.3	+1.0	0.9	+0.7	---
June 30	2.7	+0.3	2.7	+0.6	2.5	+2.2	1.8	+0.4	---
July 4	2.6	+0.3	3.1	+1.2	2.1	+0.2	2.1	+0.1	---
July 12	1.9	+0.2	2.4	+0.3	2.5	+0.2	2.5	+0.1	---
July 27	2.7	+0.2	2.8	+0.4	2.4	+0.3	2.2	+0.1	---
August 13	2.6	+0.4	2.8	+0.5	1.7	+0.0	1.7	+0.2	---
August 20	3.1	+0.7	3.1	+0.5	2.4	+0.1	2.4	+0.1	---

TABLE H-25. ANALYSIS FOR MAGNESIUM (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	2.9	+1.4	4.8	+4.6	1.4	+0.4	3.9	+2.9	2.5
May 1	1.7	+1.0	1.9	+1.6	0.8	+0.1	2.1	+0.4	0.7
May 12	3.1	+0.6	4.4	+1.7	2.9	+0.5	7.1	+5.5	---
May 21	3.0	+0.4	4.3	+1.7	3.2	+0.8	3.9	+1.3	1.25
May 28	0.7	+0.2	0.7	+0.1	0.4	+0.1	0.5	+0.3	1.7
June 5	1.0	+0.2	1.1	+0.3	1.2	+0.1	1.4	+0.5	0.9
June 6	0.9	+0.3	0.8	+0.2	0.8	+0.3	0.8	+0.6	1.1
June 7	2.0	+0.2	1.8	+0.2	1.3	+0.2	1.6	+0.4	1.1
June 9	---	----	1.4	+0.1	2.0	+0.6	1.8	+0.3	2.6
June 9	---	----	4.2	+1.8	3.2	+2.1	5.8	+2.3	---
June 10	0.3	+0.2	0.4	+0.2	0.2	+0.2	0.2	+0.1	0.5
June 12	---	----	0.7	+0.1	0.8	+0.0	0.7	+0.0	1.3
June 13	3.5	+2.3	4.4	+0.9	---	----	3.5	+0.9	---
June 16	1.2	+0.1	1.1	+0.1	1.2	+0.2	1.0	+0.1	0.6
June 19	1.1	+0.2	0.9	+0.0	0.1	+0.1	1.1	+0.2	0.8
June 19	0.8	+0.1	0.7	+0.3	0.1	+0.2	0.7	+0.3	0.8
June 20	1.6	+0.1	1.8	+0.2	1.7	+0.7	1.6	+0.4	1.0
June 20	5.9	+5.7	6.0	+5.4	---	----	10.4	+7.4	---
June 22	2.0	+0.1	2.4	+0.5	2.2	+1.0	2.4	+0.9	1.0
June 23	1.4	+0.4	1.9	+0.9	1.5	+0.5	1.7	+1.0	1.0
June 26	2.0	+0.1	2.1	+0.2	1.9	+0.5	1.8	+0.2	1.5
June 30	3.7	+1.3	3.6	+1.3	3.9	+2.0	4.1	+1.3	---
July 7	1.7	+0.4	1.7	+0.1	1.6	+0.3	1.9	+0.4	---
July 10	4.2	+0.7	3.7	+1.3	2.9	+1.2	---	----	---
July 14	2.4	+0.3	2.7	+0.5	2.2	+0.2	2.4	+0.6	2.2
July 21	1.8	+0.2	1.7	+0.4	1.8	+1.1	1.5	+0.2	1.0
July 25	4.9	+0.6	5.0	+0.6	5.0	+1.0	4.4	+0.2	---
August 4	2.0	+0.2	1.9	+0.1	2.0	+0.2	2.0	+0.3	1.5

TABLE H-26. ANALYSIS FOR CALCIUM (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
May 1	17.9	+5.7	28.6	----	20.1	+7.9	25.0	+2.2	----
May 3	27.1	+6.4	22.5	+5.9	29.0	+5.4	27.2	----	----
May 7	30.1	+3.8	30.5	+8.8	29.2	+5.4	25.6	+4.4	----
May 12	46.7	----	52.3	+5.1	44.2	+9.9	56.1	+9.2	----
May 18	29.7	----	30.7	+7.8	25.1	+1.1	28.9	----	----
May 28	19.5	+4.2	19.6	+1.2	22.8	+2.6	20.5	+5.0	----
June 5	14.9	+2.0	17.6	+4.7	19.9	+5.9	17.4	----	----
June 6	8.1	+1.9	14.2	+4.5	10.8	+2.5	17.0	+7.9	----
June 8	20.7	+1.6	23.0	+5.9	16.8	+2.0	16.0	+3.2	----
June 12	11.0	+0.6	13.1	+4.1	13.2	+1.7	12.8	+0.6	----
June 15	15.1	+2.7	16.2	+2.8	15.1	+0.1	13.5	+1.1	----
June 15	8.4	+4.5	10.3	+7.3	13.0	+0.9	11.6	+1.6	----
June 26	9.2	+5.5	13.9	+7.7	6.2	+2.5	7.7	+0.4	----
June 27	15.6	+3.6	23.1	+2.9	10.5	+1.5	8.6	+3.8	----
June 28	22.2	+3.0	25.2	+5.4	8.0	+5.6	7.2	+7.0	----
June 30	22.2	+2.3	21.1	+6.5	18.2	----	11.8	+1.8	----
July 4	23.5	+2.4	27.8	---	14.3	+1.7	14.2	+0.8	----
July 12	13.9	+0.4	18.1	+3.8	13.0	+2.0	12.6	+0.7	----
July 27	16.8	+2.3	18.1	+3.8	11.0	+1.3	9.2	+1.3	----
August 13	13.6	+4.1	15.9	+3.5	8.8	+0.6	9.0	+1.0	----
August 20	19.0	+5.1	17.2	+1.9	13.2	+1.1	12.5	+1.8	----

TABLE H-27. ANALYSIS FOR CALCIUM (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	18.8	+4.5	18.8	+8.1	8.2	+2.3	22.5	----	10.0
May 1	9.3	+4.0	9.3	+3.5	7.3	+2.1	11.8	+3.8	5.0
May 12	15.0	+3.9	18.4	+2.9	14.2	+2.5	22.7	+8.1	---
May 21	15.0	+2.4	22.4	+	14.6	+3.5	20.6	+8.3	5.8
May 28	3.2	+1.2	5.7	+2.0	4.7	+1.0	6.2	+0.8	8.5
June 5	5.7	+1.3	5.8	+1.4	6.8	+1.5	7.9	+3.4	5.0
June 6	6.2	+2.0	5.8	+2.0	6.7	+2.3	5.8	+2.5	8.0
June 7	10.0	+0.6	9.5	+0.6	6.2	+0.9	7.9	+2.2	5.2
June 9	----	+	10.5	+2.6	8.2	+2.9	7.6	+2.4	6.5
June 9	----	+	22.7	+	16.6	+	32.7	+	---
June 10	2.1	+1.7	2.4	+0.9	1.7	+1.2	1.2	+0.4	3.0
June 12	----	+	4.1	+0.3	4.5	+0.3	4.0	+0.3	5.7
June 13	19.3	+	22.6	+6.1	19.1	+	18.3	+5.8	---
June 16	6.7	+0.8	6.0	+0.5	6.2	+1.2	5.4	+0.7	3.3
June 19	6.2	+1.0	5.5	+0.0	5.6	+0.5	5.8	+0.8	4.8
June 19	5.2	+0.5	4.7	+1.5	5.5	+0.9	4.4	+1.8	---
June 20	10.5	+0.8	12.5	+2.3	11.4	+4.1	10.1	+3.1	5.3
June 20	43.2	+	38.2	+	----	+	61.8	----	---
June 22	13.7	+4.2	14.8	+6.0	14.7	+5.5	16.1	+5.0	6.5
June 23	9.2	+2.5	12.7	+4.8	9.0	+1.4	10.7	+5.9	5.3
June 26	10.3	+0.6	11.4	+1.6	9.6	+2.4	9.8	+2.2	6.5
June 30	21.8	+4.5	22.2	+3.5	21.5	+8.9	21.5	+2.3	---
July 7	7.9	+0.8	9.3	+0.8	----	+	8.3	+1.8	18.3
July 10	20.6	+2.2	18.9	+6.7	14.5	+4.2	----	+	---
July 14	9.6	+1.4	12.1	+3.4	9.1	+0.7	10.7	+2.3	7.0
July 21	8.9	+0.2	7.3	+2.4	10.0	+5.7	7.6	+2.1	6.0
July 25	22.7	+3.1	24.5	+3.1	28.8	+	20.4	+2.8	---
August 4	9.0	+1.5	9.2	+1.0	8.3	+1.2	8.9	+2.2	6.7

TABLE H-28. ANALYSIS FOR CHLORIDE (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	Canal Water
May 1	----	----	----	----	----	----	----	----	---
May 3	----	----	----	----	----	----	----	----	---
May 7	----	----	----	----	----	----	----	----	---
May 12	----	----	----	----	----	----	----	----	---
May 18	----	----	----	----	----	----	----	----	---
May 28	----	+6.0	----	+8.1	----	----	----	----	---
June 5	----	----	----	----	----	+4.6	----	----	---
June 6	----	----	----	----	98.0	----	----	----	---
June 8	----	----	----	----	----	----	----	----	---
June 12	----	----	96.0	----	84.0	----	93.7	----	---
June 15	----	----	----	----	97.0	----	96.0	----	---
June 15	88.0	----	----	----	----	----	----	----	---
June 26	----	----	----	----	----	----	----	----	---
June 27	59.7	----	----	----	79.0	----	53.0	----	---
June 28	91.0	----	99.0	----	87.0	----	78.7	----	---
June 30	99.0	+7.9	----	----	----	----	----	9.0	---
July 4	----	----	----	----	----	----	----	----	---
July 12	79.0	----	----	----	----	----	91.0	----	---
July 27	----	----	----	----	----	----	----	----	---
August 13	----	+6.8	----	+7.9	----	----	90.0	6.0	93.0
August 20	----	+9.0	----	----	----	+4.6	----	4.0	99.0

TABLE H-29. ANALYSIS FOR CHLORIDE (PPM) FOR 1974

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
May 3	79.2	+3.7	57.4	+2.3	49.9		39.0		39.5
May 3	32.7		53.8		55.5		60.0		48.7
May 21	8.9	+4.2	16.4	+3.4	5.9	+2.7	7.8	+ .8	20.5
May 29	37.3	+2.9	28.9	+4.6	28.1	+8.9	33.1	+1.4	27.7
June 6	37.5		40.5		47.3		37.8		35.3
June 7	55.3	+3.3	53.7	+1.2	48.3	+3.8	50.1	+1.2	42.4
June 8	37.9		50.7	+6.0	34.5		45.5	+9.2	42.8
June 8	52.6	+4.1	54.3	+1.7	44.6	+1.5	44.5	+ .5	
June 10	48.4	+5.3	49.7	+4.6	40.5	+ .7	40.4	+ .8	40.3
June 10									
June 14	41.3	+2.0	44.7	+3.2	37.2	+2.3	33.5	+2.6	
June 17	40.7	+4.5	41.7	+6.4	35.2	+1.3	33.3	+1.3	36.0
June 20									
June 24									
June 24	31.3	+2.8	35.5	+5.5	33.2	+2.0	32.2	+ .5	31.4
June 26	28.9	+8.6	35.2	+3.7	35.1	+3.0	36.3	+1.1	31.5
June 27									
June 27	35.6	+1.1	38.4	+4.7	35.2	+ .6	36.8	+ .3	31.5
June 28	37.2	+1.3	41.1	+7.4	39.7	+6.0	40.4	+2.2	
June 28	35.1	+2.5	34.9	+1.7	35.3	+ .6	36.7	+ .9	32.0
June 29	41.3	+2.9	41.5	+6.6	47.2	+ .8			39.0
July 1	37.4	+1.9	39.2	+4.3	38.5	+2.8	39.2	+3.0	34.0
July 3	34.0	+1.0	37.6	+ .8	35.8	+3.2	38.0	+ .9	33.0
July 3									
July 5									
July 8	39.7	+4.0	38.5	+2.9	39.6	+5.2	37.5	+1.3	
July 8	66.7						50.0	+0.0	
July 11									
July 15	36.7	+1.5	37.8	+2.1	35.7	+1.5	35.2	+ .2	34.0
July 17									
July 22			43.3	+4.6	38.9	+2.7	37.2	+ .3	31.0
July 24									
July 26	42.4	+2.6	42.8	+4.8	40.4	+2.6	39.5	+3.5	
July 29	43.4	+1.3	42.8	+2.8	35.0	+1.3	36.3	+2.0	31.5

(Continued)

TABLE H-29. (Continued)

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
August 2	35.6	+ .9	32.3	+1.4	31.3	+ .6	28.1	+1.1	
August 5	31.7	+2.5	30.9	+2.7			30.1	+2.9	
August 12	36.8	+1.2	35.0	+2.6	33.4	+ .5	34.2	+ .3	30.0
August 15									
August 16									
August 19									
August 21	36.3	+8.6	35.2	+7.5	25.2	+3.4	35.5	+8.7	23.5

TABLE H-30. ANALYSIS FOR CHLORIDE (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	46.6	+2.2	62.1		45.3	+4.6	56.1	+1.9	36.8
May 1	42.6	+1.8	53.9	+1.2	43.5	+ .6	51.1	+1.9	36.4
May 12	9.7	+2.2	20.0	+7.3	14.9	+7.2	12.7	+4.7	
May 21	35.7		36.8		29.9	+8.9	45.9		8.5
May 28	12.7	+3.6	13.9	+3.2	6.2	+3.3			32.1
June 5	31.4	+2.1	32.1	+ .8	31.3	+ .9	32.2	+1.0	30.5
June 6	31.7	+2.5	30.4	+2.5	31.3	+2.6	28.2	+4.8	19.9
June 7	22.2	+4.8	28.2	+8.5	30.8	+1.5	24.3	+4.7	25.9
June 9	19.5	+1.7			21.3	+3.2	16.4	+7.1	6.3
June 9			37.3	+1.6	30.2	+4.2	36.9	+4.1	
June 10	11.8	+1.1	12.2	+1.2	12.1	+1.9	14.2	+ .8	12.00
June 12			16.7	+3.8	15.2	+8.3	15.5	+6.9	16.00
June 13	17.5	+9.0	20.5	+1.8	30.8		13.8	+4.2	
June 16	9.7	+1.2	8.4	+3.7	12.4	+3.2	10.0	+3.2	12.1
June 19	11.4	+ .6	10.8	+1.0	13.7	+3.4	10.4	+1.8	16.50
June 19	12.4	+1.9	13.5	+2.5	14.5	+ .6	14.2	+3.3	18.20
June 20	10.5	+1.7	9.9	+2.8	10.1	+2.1	17.6		8.3
June 20	21.1		22.3				28.8	+7.0	
June 22	8.9	+2.4	9.5	+2.5	9.9	+2.0	9.0	+4.1	21.0
June 23	9.8	+4.6	9.6	+3.9	11.3	+5.1	13.6		21.8
June 26	17.5	+1.3	16.3	+3.1	18.1	+1.2	17.1	+7.6	30.5
June 30	10.8	+3.7	11.7	+5.3	14.0	+7.4	17.4		
July 7	32.7	+3.9	33.0	+4.0	44.0		38.3	+2.9	37.2
July 10	33.8	+8.1	30.8		35.6	+9.0			
July 14	33.5	+6.0	32.4	+7.3	35.7	+2.1	36.8	+7.7	32.6

TABLE H-31. ANALYSIS FOR SODIUM (PPM) FOR 1973

Date	<u>Impounded</u> Mean	<u>Recommended</u> Standard Deviation	<u>Impounded</u> Mean	<u>Excessive</u> Standard Deviation	<u>Continuous</u> Mean	<u>Recommended</u> Standard Deviation	<u>Continuous</u> Mean	<u>Excessive</u> Standard Deviation	<u>Canal</u> Water
May 1	15.5	+2.7	15.8	+1.6	14.1	+2.4	13.6	+0.9	---
May 3	17.5	+7.6	13.3	+1.5	17.2	+3.0	17.1	+7.9	---
May 7	16.1	+3.9	12.5	+2.9	14.9	+4.8	12.9	+2.7	---
May 12	25.8	+7.3	58.9	----	42.8	----	27.3	+3.2	---
May 18	23.7	----	25.3	+9.8	21.7	+0.9	19.5	+7.8	---
May 28	16.6	+5.9	14.5	+2.6	20.7	+1.9	17.0	+4.3	---
June 5	7.3	+0.8	9.8	+2.2	8.5	+0.7	7.5	+5.1	---
June 6	6.6	+2.2	12.5	+4.0	6.9	+4.7	12.7	+5.4	---
June 8	13.3	+3.2	19.2	+6.7	16.2	+3.1	11.8	+3.9	---
June 12	8.1	+1.6	8.7	+3.3	11.2	+1.1	11.3	+0.5	---
June 15	13.7	+2.7	13.9	+4.5	15.3	+0.4	13.6	+1.8	---
June 15	7.9	+3.1	8.0	+4.5	11.9	+0.9	10.4	+1.3	---
June 26	8.4	+5.8	12.5	+7.5	5.0	+1.6	5.2	+0.3	---
June 27	10.3	+3.8	13.7	+3.1	6.2	+2.0	2.9	+1.4	---
June 28	9.5	+1.3	8.0	+1.8	5.2	+3.6	3.4	+2.8	---
June 30	17.6	+3.1	15.0	+5.1	12.5	----	8.1	+2.0	---
July 4	15.2	+1.6	15.1	+3.0	14.0	----	9.0	+1.9	---
July 12	8.4	+1.2	10.0	+2.6	9.5	+0.9	8.7	+0.2	---
July 27	14.5	+1.4	14.9	+6.1	12.6	+0.9	11.3	+0.9	---
August 13	12.9	+1.8	13.2	+2.6	9.2	+0.4	9.0	+0.9	---
August 20	14.1	+2.4	15.3	+3.5	12.3	+0.5	12.4	+0.3	---

TABLE H-32. ANALYSIS FOR SODIUM (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	19.8	+3.4	22.4	+2.4	21.0	+4.4	19.5	+1.6	9.0
May 1	17.3	+2.0	19.6	+1.9	17.3	+2.6	15.3	+2.1	21.0
May 12	11.8	+2.0	10.3	+0.3	10.1	+1.4	11.4	+0.5	-
May 21	17.7	+1.0	20.6	+3.4	18.6	+2.1	18.4	+2.7	9.5
May 28	5.2	+0.8	5.0	+0.7	2.8	+1.1	5.0	+2.2	10.2
June 5	14.4	+1.3	13.7	+0.8	12.9	+0.2	15.6	+1.9	12.8
June 6	11.0	+2.3	11.3	+2.4	10.1	+1.5	9.9	+0.5	9.1
June 7	12.9	+1.3	12.5	+0.5	10.3	+0.6	10.7	+1.2	8.3
June 9	13.9	+1.4	13.7	+1.5	11.5	+1.2	12.6	+2.0	11.9
June 9	-	-	20.2	+6.1	17.8	+7.3	24.2	+5.5	-
June 10	4.5	+0.3	4.4	+0.7	4.3	+0.6	5.0	+0.8	4.4
June 12	-	-	3.9	+1.8	5.8	+0.2	4.8	+0.3	9.3
June 13	15.5	+8.2	20.7	+7.7	19.3	-	10.3	-	-
June 16	8.3	+0.9	7.0	+2.1	8.6	+1.3	6.8	+0.6	4.3
June 19	7.6	+1.2	6.0	+0.3	6.6	+1.0	6.2	+2.3	5.8
June 19	6.8	+0.5	8.2	+1.4	6.5	+0.9	6.6	+0.7	7.0
June 20	7.1	+0.4	7.8	+1.9	7.1	+2.0	7.2	+2.1	6.4
June 20	18.0	+5.5	17.7	+6.2	-	-	17.8	+5.3	-
June 22	8.4	+0.7	11.0	+1.6	9.5	+2.7	8.7	+1.9	7.5
June 23	8.1	+1.5	10.3	+2.2	7.9	+3.3	8.4	+0.8	8.2
June 26	8.3	+0.4	8.9	+0.6	7.9	+1.8	7.8	+1.3	11.0
June 30	11.7	+2.8	9.2	+8.0	14.0	+5.4	13.8	+2.1	-
July 7	11.4	+1.4	12.1	+0.4	11.1	+1.7	13.1	+0.8	-
July 10	26.9	+4.1	26.0	+4.2	22.9	+2.9	-	-	-
July 14	11.3	+1.9	12.3	+2.9	11.9	+0.6	-	-	10.3
July 21	-	-	-	-	-	-	-	-	-
July 25	16.8	+0.9	18.9	+1.0	16.6	+2.3	17.0	+1.0	-
August 4	9.2	+1.2	10.0	+1.1	10.5	+0.4	9.6	+0.5	10.8

TABLE H-33. ANALYSIS FOR HCO_3 (PPM) FOR 1975

Date	Impounded Mean	Recommended Standard Deviation	Impounded Mean	Excessive Standard Deviation	Continuous Mean	Recommended Standard Deviation	Continuous Mean	Excessive Standard Deviation	Canal Water
April 30	---	---	213.5	---	---	---	---	---	219.6
May 1	---	---	0.0	+0.0	---	---	---	---	---
May 12	---	---	0.0	+0.0	---	---	---	---	---
May 21	---	---	101.7	---	---	---	---	---	207.4
May 28	---	---	87.4	+33.6	---	---	---	---	170.8
June 5	---	---	435.1	---	---	---	---	---	164.7
June 6	---	---	144.4	---	---	---	---	---	146.4
June 7	---	---	4.1	+7.0	---	---	---	---	134.2
June 9	---	---	20.3	+21.4	---	---	---	---	225.7
June 10	---	---	26.4	+21.4	---	---	---	---	18.3
June 12	---	---	38.6	+9.3	---	---	---	---	91.5
June 16	---	---	59.0	+21.4	---	---	---	---	85.4
June 19	---	---	132.2	+33.6	---	---	---	---	109.8
June 19	---	---	150.5	+39.7	---	---	---	---	170.8
June 20	---	---	59.0	---	---	---	---	---	153.6
June 22	---	---	28.5	+49.3	---	---	---	---	195.2
June 23	---	---	---	---	---	---	---	---	256.2
June 26	---	---	136.2	---	---	---	---	---	0.0
July 7	---	---	185.0	+88.9	---	---	---	---	176.9
July 14	---	---	427.0	---	---	---	---	---	176.9
July 21	---	---	555.1	+89.9	---	---	---	---	262.3
August 4	---	---	---	---	---	---	---	---	189.1
August 15	---	---	374.1	+56.4	---	---	---	---	134.2

Appendix I. Analysis of variance for molinate,
carbofuran and carbaryl in rice paddy
water during 1973, 1974 and 1975 growing
seasons.

TABLE I-1. ANALYSIS OF VARIANCE FOR MOLINATE IN RICE PADDY WATER
SAMPLED IN 1973

Source	d.f.	MS	F
Reps	2	0.071	0.92
Times (T)	6	18.011	97.43**
Irrigation (I)	1	14.250	77.09**
Rates (R)	1	34.215	185.08**
T X I	6	1.428	7.72**
T X R	6	5.945	32.15**
I X R	1	4.535	24.53**
T X I X R	6	0.484	2.60*
Error	54	0.185	
Total	83		

* Significant at the 5% level.

** Significant at the 1% level.

TABLE I-2. ANALYSIS OF VARIANCE FOR MOLINATE IN RICE PADDY WATER
SAMPLED IN 1974

Source	d.f.	MS	F
Reps	2	0.878	1.31
Times (T)	5	36.796	47.42**
Irrigation (I)	1	0.003	-
Rates (R)	1	74.004	95.36**
T X I	5	0.488	0.63
T X R	5	10.634	13.70**
I X R	1	4.050	5.22*
T X I X R	5	0.307	0.39
Error	46	0.776	
Total	71		

* Significant at the 5% level.

** Significant at the 1% level.

TABLE I-3. ANALYSIS OF VARIANCE FOR MOLINATE IN RICE PADDY WATER
SAMPLED IN 1975

Source	d.f.	MS	F
Reps	2	1.014	3.31 *
Times (T)	6	24.644	80.53 **
Irrigation (I)	1	.492	1.61
Rates (R)	1	49.653	162.26 **
T X I	6	0.241	0.79
T X R	6	6.236	20.38 **
I X R	1	.002	.01
T X I X R	6	.053	.17
Error	54	.306	
Total	83		

*Significant at the 5% level.

**Significant at the 1% level.

TABLE I-4. ANALYSIS OF VARIANCE FOR CARBOFURAN IN RICE PADDY
WATER SAMPLED IN 1973

Source	d.f.	MS	F
Reps	2	0.017	2.42
Times (T)	6	0.483	70.44**
Irrigation (I)	1	0.007	1.05
Rates (R)	1	0.299	43.54**
T X I	6	0.001	0.13
T X R	6	0.141	20.52**
I X R	1	0.003	0.48
T X I X R	6	0.004	0.60
Error	54	0.007	
Total	83		

* Significant at the 5% level.

** Significant at the 1% level.

TABLE I-5. ANALYSIS OF VARIANCE FOR CARBOFURAN IN RICE PADDY
WATER SAMPLED IN 1974

Source	d.f.	MS	F
Reps	2	0.420	3.19
Times (T)	5	1.999	15.19**
Irrigation (I)	1	0.000	—
Rates (R)	1	3.572	27.15**
T X I	5	0.178	1.35
T X R	5	1.329	10.11**
I X R	1	0.115	0.87
T X I X R	5	0.060	0.46
Error	46	0.131	
Total	71		

* Significant at the 5% level.

** Significant at the 1% level.

TABLE I-6. ANALYSIS OF VARIANCE FOR CARBOFURAN IN RICE PADDY
WATER SAMPLED IN 1975

Source	d.f.	MS	F
Reps	2	.012	.21
Times (T)	6	.9871	17.32**
Irrigation (I)	1	.0005	.01
Rates (R)	1	3.9911	70.02**
T X I	6	.0204	.36
T X R	6	.525	9.21**
I X R	1	.0007	.01
T X I X R	6	.0176	.31
Error	54	.057	
Total	83		

* Significant at the 5% level.

** Significant at the 1% level.

TABLE I-7. ANALYSIS OF VARIANCE FOR CARBARYL IN RICE PADDY
WATER SAMPLED IN 1973

Source	d.f.	MS	F
Reps	2	0.016	1.62
Times (T)	5	0.492	49.19**
Irrigation (I)	1	0.058	5.83*
Rates (R)	1	0.229	22.91**
T X I	5	0.016	1.60
T X R	5	0.080	8.00**
I X R	1	0.017	1.68
T X I X R	5	0.005	0.51
Error	46	0.010	
Total	71		

* Significant at the 5% level.

** Significant at the 1% level.

TABLE I-8. ANALYSIS OF VARIANCE FOR CARBARYL IN RICE PADDY
WATER SAMPLED IN 1974

Source	d.f.	MS	F
Reps	2	0.064	0.61
Times (T)	5	0.521	5.03**
Irrigation (I)	1	0.759	7.32**
Rates (R)	1	2.573	24.80**
T X I	5	0.131	1.27
T X R	5	0.225	2.17
I X R	1	0.719	6.94*
T X I X R	5	0.097	0.93
Error	46	0.104	
Total	71		

* Significant at the 5% level.

** Significant at the 1% level.

TABLE I-9. ANALYSIS OF VARIANCE FOR CARBARYL IN RICE PADDY
WATER SAMPLED IN 1975

Source	d.f.	MS	F
Reps	2	1.584	1.60
Times (T)	4	5.309	5.36**
Irrigation (I)	1	.001	--
Rates (R)	1	15.973	16.13**
T X I	4	1.228	1.24
T X R	4	3.170	3.20*
I X R	1	.055	.06
T X I X R	4	1.837	1.86
Error	38	.990	
Total	59		

*Significant at the 5% level.

**Significant at the 1% level.

APPENDIX J

ANALYTICAL SOLUTION TO THE ONE-DIMENSIONAL
LINEAR, CONVECTION-DIFFUSION EQUATION

To provide a basis for comparison of the approximate numerical solutions, an analytical (exact) solution is presented in this appendix. The problem to which the solution applies is defined by equations (4), (7a), (7b), and the boundary condition at $Z = \infty$:

$$\lim_{Z \rightarrow \infty} C(Z, t) = 0, \quad t > 0 \quad (J-1)$$

The boundary condition (J-1) differs from the one for a finite column, but results obtained from use of (J-1) are identical to those obtained by use of (7d) for times, t , such that the concentration at $Z = L_c$ has not been perturbed from its initial value.

The solution to the problem thus defined has been presented by Shamir and Harleman (1967) and Nielsen, et al. (1972). It can be expressed in the form:

$$\frac{C - C_i}{C_o - C_i} = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{Z - v \cdot t}{4 \cdot D \cdot t} \right) + \exp \left(\frac{v \cdot Z}{D} \right) \cdot \operatorname{erfc} \left(\frac{Z + v \cdot t}{4 \cdot D \cdot t} \right) \right] \quad (J-2)$$

For moderate values of the term $\frac{v \cdot Z}{D}$, equation (J-2) can be evaluated on a computer using machine subroutines to obtain values for the $\operatorname{erfc} \left(\frac{Z - v \cdot t}{4 \cdot D \cdot t} \right)$ and $\exp \left(\frac{v \cdot Z}{D} \right)$ functions. For large values of $\frac{v \cdot Z}{D}$ (~160), the exponential could not be evaluated directly. It was therefore necessary in such cases to resort to an asymptotic approximation to the term $\operatorname{erfc} \left(\frac{Z + v \cdot t}{4 \cdot D \cdot t} \right)$.

According to Carslaw and Jaeger (1959), the following asymptotic expansion can be used to evaluate $\operatorname{erfc}(x)$ for large x .

$$\operatorname{erfc}(x) + \frac{e^{-x^2}}{\pi} \cdot \left(\frac{1}{x} - \frac{1}{2x^3} + \dots (-1)^{n-1} \cdot \frac{1 \cdot 3 \dots (2n-3)}{2^{n-1} \cdot x^{2n-1}} \right) \quad (J-3)$$

The error $|E|$ which results from terminating the series after $n-1$ terms is bounded according to the inequality:

$$|E| \leq E_n = \frac{1 \cdot 3 \dots (2n-1)}{2^n \cdot x^{2n+1}}$$

The advantage of using the asymptotic expansion is derived from combining the arguments of the exponential functions appearing in equations (J-2) and (J-3). When this is done the product $p = \exp(\frac{V \cdot Z}{D}) \cdot \operatorname{erfc}(\frac{Z + V \cdot T}{4 \cdot D \cdot T})$ can be expressed:

$$p \approx \frac{1}{\pi} \cdot \exp(-w^2) \cdot \left[\frac{1}{x} - \frac{1}{2 \cdot x^3} + \dots + (-1)^{n-1} \cdot \frac{1 \cdot 3 \dots (2n-3)}{2^{n-1} \cdot x^{2n-1}} \right],$$

where

$$w = \frac{V \cdot t - Z}{4 \cdot D \cdot t} \text{ and } X = \frac{V \cdot t + Z}{4 \cdot D \cdot t}.$$

The asymptotic expansion was used to evaluate p when $\frac{V \cdot Z}{D} \geq 150$. The error term $|E|$ was also evaluated to insure that the approximation was valid. A FORTRAN program was written in accordance with the procedure described above. Solutions generated from the program were used to develop the solid line curves in Figures 100 through 110.

APPENDIX K

TRANSFORMATION OF THE CHEMICAL EQUILIBRIUM EQUATIONS

The back-substitution scheme used to transform equations (46) - (51) to equations (52) - (67) is presented in this appendix. In addition, the conditions under which A_1 can be properly defined by the quadratic formula (52) are investigated.

Before proceeding with the back-substitution scheme it is helpful to first define the following terms:

$$T_{C2} = \frac{\alpha_2 \cdot C_{2T}}{Y_1 + (E_{12} + E_{12} \cdot D_{21} \cdot \gamma^8 \cdot A_1) \cdot C_1}, \quad (54a)$$

$$T_{C3} = \frac{\alpha_2 \cdot C_{2T}}{Y_1 + \gamma \cdot E_{13} \cdot C_1^{1/2}}, \quad (54b)$$

$$T_{C4} = \frac{\alpha_4 \cdot C_{4T}}{Y_1 + \gamma \cdot E_{14} \cdot C_1^{1/2}}, \quad (54c)$$

$$T_{C5} = \frac{\alpha_5 \cdot C_{5T}}{Y_1 + \gamma \cdot E_{15} \cdot C_1^{1/2}}. \quad (54d)$$

Solving for C_3 in equation (38) and substituting the result into equation (45) yields:

$$Y_1/Y_3 = \gamma E_{13} \cdot C_1^{1/2} / (C_{3T} - Y_3),$$

whereupon solving for Y_3 results in the expression:

$$Y_3 = \frac{Y_1 \cdot C_{3T}}{Y_1 + \gamma \cdot E_{13} C_1^{1/2}} = \frac{Y_1}{\alpha_3} \cdot T_{C3}. \quad (65)$$

Following a similar procedure with equations (39), (46), (40) and (47) yields:

$$Y_4 + \frac{Y_1 \cdot C_{4T}}{Y_1 + \gamma \cdot E_{14} \cdot C_1^{\frac{1}{2}}} = \frac{Y_1}{\alpha_4} \cdot T_{C4} \quad (66)$$

and

$$Y_5 = \frac{Y_1 \cdot C_{5T}}{Y_1 + \gamma \cdot E_{15} \cdot C_1^{\frac{1}{2}}} = \frac{Y_1}{\alpha_5} \cdot T_{C5} \quad (67)$$

Back-substituting equations (65), (66) and (67) into equations (45), (46) and (47), respectively, produces C_3 , C_4 and C_5 :

$$C_3 = \left(\frac{E_{13}}{\alpha_3} \right) \cdot (\gamma C_1^{\frac{1}{2}}) \cdot T_{C3} \quad (56)$$

$$C_4 = \left(\frac{E_{14}}{\alpha_4} \right) \cdot (\gamma C_1^{\frac{1}{2}}) \cdot T_{C4} \quad (57)$$

$$C_5 = \left(\frac{E_{15}}{\alpha_5} \right) \cdot (\gamma C_1^{\frac{1}{2}}) \cdot T_{C5} \quad (58)$$

Substituting equation (50) into equation (37) and solving the resulting equation for C_2 , we get:

$$C_2 = \frac{(C_{2T} - Y_2)}{(1 + \gamma^8 \cdot D_{21} \cdot A_1)} \quad .$$

Substituting the right-hand side of the above equation into equation (44) and solving for Y_2 produces:

$$Y_2 = \frac{Y_1 \cdot C_{2T}}{Y_1 + (E_{12} + E_{12} \cdot D_{21} \cdot \gamma^8 \cdot A_1) \cdot C_1} = \frac{Y_1}{\alpha_2} \cdot T_{C2} \quad (64)$$

Substituting equation (64) into (44) and solving for C_2 yields:

$$C_2 = \frac{E_{12}}{\alpha_2} \cdot C_1 \cdot T_{C2} \quad (55)$$

Inspection of equations (54a) through (58) and (64) through (67) reveals

that $Y_2, C_2, Y_3, C_3, Y_4, C_4, Y_5$, and C_5 are defined as functions of Y_1, A_1, C_1 , and γ . It will now be shown that Y_1 can be obtained as a function of A_1, C_1 , and γ and that A_1 can be obtained as a function of C_1 and γ , only.

Substituting equation (49) into equation (36) provides Y_1 as a function of A_1, C_1 and γ :

$$Y_1 = C_{1T} - C_1 \cdot (1 + D_{11} \cdot \gamma^8 \cdot A_1) . \quad (53)$$

Substituting equations (49) and (50) into equation (41), we get:

$$A_{1T} = A_1 \cdot (1 + \gamma^8 \cdot D_{11} \cdot C_1 + \gamma^8 \cdot D_{21} \cdot C_2) .$$

Finally, substituting equations (53) and (55) into the above expression and using the definition of T_{C2} from equation (54a), we get:

$$A_{1T} = A_1 \cdot \left\{ 1 + \gamma^8 C_1 \left[D_{11} + \frac{D_{21} \cdot E_{12} \cdot C_{2T}}{C_{1T} - C_1 \cdot (1 + D_{11} \cdot \gamma^8 \cdot A_1) + (E_{12} + E_{12} \cdot D_{21} \cdot \gamma^8 \cdot A_1) \cdot C_1} \right] \right\} , \quad (K-1)$$

which defines A_1 as implicit function of C_1 and γ .

Multiplying both sides of (K-1) by the denominator of the quotient term results in a quadratic equation in A_1 . Upon rearrangement, the quadratic may be expressed as:

$$F_1 = AAA \cdot A_1^2 + BBB \cdot A_1 + CCC = 0 ,$$

where

$$AAA = \gamma^8 \cdot (1 + D_{11} \cdot C_1 \cdot \gamma^8) \cdot (D_{21} - \frac{D_{11}}{E_{12}}) ,$$

$$BBB = (1 + D_{11} \cdot C_1 \cdot \gamma^8) \cdot (1 + \frac{C_{1T}}{E_{12} \cdot C_1} - \frac{1}{E_{12}}) + \gamma^8 \cdot [D_{21} \cdot C_{2T} + A_{1T} \cdot (\frac{D_{11}}{E_{12}} - D_{21})] ,$$

and

$$CCC = A_{1T} \cdot (\frac{1}{E_{12}} - \frac{C_{1T}}{E_{12} \cdot C_1} - 1) .$$

This quadratic may be solved for A_1 by the quadratic formula:

$$A_1 = \frac{-BBB \pm \sqrt{BBB^2 - 4 \cdot AAA \cdot CCC}}{2 \cdot AAA} , \quad (52)$$

provided (a) an unambiguous choice of sign can be made, (b) the discriminant, $d = BBB^2 - 4 \cdot AAA \cdot CCC$, is non-negative, and (c) $AAA \neq 0$.

To facilitate the discussion of conditions (a), (b), and (c), the following additional notation is introduced:

$$k_1 = (1 + D_{11} \cdot C_1 \cdot \gamma^8) ,$$

$$k_2 = \gamma^8 \cdot \left(\frac{D_{11}}{E_{12}} - D_{21} \right) \cdot A_{1T} ,$$

$$k_3 = \frac{1}{E_{12}} \cdot \left(1 - \frac{C_{1T}}{C_1} \right) - 1 ,$$

and

$$k_4 = \gamma^8 \cdot D_{21} \cdot C_{2T} .$$

Using this notation we have:

$$AAA = -k_1 \cdot k_2 / A_{1T} ,$$

$$BBB = -k_1 \cdot k_3 + k_4 + k_2 ,$$

and

$$d = (-k_1 \cdot k_3 + k_4 + k_2)^2 + 4 \cdot k_1 \cdot k_2 \cdot k_3 .$$

The inverse dissociation constants D_{11} and D_{21} , as well as the exchange coefficient, E_{12} , are always positive numbers. The total concentrations C_{2T} and A_{1T} are non-negative, and since it is required that $Q < C_1 \leq C_{1T}$ for equation (61) to be solvable, C_1 and C_{1T} are positive. In practice, C_1 is forced to be positive in the programmed version of the iterative solution technique. Finally, examination of equation (61) reveals that $\exp(-1.17) \leq \gamma \leq 1$. With this information it is evident that the following inequalities are always satisfied:

$$k_1 > 1 ,$$

$$k_3 \leq -1 ,$$

$$k_4 \geq 0 ,$$

and

$$CCC \leq 0.$$

The conditions (a), (b), and (c) must be investigated for the cases: (1) $k_2 > 0$, (2) $k_2 < 0$, and (3) $k_2 = 0$.

Case 1: $k_2 > 0$

Since $-k_1 \cdot k_3 > 0$ and $k_4 > 0$, we have:

$$\begin{aligned} d &\geq (-k_1 \cdot k_3 + k_2)^2 + 4 \cdot k_1 \cdot k_2 \cdot k_3 \\ &= (k_1 \cdot k_3)^2 + 2 \cdot k_1 \cdot k_2 \cdot k_3 + k_2^2 \\ &= (k_1 \cdot k_3 + k_2)^2 \geq 0, \end{aligned}$$

so that condition (b) is met. The term $-4 \cdot A \cdot C = 4 \cdot k_1 \cdot k_2 \cdot k_3 < 0$, and therefore $|BBB| = \sqrt{BBB^2} \geq \sqrt{d}$. Since BBB is the sum of three non-negative terms, it is non-negative, i.e. $BBB \geq 0$. In addition, $AAA = k_1 \cdot k_2 / A_{1T}$ is negative so that

$$\frac{-BBB \pm \sqrt{d}}{2 \cdot AAA}$$

is non-negative regardless of the choice of sign. However, it is desirable that $A_1 \rightarrow 0$ as $A_{1T} \rightarrow 0$. Since the product $4 \cdot AAA \cdot CCC \rightarrow 0$ as $A_{1T} \rightarrow 0$, $\sqrt{d} \rightarrow BBB$ as $A_{1T} \rightarrow 0$. Therefore a (+) sign in front of the radical will result in a zero-limit for A_1 , when $A_{1T} \rightarrow 0$. The minus sign in front of the radical yields:

$$A_1 \rightarrow -BBB/AAA \neq 0, \text{ as } A_{1T} \rightarrow 0.$$

It can be concluded from the above that the (+) sign is the proper choice in this case.

Case 2: $k_2 < 0$

In this case, $-4 \cdot AAA \cdot CCC = 4 \cdot k_1 \cdot k_2 \cdot k_3 > 0$, so $d > 0$. Moreover, $AAA > 0$ and $|BBB| < \sqrt{d}$ so that A_1 will be non-negative if the (+) sign is used and negative if the (-) sign is used. Again, the proper choice is the (+) sign.

Case 3: $k_2 = 0$

This case can arise in two ways. Either A_{1T} must be zero or $(D_{21} - \frac{D_{11}}{E_{12}})$ must be zero. The situation where $A_{1T} \rightarrow 0$ was discussed under Case 1. In the event that the term $(D_{21} - \frac{D_{11}}{E_{12}}) = 0$, $AAA = 0$, so any discussion of the quadratic formula would be superfluous. The defining equation (52) for A_1 is linear in A_1 for this case so the computational procedure requires specialized treatment.

The final step in the overall transformation scheme is to obtain (54) by substituting (52), (53), (54), and (58) into (48). The equations (42), (43), (49), (50), and (51) appear unmodified in the new system as equations (59), (60), (62), (63), and (61), respectively. This completes the description of the back-substitution process used to obtain Table 67.

APPENDIX L
LISTING OF THE MODEL

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0001      DIMENSION WTMOLC(8),QUNPAD(8),QUANIR(8)
0002      DIMENSION ISOL(8)
0003      COMMON K,I,C1T,C2T,C3T,C4T,C5T,A1T,A2T,A3T,C1,C2,C3,C4,C5,A1,A2,A3
0004      COMMON CSTOS(8),OUTFLO(8),PASTO(8),CAOD(8)
0005      COMMON ISTO,SOSTO(8),DELPA(8),CSTO(8)
0006      COMMON X11(25), X21(25), DX11(225), DX21(225)
0007      COMMON AMPEV,QTOT,TIMAX,ICHG
0008      COMMON DRAIN1,SWAT( 25),TAUO
0009      COMMON RIONRT(8),WTMOL(8),IPERC( 25),IFERT(8),IRCONC(8)
0010      COMMON DELT,DELZ,DIFCOF,DIFEXP
0011      COMMON VAL1(8),DIFUS(8),IDAY
0012      COMMON NDOON,NDON1,ML1,MLND,MLNDO1
0013      COMMON DIFX1,DIFX2
0014      COMMON MLON,NDER1,NION1,MLIN
0015      COMMON ALP2,ALP3,ALP4,ALP5,E12,E13,E14,E15,D11,D21
0016      COMMON ITHET,NDER,NSULF,NDICAT,NMONCA,NMONAN,NION,M
0017      COMMON CT(225),THETA1( 25),RHOB( 25),DCC(1800)
0018      COMMON DGAMA(225),DGAMA8(225),DELC(225),CEC(25)
0019      COMMON IFLAG( 25),GAMA( 25),C(200),GAMA8(25)
0020      COMMON IGAM, ML2,      TEMX
0021      COMMON Y11(25)
0022      COMMON H
0023      READ(5,101) M,NDICAT,NMONCA,NSULF,NMONAN,ITHET
0024      READ(5,101) IGAM,ML2,ICHG
0025      101 FORMAT(10I3)
0026      TEMX = 1.17202
0027      WRITE(6,1300)M,NDICAT,NMONCA,NSULF,NMONAN,ITHET
0028      1300 FORMAT(/10X,'M = ',I3,' NDICAT = ',I2,' NMONCA = ',I2,
0029      1 ' NSULF = ',I3,' NMONAN = ',I3,' ITHET = ',I3)
0029      WRITE(6,1301)IGAM,ML2,ICHG
0030      1301 FORMAT(/5X,'PRINT=OUT INTERVALS OF CONCENTRATIONS ',
0031      1 'IGAM = ',I3,' ML2 = ',I3,' ICHG = ',I3)
0031      NION = NDICAT+NMONCA+ NMONAN+NSULF
0032      NDER = NION
0033      IF(ITHET.NE.0) NDER = NION+1
0034      NDON1 = NION+NDER
0035      NDON = NDON1-NDER
0036      ML1 = M+1
0037      MLND = ML1+NDER

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0038      MLND01 = ML1*NDON1
0039      MLON = ML1*NDON
0040      NDER1 = NDER=1
0041      NION1 = NION=1
0042      MLIN = ML1*NION
0043      READ(5,102) (VAL1(I),I=1,NION)
0044      READ(5,102) (DIFUS(I),I=1,NION)
0045      READ(5,102) DIFX1,DIFX2
0046      READ(5,102) DIFCOF,DIFEXP,TIMAX,TPRIN
0047      READ(5,102) D11,D21
0048      102 FORMAT(5E16.4)
0049      WRITE(6,1311)TIMAX
0050      1311 FORMAT(/5X,'TOTAL SIMULATED TIME (MIN)',22X,'TIMAX   = ',E16.4)
0051      WRITE(6,1312)TPRIN
0052      1312 FORMAT(/5X,' PRINT=OUT INTERVALS OF CONCENTRATIONS (DAYS),4X,TPRIN
           1   = ',E16.4)
0053      READ(5,102) DELT,Q1,DELZ,TPULSE
0054      READ(5,102) E12,E13,E14,E15,CEC1
0055      READ(5,103) (CEC(K),K=1,M)
0056      READ(5,103) (RHOB(K),K=1,M)
0057      READ(5,103)(THETA1(K),K=1,M)
0058      103 FORMAT(8F10.4)
0059      WRITE(6,1316)Q1
0060      1316 FORMAT(/5X,'Q1',54X,'= ',E16.4)
0061      WRITE(6,1318)TPULSE
0062      1318 FORMAT(/5X,'TPULSE',50X,'= ',E16.4)
0063      WRITE(6,205) E12,E13,E14,E15
0064      205 FORMAT(1H1//5X,' EXCHANGE COEFFICIENTS',5X,'E12 = ',F6.2,5X,'E13 =
           1',F6.2,5X,'E14 = ',F6.2,5X,'E15 = ',F6.2)
0065      WRITE(6,247) DIFCOF,DIFEXP,D11,D21
0066      247 FORMAT(/10X,'DIFCOF = ',E10.4,'DIFEXP = ',E10.4,' D11 = ',E10.4,
           1' D21 = ',E10.4/)
0067      WRITE(6,206)
0068      206 FORMAT(///' VALENCE AND DIFFUSION COEFFICIENT OF EACH ION'/)
0069      DO 240 I=1,NION
0070      VV = VAL1(I)
0071      DD = DIFUS(I)
0072      240 WRITE(6,207) I,VV,DD
0073      207 FORMAT(/10X,' ION',13,5X,F6.2,E12.4)
0074      WRITE(6,245) DIFX1,DIFX2

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0075      245 FORMAT(//, '          DIFX1 = '.E12.4, '          DIFX2 = '.E12.4/)
0076      WRITE(6,208) DELT, DELZ
0077      208 FORMAT(//10X, 'DELTA T = '.E12.4, 5X, 'DELTA Z = '.E12.4)
0078      WRITE(6,209)
0079      209 FORMAT(1H1//10X, 'CATION EXCHANGE CAPACITY, BULK DENSITY, AND WATER
          1 CONTENT'///)
0080      DO 241 K=1,M
0081      DEP = (K-1)*DELZ
0082      CCE = CEC(K)
0083      RB = RHOB(K)
0084      TTH = THETA1(K)
0085      241 WRITE(6,242) DEP,CCE,RB,TTH
0086      242 FORMAT(10X, 'DEPTH = ', 4E12.4/)
0087      DZ1000 = DELZ+THETA1(2)
0088      TP = 0.0
0089      GAM0 = 0.9
0090      IF(IGAM.EQ.1) GAM0 = 1.0
0091      JK3 = 1
0092      IK1 = 1
0093      JK = 1
0094      WRITE(6,1328)
0095      1328 FORMAT(//, ' TOTAL CONCEN. OF ION IK AT GRID PT. K (MOL L-1)')
0096      DO 1 K=1,M
0097      IK2 = IK1+NIONI
0098      READ(5,102)(CT(IK), IK=IK1, IK2)
0099      WRITE(6,1330) (CT(IK), IK = IK1, IK2)
0100      1330 FORMAT(4X, 8E16.4)
0101      C(IK1) = 0.01*CT(IK1)
0102      X11(K) = 0.0
0103      X21(K) = 0.0
0104      GAMA(K) = GAM0
0105      IFLAG(K) = 1
0106      JK1 = JK3
0107      DO 11 J=1,NDER
0108      DCC(JK1) = 0.0
0109      DELC(JK) = 0.0
0110      DGAMA(JK) = 0.0
0111      DX11(JK) = 0.0
0112      DX21(JK) = 0.0

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0113          JK1 = JK1+1
0114      11 JK = JK+1
0115          JK3 = JK3+NDON1
0116      1 IK1 = IK1+NION
0117      DO 20 I=2,NION
0118      20 C(I) = 0.0
0119          READ(5,101) NDAYS,NOPT
0120          WRITE(6,1331)NDAYS
0121      1331 FORMAT(/5X,'# DAYS OF SIMULATION',25X,'NDAYS'   = ',13)
0122          WRITE(6,1332)NOPT
0123      1332 FORMAT(5X,'# OF OPTIONS',36X,'NOPT'   = ',13)
0124          READ(5,102) (RIONRT(I),I=1,NION)
0125          READ(5,102) (WTMOL(I),I=1,NION)
0126          READ(5,102) SUNTIM,DAYLNG
0127          WRITE(6,1333)
0128      1333 FORMAT(/' FACTOR FOR ION (I) UPTAKE BY ROOTS (MG/CM3(H2O)) (RIONR
          IT)')
0129          WRITE (6,1335) (RIONRT(K),K=1,6)
0130      1335 FORMAT (/1X,8F16.4)
0131          WRITE(6,1336)
0132      1336 FORMAT(/' GRAM MOL WT. OF ION (I) PER MOL OF ION (I) (WTMOL)')
0133          DO1337I=1,NION
0134          FF=WTMOL(I)
0135      1337 WRITE(6,1338)I,FF
0136      1338 FORMAT(/10X,' I',15,5X,E16.4)
0137          WRITE(6,1339)SUNTIM
0138      1339 FORMAT(/5X,'SUNUP TIME (HRS)',32X,'SUNTIM' = ',E16.4)
0139          WRITE(6,1340)DAYLNG
0140      1340 FORMAT(/5X,'LENGTH OF DAYLIGHT PERIOD (HRS)',17X,'DAYLNG' = ',E16.
          14)
0141          WRITE(6,250)
0142      250 FORMAT(/25X,'COEFFICIENTS FOR ION UPTAKE BY ROOTS(MG/ML)')//)
0143          WRITE(6,251) (RIONRT(I),I=1,NION)
0144      251 FORMAT(8E13.4/)
0145          WRITE(6,252)
0146      252 FORMAT(/25X,'MOLECULAR WEIGHTS OF IONS')//)
0147          WRITE (6, 1350)
0148      1350 FORMAT(1X,'          CA          MG          NA          K
          U          NH4          CL          HCO3          SO4 '/)

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0149      WRITE(6,251)(WTMOL(I),I=1,NION)
0150      WRITE(6,253) DAYLNG
0151      253 FORMAT(//10X,'DAYLENGTH(HRS) = ',F4.1/)
0152      FACSOL = 1.0E+02 / (THETA1(2) * DELZ)
0153      SINTOT = 0.0
0154      RPI = 3.141592
0155      CONS = RPI/((120.*DAYLNG)
0156      TAU0 = RPI/(DAYLNG*60.0)
0157      NDEL = DAYLNG*60.0/DELT
0158      TJ = -DELT/2.0
0159      DO 30 J=1,NDEL
0160      TJ = TJ+DELT
0161      TAUJ = TAU0*TJ
0162      30 SINTOT = SINTOT+SIN(TAUJ)
0163      AMP = 1./(SINTOT*DELT)
0164      HSOIL = 0.5*THETA1(1)*DELZ
0165      H = HSOIL
0166      QTOT = 0.0
0167      DO 10 I=1,NION
0168      RIONRT(I) = RIONRT(I)/WTMOL(I)
0169      10 WTMOLC(I) = WTMOL(I)*100.0
0170      DO 1000 IDAY = 1,NDAYS
0171      READ(5,104) (IPERC(K),K=1,M)
0172      READ(5,105) IRDEP,IPREC,IDRAIN,IEVAP,ITRANS,(IFERT(I1),I1 = 1,
1NION),(IRCONC(I1),I1 = 1,NION)
0173      READ(5,105)(ISOL(I), I = 1, NION)
0174      READ(5,104) IRUNOF
0175      104 FORMAT(20I4)
0176      105 FORMAT(3X,2I13)
0177      WRITE(6,201)
0178      201 FORMAT(//////////25X,'NEW DAY'///)
0179      WRITE(6,1345)
0180      1345 FORMAT(///' FERTILIZER ADDED AT GRID PT. 1 (KGHA=1 DAY=1)(IFERT)')
0181      WRITE (6,1352) (IFERT(I1),I1=1,8)
0182      WRITE(6,1351)
0183      1351 FORMAT(///' AMT. OF FERTILIZER AT SECOND CELL GRID PT.2 (KGHA=1) (I
1SOL)')
0184      WRITE (6,1352) (ISOL(I), I = 1,8)
0185      1352 FORMAT (8I7)

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0186      RUNOF = IRUNOF * 0.1
0187      DRAIN = IDRAIN*0.1
0188      DRAIN1 = DRAIN/1440.0
0189      DTDRA = DELT*DRAIN1
0190      PRECIP = IPREC*0.1
0191      EVAP = IEVAP*0.1
0192      TRANS = ITRANS*0.1
0193      DEPIR = IRDEP*0.1
0194      IF(NOPT.EQ.1) GO TO 2500
0195      IF((H-HSOIL).LT.4.0) DEPIR =      10.0-H-HSOIL
0196 2500 CONTINUE
0197      WRITE(6,256) IDAY
0198      256 FORMAT(5X,'DAY = ',I3,5X,'LEACHED   RAINED   EVAPORATION   TRANSP
          1IRATION IRRIGATION   RUNOFF(ALL IN CM)')
0199      WRITE (6,257) DRAIN,PRECIP,EVAP,TRANS,DEPIR,RUNOF
0200      257 FORMAT (22X,F4.2,4X,F5.2,9X,F4.2,11X,F4.2,10X,F5.2,8X,F5.2//)
0201      WRITE(6,254)
0202      254 FORMAT(/25X,'PERCENTAGE OF TRANSPIRATION EXTRACTED FROM LAYERS')
0203      WRITE(6,255) (IPERC(K),K=1,ML1)
0204      255 FORMAT(/10X,10 I5)
0205      AMPTR = AMP*TRANS
0206      AMPEV = AMP*EVAP
0207      HQ = H
0208      H = HQ + DEPIR + PRECIP - RUNOF
0209      H1 = HQ-HSOIL
0210      H2 = H-HSOIL
0211      WRITE(6,258) H1,H2
0212      258 FORMAT(/10X,'DEPTH OF PADDY WATER BEFORE AND AFTER TODAYS PRECIP A
          1ND IRRIG',F6.2,5X,F6.2,'CM'//)
0213      K11 = NION + 1
0214      DO 2000 I=1,NION
0215      SOL2 = ( FACSOL * ISOL(I)) / WTMOL(I)
0216      CT(K11) = CT(K11) + SOL2
0217      K11 = K11 + 1
0218      QUANIR(I) = 0.1*DEPIR*IRCONC(I)
0219      QUANAD = QUANIR(I)+IFERT(I)

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```

0220         DELC1 = ((H0=H)*CT(I)+QUANAD/WTMOLC(I))/H
0221         CT(I) = CT(I)+DELC1
0222         IK = NION+I
0223         CSTOS(I) = 0.0
0224         DO 21 K=2,ML1
0225             CSTOS(I) = CSTOS(I)+CT(IK)
0226     21 IK = IK+NION
0227         DELC(I) = DELC1
0228     2000 CONTINUE
0229         WRITE(6,265)
0230     265 FORMAT(/ /10X,'CONCENTRATION OF IONS IN TODAYS IRRIG.(PPM)')
0231         WRITE(6,255)(IRCONC(I),I=1,NION)
0232         WRITE(6,266)
0233     266 FORMAT(/ /10X,'KG/HA OF IONS AS FERTILIZER')
0234         WRITE(6,255)(IFERT(I),I=1,NION)
0235         DO 3000 K=1,M
0236             SWAT(K) = 0.01*IPERC(K)*AMPTR
0237             IF(SWAT(K).GT.0.0) IFLAG(K) = 1
0238     3000 CONTINUE
0239         DO 62 I=1,NION
0240             OUTFLO(I) = 0.0
0241             CSTO(I) = 0.0
0242     62 PASTO(I) = CT(I)*H
0243             CALL SOIL
0244             THETS = THETA1(I)
0245             THETA1(I) = 2.*H/DELZ
0246             CALL EQUIL
0247             THETA1(I) = THETS
0248             DO 40 I=1,NION
0249                 OUTFLO(I) = WTMOL(I)*(0.5*DELT*OUTFLO(I)+CSTO(I))*DTDRA
0250     40 CONTINUE
0251             DO 60 I=1,NION
0252                 CADD(I) = 0.0
0253                 IK = NION+I
0254                 DO 61 K=2,ML1
0255                     CADD(I) = CADD(I)+CT(IK)
0256     61 IK = IK+NION
0257                 SOSTO(I) = DZ1000*WTMOL(I)*(CADD(I)-CSTOS(I))
0258                 CSTOS(I) = CADD(I)

```

```

0259      QUNPAD(I) = C(I)*WTMOL(I)*1000.0
0260      60 DELPA(I) = WTMOL(I)*(H*CT(I)-PASTO(I))
0261      T11 = 1000.*X11(I)*WTMOL(I)
0262      T21 = 1000.*X21(I)*WTMOL(2)
0263      QUNPAD(1) = QUNPAD(1)+T11
0264      QUNPAD(2) = QUNPAD(2)+T21
0265      QUNPAD(NION) = QUNPAD(NION)+T11+T21
0266      IK = NION+1
0267      DO 65 K=2,NL1
0268      DELC(IK) = 0.0
0269      65 IK=IK+NION
0270      WRITE(6,259)
0271      259 FORMAT(/10X,'CONCENTRATION OF IONS(MG/L) AT END PREVIOUS DAY
      1PADDY WATER'/)
0272      WRITE(6,260)(QUNPAD(I),I=1,NION)
0273      260 FORMAT(/10X,5E16.4/10X,3E16.4)
0274      QTOT = QTOT*DELT
0275      WRITE(6,261) QTOT
0276      261 FORMAT(/10X,'TOTAL WATER ENTERING SOIL OVER LAST DAY',10X,F6.3,
      1'CM'/)
0277      WRITE(6,262)
0278      262 FORMAT(/5X,' NET GAIN(MGM) OF EACH ION OVER LAST DAY=PADDY WATER
      1AND SOIL SURFACE'/)
0279      WRITE(6,251)(DELP(I),I=1,NION)
0280      WRITE(6,263)
0281      263 FORMAT(/5X,'NET STORAGE OF EACH ION IN SOIL BELOW SURFACE'/)
0282      WRITE(6,251)(SOSTO(I),I=1,NION)
0283      WRITE(6,264)
0284      264 FORMAT(/5X,'NET LOSS OF EACH ION FROM BOTTOM OF PROFILE'/)
0285      WRITE(6,251) (OUTFLO(I),I=1,NION)
0286      TP = TP+1.0
0287      IF(TP.LT.TPRIN) GO TO 1001
0288      TP = 0.0
0289      WRITE(6,243)
0290      243 FORMAT(/40X,'SOLUTION CONTRATIONS'//)
0291      WRITE(6,202)
0292      202 FORMAT(7X,'C1',14X,'C2',14X,'C3',14X,'C4',14X,'C5',14X,'C6',14X,
      1'C7',14X,'C8'//)
0293      IM1 = 1
0294      DO 2001 K=1,M

```

```

0295         IM2 = IM1+NION1
0296         WRITE(6,203)(C(I),I=IM1,IM2)
0297 2001 IM1 = IM1+NICN
0298     203 FORMAT(/8(2X,E12.4,2X))
0299         WRITE(6,246)
0300     246 FORMAT(1H1//40X,' ION TOTALS'//)
0301         WRITE(6,202)
0302         IM1 = 1
0303         DO 2002 K=1,M
0304             IM2 = IM1+NICN1
0305             WRITE(6,203) (CT(I),I=IM1,IM2)
0306 2002 IM1 = IM1+NION
0307             IK = (ML2-1)*NION+1
0308             DO 964 K=ML2,ML1
0309                 KK1 = (K-1)*NION+1
0310                 KK2 = KK1
0311                 Y1P = Y11(K)
0312                 IF(NDICAT.EQ.1) GO TO 2003
0313                 KK2 = KK2+1
0314                 Y2P = Y1P*C(KK2)/(E12*C(KK1))
0315 2003 IF(NMONCA.EQ.0) GO TO 2004
0316                 GAMRTC = GAMA(K)*SQRT(C(KK1))
0317                 KK2 = KK2+1
0318                 Y3P = Y1P*C(KK2)/(E13*GAMRTC)
0319                 IF(NMONCA.EQ.1) GO TO 2004
0320                 KK2 = KK2+1
0321                 Y4P = Y1P*C(KK2)/(E14*GAMRTC)
0322                 IF(NMONCA.EQ.2) GO TO 2004
0323                 KK2 = KK2+1
0324                 Y5P = Y1P*C(KK2)/(E15*GAMRTC)
0325 2004 CONTINUE
0326                 GAP = GAMA(K)
0327                 X1P = X11(K)
0328                 X2P = X21(K)
0329                 KK1 = KK1+NION
0330                 CHG = 0.0
0331                 DO 963 I=1,NION
0332                     CHG = CHG+VAL1(I)*C(IK)
0333 963 IK = IK+1

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```
0334          IFL = IFLAG(K)
0335      964 CONTINUE
0336      1001 CONTINUE
0337          QTOT = 0.0
0338      1000 CONTINUE
0339          STOP
0340          END
```

```

0001      SUBROUTINE SOIL
0002      DIMENSION DTDEN1(9),DTDEN2(9),DTNUM1(9),DTNUM2(9)
0003      DIMENSION          VAL2(8),DSTR1(9),DSTR2(9)
0004      DIMENSION DFL(9),CAV(9),DXSI1(9),DXSI2(9)
0005      DIMENSION DX11A1(9),DX11A2(9),DX11G1(9),DX11G2(9)
0006      DIMENSION DX21A1(9),DX21A2(9),DX21G1(9),DX21G2(9)
0007      DIMENSION          DDFL1(72),DDFL2(72)
0008      DIMENSION THETA2(25),DTKET(25),DEC(25),THEINV(25)
0009      DIMENSION COF3(25),COF4(25),COF42(25)
0010      DIMENSION FLC(200),G(225),TCTHE(200)
0011      DIMENSION DTHDT(25),Q(25),          DZ11(9),DZ12(9),ZZZ(9)
0012      DIMENSION DC(200),COF4(200),COF1(200)
0013      DIMENSION DCC1(1800),DCC2(1800),DFLC1(1800),DFLC2(1800)
0014      DIMENSION DG1(1800),DG2(1800),DG3(1800)
0015      DIMENSION SNKION(200)
0016      COMMON K,I,C1T,C2T,C3T,C4T,C5T,A1T,A2T,A3T,C1,C2,C3,C4,C5,A1,A2,A3
0017      COMMON CSTOS(8),OUTFLO(8),PASTO(8),CAOD(8)
0018      COMMON ISTO,SOSTO(8),DELPA(8),CSTO(8)
0019      COMMON X11( 25),X21( 25),DX11(225),DX21(225)
0020      COMMON AMPEV,QTOT,TIMAX,ICMG
0021      COMMON DRAIN1,SWAT( 25),TAU0
0022      COMMON RIONRT(8),WTMOL(8),IPERC( 25),IFERT(8),IRCONC(8)
0023      COMMON DELT,DELZ,DIFCOF,DIFEXP
0024      COMMON VAL1(8),DIFUS(8),IDAY
0025      COMMON NDOON,NDON1,ML1,MLND,MLNDOO1
0026      COMMON DIFX1,DIFX2
0027      COMMON MLON,NDER1,NION1,MLIN
0028      COMMON ALP2,ALP3,ALF4,ALP5,E12,E13,E14,E15,D11,D21
0029      COMMON ITHET,NDER,NSULF,NDICAT,NMONCA,NMONAN,NION,M
0030      COMMON CT(225),THETA1( 25),RHOB( 25),DCC(1800)
0031      COMMON DGAMA(225),DGAMA8(225),DELC(225),CEC(25)
0032      COMMON IFLAG( 25),GAMA( 25),C(200),GAMA8(25)
0033      COMMON IGAM, ML2,          TEMX
0034      COMMON Y11(25)
0035      COMMON H
0036      TIM = 0.0
0037      DHDT = -DRAIN1
0038      DT2 = DELT/2.0
0039      DZINV = 1./DELZ

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0040      GAM1 = 1.0
0041      GAM8 = 1.0
0042      DGAM11 = 0.0
0043      DGAM12 = 0.0
0044      DGAM81 = 0.0
0045      DGAM82 = 0.0
0046      XSI = 0.0
0047      XSI1 = 0.0
0048      TXSI1 = 0.0
0049      DZINV2 = DZINV*DZINV
C      *****
C      *****
0050      DO 2 I=1,NION
0051      2 VAL2(I) = VAL1(I)*VAL1(I)
C
C
0052      2020 CONTINUE
0053      Q(M) = DRAIN1
0054      TAU = TAU0*(TIM+DT2)
0055      FAC1 = SIN(TAU)
0056      IF(FAC1.LE.0.0) FAC1 = 0.0
0057      FAC = FAC1/DELZ
0058      THETA2(M) = THETA1(M)
0059      DTHET(M) = 0.0
0060      MLL1 = ML1-1
0061      DO 3 K=1,ML1
0062      DTHET(K) = 0.0
0063      THETA2(K) = THETA1(K)
0064      KINV = M-K
0065      KPIN = KINV+1
0066      SNKWAT = SWAT(KINV)*FAC1
0067      IK = (KINV-1)*NION
0068      DO 333 I=1,NION
0069      IK = IK+1
0070      333 SNKION(IK) = SNKWAT*RIONRT(I)/DELZ
0071      3 Q(KINV) = Q(KPIN)+SNKWAT
0072      QTOT = QTOT+Q(1)
0073      DHDT0 = DHDT
0074      DHDT = (-AMPEV*FAC1-Q(1))

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0075      DTHET(1) = (DHDT0+DHDT)*DZINV
0076      DELC(NDER) = 2.*DHDT*DZINV
0077      G(NDER) = DTHET(1)
0078      THETS1 = H*2./DELZ
0079      H = H+DT2*DHDT
0080      2030 THEAV2 = 0.5*(THETA1(1)+THETA2(1))
0081      IK1 = NION+1
0082      KND = NDER+NDER
0083      DO 45 K=2,M
0084      THEAV1 = THEAV2
0085      THEAV2 = 0.5*(THETA1(K)+THETA2(K))
0086      THEINV(K) = 1./THEAV2
0087      THETA = 0.5*(THEAV1+THEAV2)
0088      DTHDT(K) = DTHET(K)*THEINV(K)
0089      TZ4 = Q(K)
0090      COF3(K) = TZ4*DZINV
0091      TZ1 = 0.66*THETA
0092      TZ5 = 1./THETA
0093      TZ2 = DIFCOF*THETA*(TZ4*TZ5)**DIFEXP
0094      TZ3 = DZINV2
0095      DELC(KND) = THETA2(K)-THETA1(K)
0096      G(KND) = DTHET(K)
0097      KND = KND+NDER
0098      DO 4 I=1,NICN
0099      TCTHE(IK1) = 0.0
0100      DC(IK1) = DIFUS(I)*TZ1+TZ2
0101      COF1(IK1) = VAL1(I)*DC(IK1)
0102      COF4(IK1) = -DC(IK1)*TZ3
0103      4 IK1 = IK1+1
0104      DIX11 = DIFX1*TZ1+TZ2
0105      DIX21 = DIFX2*TZ1+TZ2
0106      COF41(K) = -DIX11*TZ3
0107      45 COF42(K) = -DIX21*TZ3
0108      I1 = NICN
0109      DO 46 I=1,NION
0110      I1 = I1+1
0111      46 COF4(I1) = 2.0*COF4(I1)
0112      COF41(2) = 2.0*COF41(2)
0113      COF42(2) = 2.0*COF42(2)

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0114      2000 CONTINUE
0115          THETS = THETA1(1)
0116          THETA1(1) = THETS1
0117          CALL EQUIL
0118          THETA1(1) = THETS
0119          J1 = 1
0120          DO 6 K=1,ML1
0121              DO 61 I=1,NICN
0122                  DO 61 J=1,NDER
0123                      DCC1(J1) = 0.5*DCC(J1)
0124                      DCC2(J1) = VAL2(I)*DCC1(J1)
0125          61 J1 = J1+1
0126          6 CONTINUE
0127              IF(NSULF.EQ.0) GO TO 51
0128                  K1 = 1
0129                  K2 = 2
0130                  K3 = NION
0131                  J1 = 1
0132                  J2 = 1
0133                  JK1 = 1
0134                  JK2 = NDER+1
0135                  JK6 = NDCN+1
0136                  DO 57 K=1,ML1
0137                      IF1 = IFLAG(K)
0138                      IF(IF1.EQ.0) GO TO 55
0139                      ZZ = GAMA8(K)*C(K3)
0140                      X11(K) = ZZ*C(K1)*D11
0141                      DO 54 J=1,NDER
0142                          ZZ1 = DGAMA8(J1)*C(K3)
0143                          ZZ2 = GAMA8(K)*DCC(JK6)
0144                          ZZZ(J) = ZZ1+ZZ2
0145                          DX11(J1) = D11*(C(K1)*ZZZ(J)+DCC(JK1)*ZZ)
0146                          J1 = J1+1
0147                          JK1 = JK1+1
0148          54 JK6 = JK6+1
0149                  JK1 = JK1+NDCN
0150                  JK6 = JK6+NDCN
0151                  IF(NDICAT.EQ.1) GO TO 53
0152                  X21(K) = ZZ*C(K2)*D21

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0153          DO 56 J=1,NDER
0154          DX21(J2) = D21*(C(K2)*ZZZ(J)+DCC(JK2)*ZZ)
0155          J2 = J2+1
0156          56 JK2 = JK2+1
0157             JK2 = JK2+NDON
0158             GO TO 53
0159          55 J1 = J1+NDER
0160             J2 = J2+NDER
0161             JK1 = JK1+NDON1
0162             JK2 = JK2+NDON1
0163             JK6 = JK6+NDON1
0164          53 K1 = K1+NION
0165             K2 = K2+NION
0166             K3 = K3+NION
0167          57 CONTINUE
0168          51 CONTINUE
C          *****
C          *****
C
C          BOUNDARY CONDITIONS START
C
0169          X11(M) = X11(ML1)
0170          X21(M) = X21(ML1)
0171          JM1 = MLND+1
0172          JM2 = JM1+NDER1
0173          DO 6004 J=JM1,JM2
0174             J1 = J-NDER
0175             DX11(J) = DX11(J1)
0176          6004 DX21(J) = DX21(J1)
0177             JM1 = MLND01+1
0178             JM2 = JM1+NDON1+1
0179             DO 6005 J=JM1,JM2
0180                J1 = J-NDON1
0181                DCC1(J) = DCC1(J1)
0182                DCC2(J) = DCC2(J1)
0183          6005 DCC(J) = DCC(J1)
0184             JM1 = MLIN+1
0185             JM2 = MLIN+NION
0186             DO 6006 J=JM1,JM2

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0187          J1 = J=NION
0188      6006 C(J) = C(J1)
C
C
C
C          BOUNDARY CONDITIONS END
C
C          *****
0189          IM1 = 1
0190      2050 CONTINUE
0191          DO 501 K=2,M
0192              KMIN1 = K-1
0193              I1 = IFLAG(K)
0194              IF(I1.EQ.0) GO TO 501
0195              IF(K.NE.2) GO TO 62
0196              IJ1 = 1
0197              DO 63 I=1,NICN
0198                  DO 63 J=1,NDER
0199                      IJ2 = IJ1+NDON1
0200                      DCC1(IJ1) = DCC(IJ1)
0201                      DCC1(IJ2) = 0.0
0202                      DCC2(IJ1) = VAL2(I)*DCC1(IJ1)
0203                      DCC2(IJ2) = 0.0
0204              63 IJ1 = IJ1+1
0205              62 CONTINUE
0206              DO 50 J= 1,NDER
0207                  DSTR1(J) = 0.0
0208                  DSTR2(J) = 0.0
0209                  DTDEN1(J) = 0.0
0210                  DTDEN2(J) = 0.0
0211                  DTNUM1(J) = 0.0
0212                  DTNUM2(J) = 0.0
0213              50 CONTINUE
0214                  STR = 0.0
0215                  TDEN = 0.0
0216                  TNUM = 0.0
0217                  IK3 = (K-1)*NION
0218                  IJJ = IK3*NDER
0219                  IK1 = IK3+1
0220                  DO 110 I=1,NION
0221                      IK2 = IK1-NICN

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0222      CAV(I) = 0.5*(C(IK1)+C(IK2))
0223      IF(K.EQ.2) CAV(I) = C(IK2)
0224      TD = VAL2(I)*CAV(I)
0225      STR = STR+TD
0226      DFL(I) = COF4(IK1)*(C(IK1)-C(IK2))
0227      TNUM = TNUM-VAL1(I)*DFL(I)
0228      TDEN = TDEN+TD*DC(IK1)
0229      IJ = (I-1)*NDER+1
0230      IJ1 = IJJ+IJ
0231      DO 100 J=1,NDER
0232      IJ2 = IJ1-NDON1
0233      DSTR1(J) = DSTR1(J)+DCC2(IJ1)
0234      DSTR2(J) = DSTR2(J)+DCC2(IJ2)
0235      DTDEN1(J) = DTDEN1(J)+DC(IK1)*DCC2(IJ1)
0236      DTDEN2(J) = DTDEN2(J)+DC(IK1)*DCC2(IJ2)
0237      DDFL1(IJ) = COF4(IK1)*DCC(IJ1)
0238      DDFL2(IJ) = -COF4(IK1)*DCC(IJ2)
0239      DTNUM1(J) = DTNUM1(J)-VAL1(I)*DDFL1(IJ)
0240      DTNUM2(J) = DTNUM2(J)-VAL1(I)*DDFL2(IJ)
0241      IJ1 = IJ1+1
0242      IJ = IJ+1
0243      IK1 = IK1+1
0244      110 CONTINUE
0245      IF(ICHG.EQ.1) GO TO 196
0246      XSI1 = 1./TDEN
0247      TXSI1 = -XSI1*XSI1
0248      XSI = TNUM*XSI1
0249      196 CONTINUE
0250      DO 200 J=1,NDER
0251      DXSI11 = TXSI11*DTDEN1(J)
0252      DXSI12 = TXSI11*DTDEN2(J)
0253      DXSI1(J) = TNUM*DXSI11+XSI1*DTNUM1(J)
0254      DXSI2(J) = TNUM*DXSI12+XSI1*DTNUM2(J)
0255      200 CONTINUE
0256      IF(NSULF.EQ.0) GO TO 210
0257      J1J = (K-1)*NDON1+1
0258      J2J = J1J+NDER
0259      JNJ = J1J+NDON
0260      JK11 = NDER*(K-1)+1

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```

0261      JK1 = JK11
0262      IF((GAM.EQ.1) GO TO 222
0263      U = SQRT(0.5*STR)
0264      TU = 0.25/U
0265      TU1 = -TEMX / (1.0 + U)
0266      TU2 = TU1/(1.+U)
0267      U1 = U*TU1
0268      GAM1 = EXP(U1)
0269      GAM2 = GAM1*GAM1
0270      GAM4 = GAM2*GAM2
0271      GAM8 = GAM4*GAM4
0272      GAM78 = 8.*GAM8/GAM1
0273      222 CONTINUE
0274      Z1 = GAM8*CAV(NION)
0275      X11A = D11*Z1*CAV(1)
0276      X11G = COF41(K)*(X11(K)-X11(KMIN1))
0277      DO 220 J=1,NDER
0278      JMJ = JNJ+NDON1
0279      J1J = J1J+NDON1
0280      JK2 = JK1+NDER
0281      IF((GAM.EQ.1) GO TO 223
0282      DU1 = TU*DSTR1(J)
0283      DU2 = TU*DSTR2(J)
0284      DU11 = TU2*DU1
0285      DU12 = TU2*DU2
0286      DGAM11 = GAM1*DU11
0287      DGAM12 = GAM1*DU12
0288      DGAM81 = GAM78*DGAM11
0289      DGAM82 = GAM78*DGAM12
0290      223 CONTINUE
0291      DZ11(J) = GAM8*DCC1(JNJ)+CAV(NION)*DGAM81
0292      DZ12(J) = GAM8*DCC1(JMJ)+CAV(NION)*DGAM82
0293      DX11A1(J) = D11*(DZ11(J)*CAV(1)+Z1*DCC1(J1J))
0294      DX11A2(J) = D11*(DZ12(J)*CAV(1)+Z1*DCC1(J1J))
0295      DX11G1(J) = COF41(K)*DX11(JK1)
0296      DX11G2(J) = -COF41(K)*DX11(JK2)
0297      JNJ = JNJ+1
0298      J1J = J1J+1
0299      220 JK1 = JK1+1

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0300      IF (NDICAT.EQ.0) GO TO 210
0301      X21A = D21*Z1*CAV(2)
0302      X21G = COF42(K)*(X21(K)-X21(KMIN1))
0303      JK1 = JK11
0304      DO 221 J=1,NDER
0305      JJ2 = JJ2+NDCN1
0306      JK2 = JK1+NDER
0307      DX21A1(J) = D21*(DZ11(J)*CAV(2)+Z1*DCC1(JJ2))
0308      DX21A2(J) = D21*(DZ12(J)*CAV(2)+Z1*DCC1(JJ2))
0309      DX21G1(J) = COF42(K)*DX21(JK1)
0310      DX21G2(J) = -COF42(K)*DX21(JK2)
0311      JK1 = JK1+1
0312 221 JJ2 = JJ2+1
0313 210 CONTINUE
0314      IK1 = IK3+1
0315      DO 300 I=1,NION
0316      TX11 = COF3(K)+COF1(IK1)*XS1
0317      FLC(IK1) = DFL(I)+TX11*CAV(I)
0318      IJ = (I-1)*NDER+1
0319      IJ1 = IJJ+IJ
0320      DO 310 J=1,NDER
0321      IJ2 = IJ1+NDCN1
0322      DTX111 = COF1(IK1)*DXS11(J)
0323      DTX112 = COF1(IK1)*DXS12(J)
0324      DFLC1(IJ1) = DDFL1(IJ)+TX11*DCC1(IJ1)+CAV(I)*DTX111
0325      DFLC2(IJ1) = DDFL2(IJ)+TX11*DCC1(IJ2)+CAV(I)*DTX112
0326      IJ = IJ+1
0327 310 IJ1 = IJ1+1
0328      IK1 = IK1+1
0329 300 CONTINUE
0330      IF (K.NE.2) GO TO 65
0331      IJ1 = 1
0332      DO 66 I=1,NION
0333      DO 66 J=1,NDER
0334      IJ2 = IJ1+NDCN1
0335      DCC1(IJ1) = 0.5*DCC(IJ1)
0336      DCC1(IJ2) = 0.5*DCC(IJ2)
0337      DCC2(IJ1) = VAL2(I)*DCC1(IJ1)
0338      DCC2(IJ2) = VAL2(I)*DCC1(IJ2)
0339 66 IJ1 = IJ1+1

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```

0340      65 CONTINUE
0341      IF(NSULF.EQ.0) GO TO 501
0342      TZ1 = X11G+COF3(K)*X11A
0343      K1K = IK3+1
0344      KNK = IK3+N1CN
0345      FLC(K1K) = FLC(K1K)+TZ1
0346      FLC(KNK) = FLC(KNK)+TZ1
0347      J1K = (K-1)*NDON1+1
0348      J2K = J1K+NDER
0349      JNKK = J1K+NDON
0350      JNK = JNKK
0351      DO 500 J=1,NDER
0352      DTZ11 = DX11G1(J)+COF3(K)*DX11A1(J)
0353      DTZ12 = DX11G2(J)+COF3(K)*DX11A2(J)
0354      DFLC1(J1K) = DFLC1(J1K)+DTZ11
0355      DFLC2(J1K) = DFLC2(J1K)+DTZ12
0356      DFLC1(JNK) = DFLC1(JNK)+DTZ11
0357      DFLC2(JNK) = DFLC2(JNK)+DTZ12
0358      J1K = J1K+1
0359      500 JNK = JNK+1
0360      IF(NDICAT.EQ.1) GO TO 501
0361      JNK = JNKK
0362      K2K = IK3+2
0363      TZ2 = X21G+COF3(K)*X21A
0364      FLC(K2K) = FLC(K2K)+TZ2
0365      FLC(KNK) = FLC(KNK)+TZ2
0366      DO 502 J=1,NDER
0367      DTZ21 = DX21G1(J)+COF3(K)*DX21A1(J)
0368      DTZ22 = DX21G2(J)+COF3(K)*DX21A2(J)
0369      DFLC1(J2K) = DFLC1(J2K)+DTZ21
0370      DFLC2(J2K) = DFLC2(J2K)+DTZ22
0371      DFLC1(JNK) = DFLC1(JNK)+DTZ21
0372      DFLC2(JNK) = DFLC2(JNK)+DTZ22
0373      J2K = J2K+1
0374      502 JNK = JNK+1
0375      501 CONTINUE
0376      IF(ITHET.EQ.0) GO TO 651
0377      IK = N1CN+1
0378      DO 650 K=2,ML1

```



```

0379      DO 650 I=1,N(CN
0380      TCTHE(IK) = CT(IK)*DTHDT(K)
0381      650 IK=IK+1
0382      651 CONTINUE
0383      COFH1 = -DELZ/H
0384      COFH2 = -DHDT/H
0385      DO 510 I=1,N(CN
0386      I1 = I+NION
0387      CTHT = -CT(I)*DHDT
0388      G(I) = (-DELZ*(FLC(I1)+SNKION(I))+CTHT)/H
0389      IJ = (I-1)*NDER+1
0390      II = IJ+I-1
0391      DO 511 J=1,NDER
0392      IJ1 = IJ+ND(CN1
0393      DG1(IJ) = COFH1*DFLC2(IJ1)
0394      DG2(IJ) = 0.0
0395      DG3(IJ) = COFH1*DFLC1(IJ1)
0396      511 IJ = IJ+1
0397      510 DG1(II) = DG1(II)+COFH2
0398      DO 670 K=2,ML1
0399      KMIN1 = K-1
0400      KP1 = K+1
0401      I1 = IFLAG(K)
0402      I2 = IFLAG(KP1)
0403      IF(I1.EQ.0.AND.I2.EQ.0) GO TO 670
0404      IKK = (K-1)*NION
0405      IK2 = (K-1)*NDER+1
0406      IJK1 = IKK*NDER+1
0407      IK1 = IKK+1
0408      IK3 = IK1+NION
0409      DO 600 I=1,N(CN
0410      G(IK2) = THEINV(K)*(FLC(IK1)-FLC(IK3)-SNKION(IK1))-TCTHE(IK1)
0411      IJK3 = IJK1+NDON1
0412      IIK = IJK1+I-1
0413      DO 660 J=1,NDER
0414      DG1(IJK1) = THEINV(K)*(DFLC1(IJK1)-DFLC2(IJK3))
0415      DG2(IJK1) = THEINV(K)*DFLC2(IJK1)
0416      DG3(IJK1) = -THEINV(K)*DFLC1(IJK3)
0417      IJK1 = IJK1+1
0418      660 IJK3 = IJK3+1

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```

0419      DG1(IK) = DG1(IK)-DTHOT(K)
0420      IK1 = IK1+1
0421      IK2 = IK2+1
0422      IK3 = IK3+1
0423      600 CONTINUE
0424      670 CONTINUE
0425      JM1 = MLND+1
0426      JM2 = JM1+NDER1
0427      DO 680 J=JM1,JM2
0428      J1 = J-NDER
0429      680 G(J) = G(J1)
0430      I1 = JM1
0431      I2 = MLIN
0432      DO 897 I=1,NION
0433      OUTFLO(I) = OUTFLO(I)+G(I1)
0434      I1 = I1+1
0435      I2 = I2+1
0436      897 CSTO(I) = CSTO(I)+C(I2)
0437      IF(NSULF.EQ.0) GO TO 896
0438      X1TT = X11(ML1)
0439      X2TT = X21(ML1)
0440      CSTO(1) = CSTO(1)+X1TT
0441      CSTO(2) = CSTO(2)+X2TT
0442      CSTO(NION) = CSTO(NION)+X1TT+X2TT
0443      896 CONTINUE
0444      CH = 1.0E-8
0445      JK11 = NDER+1
0446      IJK = NION+1
0447      IK = NION+1
0448      DO 800 K=2,ML1
0449      IK1 = (K-1)*NDER+1
0450      DO 801 I=1,NION
0451      TT = 0.0
0452      JK1 = JK11
0453      JK2 = JK1-NDER
0454      JK3 = JK1+NDER
0455      DO 802 J=1,NDER
0456      TT1 = DG1(IJK)*G(JK1)
0457      TT2 = DG2(IJK)*G(JK2)

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0458      TT3 = DG3(IJK)*G(JK3)
0459      TT = TT+TT1+TT2+TT3
0460      IJK = IJK+1
0461      JK1 = JK1+1
0462      JK2 = JK2+1
0463      802 JK3 = JK3+1
0464      DELC(IK) = DELT*(G(IK1)+DT2*TT)
0465      CT(IK) = CT(IK)+DELC(IK)
0466      IK1 = IK1+1
0467      801 IK = IK+1
0468      JK11 = JK11+NDER
0469      800 CONTINUE
0470      IJ = 1
0471      J1 = 1
0472      DO 803 I = 1,NION
0473      TT = 0.0
0474      DO 804 J=1,NDER
0475      J3 = J1+NDER
0476      TT1 = DG1(IJ)*G(J1)
0477      TT3 = DG3(IJ)*G(J3)
0478      TT = TT+TT1+TT3
0479      IJ = IJ+1
0480      804 J1 = J1+1
0481      J1 = 1
0482      DELC(I) = DELT*(G(I1)+DT2*TT)
0483      803 CT(I) = CT(I)+DELC(I)
0484      IM1 = MLIN+1
0485      IM2 = IM1+NION1
0486      DO 701 I=IM1,IM2
0487      I1 = I-NION
0488      701 CT(I) = CT(I1)
0489      H = H+DT2*DHDT
0490      TIM = TIM+DELT
0491      IF(TIM.GE.TIMAX-1.E-6) RETURN
0492      GO TO 2020
0493      END

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0001      SUBROUTINE ECUIL
0002      DIMENSION DCCS(72)
0003      COMMON K,I,C1T,C2T,C3T,C4T,C5T,A1T,A2T,A3T,C1,C2,C3,C4,C5,A1,A2,A3
0004      COMMON CSTOS(8),OUTFLO(8),PASTO(8),CADD(8)
0005      COMMON ISTO,SOSTO(8),DELP(8),CSTO(8)
0006      COMMON X11( 25),X21( 25),DX11(225),DX21(225)
0007      COMMON AMPEV,QTOT,TIMAX,ICHG
0008      COMMON DRAIN1,SWAT( 25),TAU0
0009      COMMON RIONRT(8),WTMOL(8),IPERC( 25),IFERT(8),IRCONC(8)
0010      COMMON DELT,DELZ,DIFCOF,DIFEXP
0011      COMMON VAL1(8),DIFUS(8),ICAY
0012      COMMON NDO1,NDO11,ML1,MLND,MLND01
0013      COMMON DIFX1,DIFX2
0014      COMMON MLON,NDER1,NION1,MLIN
0015      COMMON ALP2,ALP3,ALP4,ALP5,E12,E13,E14,E15,D11,D21
0016      COMMON ITHET,NDER,NSULF,NDICAT,NMONCA,NMONAN,NION,M
0017      COMMON CT(225),THETZ( 25),RHOZ( 25),DCC(1800)
0018      COMMON DG(225),DG8(225),DELC(225),CEC1( 25 )
0019      COMMON IFLAG( 25),GAMA( 25),C(200),GAMA8(25)
0020      COMMON IGAM, ML2,          TEMX
0021      COMMON Y11(25)
0022      COMMON H
0023      GAMLIN = EXP(-TEMX)
0024      ML1 = M-1
0025      DO 5001 K=ML2,ML1
0026      I1 = IFLAG(K)
0027      IF(I1.EQ.0) GO TO 5001
0028      KDER = (K-1)*NDER
0029      JK = KDER+1
0030      KON = (K-1)*NION
0031      KKK = KON*NDER+1
0032      KK = KON+1
0033      C10 = C(KK)
0034      GAM0 = GAMA(K)
0035      DO 5002 J=1,NDER
0036      C10 = C10+DCC(KKK)*DELC(JK)
0037      GAM0 = GAM0+DG(JK)*DELC(JK)
0038      KKK = KKK+1
0039      5002 JK = JK+1

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0040      IF(C10 .LT.0.0) C10 = 0.5 * C(KK)
0041      CEC = CEC1(K)
0042      THETA = THETZ(K)
0043      RHOB = RHOZ(K)
0044      T1 = THETA/RHOB
0045      ALP1 = 200.*T1
0046      ALP2 = ALP1
0047      ALP3 = 100.*T1
0048      ALP4 = ALP3
0049      ALP5 = ALP4
0050      FC21 = E12/ALP2
0051      FC31 = E13/ALP3
0052      FC41 = E14/ALP4
0053      FC51 = E15/ALP5
0054      C1 = C10
0055      GAM1 = GAM0
0056      F15 = 1./E12
0057      F11 = D21-D11*F15
0058      C2T = 0.0
0059      C3T = 0.0
0060      C4T = 0.0
0061      C5T = 0.0
0062      A1T = 0.0
0063      A2T = 0.0
0064      A3T = 0.0
0065      K1 = KDN + 1
0066      C1T = CT(K1)
0067      K1 = K1+1
0068      IF(NDICAT.EQ.1) GO TO 2003
0069      C2T = CT(K1)
0070      K1 = K1+1
0071      2003 IF(NMONCA.EQ.0) GO TO 2006
0072      C3T = CT(K1)
0073      K1 = K1+1
0074      IF(NMONCA.EQ.1) GO TO 2006
0075      C4T = CT(K1)
0076      K1 = K1+1
0077      IF(NMONCA.EQ.2) GO TO 2006
0078      C5T = CT(K1)

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0079      K1 = K1+1
0080      2006 IF(NMONAN.EQ.0) GO TO 2008
0081      A2T = CT(K1)
0082      K1 = K1+1
0083      IF(NMONAN.EQ.1) GO TO 2008
0084      A3T = CT(K1)
0085      K1 = K1+1
0086      2008 IF(NSULF.EQ.0) GO TO 2009
0087      A1T = CT(K1)
0088      2009 CONTINUE
0089      F19 = D21*C2T
0090      F101 = -A1T*F11
0091      F102 = F19 + F101
0092      F31 = D21 * E12
0093      F302 = ALP2 * C2T
0094      F303 = ALP3 * C3T
0095      F304 = ALP4 * C4T
0096      F305 = ALP5 * C5T
0097      DO 500 N = 1,20
0098      ICONT = 0
0099      GAM2 = GAM1*GAM1
0100      GAM4 = GAM2*GAM2
0101      GAM8 = GAM4*GAM4
0102      GAM7 = GAM8/GAM1
0103      F12 = D11*GAM8
0104      F103 = F102*GAM8
0105      F105 = F11*GAM8
0106      BET2 = F31*GAM8
0107      BET3 = GAM1*E13
0108      BET4 = GAM1*E14
0109      BET5 = E15*GAM1
0110      F13C1 = F12
0111      F14C1 = F13C1
0112      F32A1 = BET2
0113      AAAC1 = F105*F12
0114      DO 300 I = 1,20
0115      350 CONTINUE
0116      ICONT = ICONT+1
0117      IF (ICONT .LE. 20) GOTO 1313

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```

0118      WRITE (6,1314)
0119 1314 FORMAT(1X, ' AT STOP IN EQUAL ' )
0120      STOP
0121 1313 CONTINUE
0122      F13 = C1*F12
0123      F16 = F15/C1
0124      F14 = 1.+F13
0125      F17 = C1T*F16
0126      F18 = 1. + F17 - F15
0127      F104 = F14 * F18
0128      AAA = F14 * F105
0129      BBB = F104 + F103
0130      CCC = -A1T * F18
0131      A2A = 2. * AAA
0132      DISC = BBB*BBB - 4. * AAA * CCC
0133      DISCRT = SQRT(DISC)
0134      A1 = (-BBB + DISCRT) / A2A
0135      F21 = F12 * A1
0136      F22 = 1. + F21
0137      F32 = E12 + BET2*A1
0138      F1A1 = A2A*A1 + BBB
0139      F1A1I = 1./F1A1
0140      F16C1 = -F16/C1
0141      F17C1 = C1T*F16C1
0142      F18C1 = F17C1
0143      F104C1 = F14*F18C1 + F18*F14C1
0144      BBBC1 = F104C1
0145      CCCC1 = -A1T*F18C1
0146      A1SQ = A1*A1
0147      F1C1 = A1SQ*AAAC1+A1*BBBC1+CCCC1
0148      A1C1 = -F1C1/F1A1
0149      DA1C1 = A1C1
0150      F23 = C1*F22
0151      Y1A1 = -F13
0152      Y1C1 = -F22
0153      DY1C1 = Y1C1+Y1A1*DA1C1
0154      Y1 = C1T - F23
0155      IF(Y1.GT.0.0) GO TO 400
0156      C1 = 0.1*C1

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```

0157          GO TO 350
0158      400 F33 = F32*C1
0159          ICONT = 0
0160          CIRT = SQRT(C1)
0161          CIRT1 = 0.5/CIRT
0162          F34 = BET3*CIRT
0163          F35 = CIRT*BET4
0164          F36 = BET5*CIRT
0165          F37 = Y1 + F33
0166          F38 = Y1 + F34
0167          F39 = Y1 + F35
0168          F301 = Y1 + F36
0169          F37I = 1./F37
0170          F38I = 1./F38
0171          F39I = 1./F39
0172          F301I = 1./F301
0173          TC2 = F302*F37I
0174          TC3 = F303*F38I
0175          TC4 = F304*F39I
0176          TC5 = F305*F301I
0177          F310 = ALP1 + TC2 + TC3 + TC4 + TC5
0178          F311 = Y1*F310
0179          F3 = F311 * CEC
0180          F33A1 = C1*F32A1
0181          DTC2 = -TC2*F37I
0182          DTC3 = -TC3*F38I
0183          DTC4 = -TC4*F39I
0184          DTC5 = -TC5*F301I
0185          F33C1 = F32
0186          DF33C1 = F33C1+F33A1*DA1C1
0187          DF34C1 = BET3*CIRT1
0188          DF35C1 = BET4*CIRT1
0189          DF36C1 = BET5*CIRT1
0190          DF37C1 = DY1C1+DF33C1
0191          DF38C1 = DF34C1+DY1C1
0192          DF39C1 = DF35C1+DY1C1
0193          DF301C = DF36C1 + DY1C1
0194          DTC2C1 = DTC2*DF37C1
0195          DTC3C1 = DTC3*DF38C1

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0196      DTC4C1 = DTC4*DF39C1
0197      DTC5C1 = DTC5*DF301C
0198      DF310C = DTC2C1+DTC3C1+DTC4C1+DTC5C1
0199      DF311C = Y1*DF310C+F310*DY1C1
0200      DF3C1 = DF311C
0201      DF3C11 = 1./DF3C1
0202      T1 = Y1*((ABS(TC2) + ABS(TC3) + ABS(TC4) + ABS(TC5) + ABS(ALP1)))
          1+ABS(CEC)
0203      IF(ABS(F3/T1).LT.1.E-5) GO TO 301
0204      DC1 = -F3*DF3C11
0205      C1 = C1 + DC1
0206      IF(C1.LT.0.0) C1 = .5*(C1 - DC1)
0207      IF(C1.GT.C1T) C1 = .5*(C1 - DC1 + C1T)
0208      300 CONTINUE
0209      WRITE(6,302)
0210      302 FORMAT('//25X,' FLAGC'//')
0211      301 CONTINUE
0212      GAM78 = 8.*GAM7
0213      GAM78D = GAM78*D11
0214      GAM780 = C1*GAM78D
0215      F12G = GAM78D
0216      F105G = F11*GAM78
0217      F13G = GAM780
0218      F14G = F13G
0219      AAAG = F14*F105G + F105*F14G
0220      F103G = F102*GAM78
0221      F104G = F18*F14G
0222      BBBG = F104G + F103G
          C      WE NOTE THAT CCCG = 0
0223      FIG = A1SQ*AAAG+A1*BBBG
0224      A1G = -F1G*F1A11
0225      F21G = A1*F12G
0226      F22G = F21G
0227      F23G = A1*GAM780
0228      Y1G = -F23G
0229      BET2G = F31 * GAM78
0230      Y1GC1 = Y1G + Y1A1*A1G
0231      BET3G = E13
0232      BET4G = E14

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0233	BET5G = E15
0234	F32G = A1*BET2G
0235	F33G = C1*F32G
0236	F33GC1 = F33G*F33A1*A1G
0237	F37GC1 = Y1GC1+F33GC1
0238	F34GC1 = BET3G*C1RT
0239	F35GC1 = BET4G*C1RT
0240	F36GC1 = BET5G*C1RT
0241	F38GC1 = Y1GC1+F34GC1
0242	F39GC1 = Y1GC1+F35GC1
0243	F301GC = Y1GC1+F36GC1
0244	TC2GC1 = DTC2*F37GC1
0245	TC3GC1 = DTC3*F38GC1
0246	TC4GC1 = DTC4*F39GC1
0247	TC5GC1 = DTC5*F301GC
0248	F3GC1 = Y1*(TC2GC1+TC3GC1+TC4GC1+TC5GC1)+F310*Y1GC1
0249	DF3C1I = 1./DF3C1
0250	DC1G = -F3GC1*DF3C1I
0251	DA1G = A1G+DA1C1*DC1G
0252	DY1G = Y1GC1 + DY1C1*DC1G
0253	DTC2G = TC2GC1+DTC2C1*DC1G
0254	DTC3G = TC3GC1+DTC3C1*DC1G
0255	DTC4G = TC4GC1+DTC4C1*DC1G
0256	DTC5G = TC5GC1+DTC5C1*DC1G
0257	GAC1 = GAM1*C1RT
0258	GAMRTC = GAM1*C1RT1
0259	DGAC1G = C1RT+GAMRTC*DC1G
0260	FC22 = FC21*C1
0261	FC32 = FC31*GAC1
0262	FC42 = FC41*GAC1
0263	FC52 = FC51*GAC1
0264	C2 = FC22*TC2
0265	C3 = FC32*TC3
0266	C4 = FC42*TC4
0267	C5 = FC52*TC5
0268	DFC22G = FC21*DC1G
0269	DFC32G = FC31*DGAC1G
0270	DFC42G = FC41*DGAC1G
0271	DFC52G = FC51*DGAC1G

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0272      DC2G = TC2*DFC22G+FC22*DT C2G
0273      DC3G = TC3*DFC32G+FC32*DT C3G
0274      DC4G = TC4*DFC42G+FC42*DT C4G
0275      DC5G = TC5*DFC52G+FC52*DT C5G
0276      U1 = 2.*(C1 + C2 + A1)
0277      U2 = .5*(C3 + C4 + C5 + A2T + A3T)
0278      U3 = U1 + U2
0279      DU1G = 2.*(DC1G + DC2G + DA1G)
0280      DU2G = .5 * (DC3G + DC4G + DC5G )
0281      DU3G = DU1G + DU2G
0282      U = SQRT(U3)
0283      UP5 = 0.5/U
0284      DUG = UP5*DU3G
0285      U5 = 1./(1. + U)
0286      USU5 = U*U5
0287      DU5G = USU5*DUG
0288      U6 = TEMX * U5
0289      DUG6 = TEMX * DUG5
0290      U4 = U * U6
0291      DU4G = U*DU6G + U6*DUG
0292      EXPU = EXP(-U4)
0293      DEXPUG = -EXPU*DU4G
0294      F4 = GAM1 - EXPU
0295      DF4G = -DEXPUG + 1.0
0296      IF((GAM.EQ.1) GO TO 550
0297      T2 = ABS(GAM1) + ABS(EXPU)
0298      IF(ABS(F4/T2).LT.1.E-5) GO TO 550
0299      DGAM1 = -F4/DF4G
0300      GAMOLD = GAM1
0301      GAM1 = GAM1 + DGAM1
0302      IF(GAM1.LT.GAMLIM) GAM1 = .5*(GAM1 - DGAM1 + GAMLIM)
0303      IF(GAM1.GT.1.0) GAM1 = .5*(GAM1 - DGAM1 + 1.0)
0304      GAMNEW = GAM1
0305      D2GAM1 = GAMNEW - GAMOLD

C
C      NOTE THAT IF NIETHER OF THE PRECEEDING TWO CONDITIONS IS ENCOUNTERED,
C      THE VALUE OF D2GAM1 IS EXACTLY THAT OF DGAM1.
C

0306      C1 = C1 + DC1G*D2GAM1

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0307          IF(C1.LT.0.0) C1 = .5*(C1 - DC1G*D2GAM1)
0308          IF(C1.GT.C1T) C1 = .5*(C1 - DC1G * D2GAM1 + C1T)
0309          500 CONTINUE
0310          WRITE(6,551)
0311          551 FORMAT(/25X,' FLAGG'//)
0312          STOP
0313          550 CONTINUE
C *****
C *   CALCULATION OF DERIVATIVE OF F1 WITH RESPECT TO CJT; C1, GAM1   *
C *   CONSTANT                                                         *
C *****
0314          DF4GI = 1./DF4G
0315          F17C1T = F16
0316          F18C1T = F17C1T
0317          F1041T = F14*F18C1T
0318          BBBC1T = F1041T
0319          CCCC1T = - A1T*F18C1T
0320          F1C1T = A1*BBBC1T + CCCC1T
0321          AC1TCG = -F1C1T*F1A1I
0322          Y1C1T = 1.
0323          YC1TCG = Y1C1T + Y1A1*AC1TCG
0324          TC2A1 = DTC2*F33A1
0325          TC2Y1 = DTC2
0326          TC3Y1 = DTC3
0327          TC4Y1 = DTC4
0328          TC5Y1 = DTC5
0329          T2C1CG = TC2A1*AC1TCG + TC2Y1*YC1TCG
0330          T3C1CG = TC3Y1*YC1TCG
0331          T4C1CG = TC4Y1*YC1TCG
0332          T5C1CG = TC5Y1*YC1TCG
0333          F3101T = T2C1CG + T3C1CG + T4C1CG + T5C1CG
0334          F3111T = Y1*F3101T + F310*YC1TCG
0335          F3C1T = F3111T
0336          C1C1TG = -F3C1T*DF3C1I
0337          A1C1TG = AC1TCG + A1C1*C1C1TG
0338          Y1C1TG = YC1TCG + DY1C1*C1C1TG
0339          T2C1TG = T2C1CG+DTC2C1*C1C1TG
0340          T3C1TG = T3C1CG+DTC3C1*C1C1TG
0341          T4C1TG = T4C1CG+DTC4C1*C1C1TG

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0342      T5C1TG = T5C1CG+DTC5C1*C1C1TG
0343      C2C1 = TC2*FC2I
0344      C3C1 = TC3*FC3I *GAMRTC
0345      C4C1 = TC4*FC4I *GAMRTC
0346      C5C1 = TC5*FC5I *GAMRTC
0347      C2TC2 = FC22
0348      C3TC3 = FC32
0349      C4TC4 = FC42
0350      C5TC5 = FC52
0351      C2C1TG = C2C1*C1C1TG + C2TC2*T2C1TG
0352      C3C1TG = C3C1*C1C1TG + C3TC3*T3C1TG
0353      C4C1TG = C4C1*C1C1TG + C4TC4*T4C1TG
0354      C5C1TG = C5C1*C1C1TG + C5TC5*T5C1TG
0355      U1C1TG = 2.0 * (C1C1TG + C2C1TG + A1C1TG)
0356      U2C1TG = 0.5* (C3C1TG + C4C1TG + C5C1TG)
0357      U3C1TG = U1C1TG + U2C1TG
0358      UC1TG = UP5*U3C1TG
0359      U5C1TG = U5U5*UC1TG
0360      U6C1TG = TEMX * U5C1TG
0361      U4C1TG = U*U6C1TG + UC1TG * U6
0362      EX1UDG = -EXPU*U4C1TG
0363      F4C1TG = -EX1UDG
0364      GAMC1T = -F4C1TG*DF4GI
0365      IF (IGAM.EQ.1) GAMC1T = 0.0
0366      DC1C1T = C1C1TG + DC1G *GAMC1T
0367      DA1C1T = A1C1TG + DA1G *GAMC1T
0368      DY1C1T = Y1C1TG + DY1G *GAMC1T
0369      DC2C1T = C2C1TG + DC2G *GAMC1T
0370      DC3C1T = C3C1TG + DC3G *GAMC1T
0371      DC4C1T = C4C1TG + DC4G *GAMC1T
0372      DC5C1T = C5C1TG + DC5G *GAMC1T
0373      DA2C1T = 0.0
0374      DA3C1T = 0.0
0375      IKK = KCN+1
0376      JKK = KDER+1
0377      DCCS(1) = DC1C1T
0378      DCCS(2) = DC2C1T
0379      DCCS(3) = DC3C1T
0380      DCCS(4) = DC4C1T

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0381      DCCS(5) = DC5C1T
0382      DCCS(6) = DA2C1T
0383      DCCS(7) = DA3C1T
0384      DCCS(8) = DA1C1T
0385      DG(JKK) = GAMC1T
0386      DG8(JKK) = GAM78*GAMC1T
0387      C(IKK) = C1
0388      JKK = JKK+1
0389      KK1 = JKK
0390      IKK = IKK+1
0391      K1 = 9
0392      K2 = 10
0393      K3 = 11
0394      K4 = 12
0395      K5 = 13
0396      K6 = 14
0397      K7 = 15
0398      K8 = 16
0399      IF(NDICAT.EQ.1) GO TO 7001
0400      F19C2T = D21
0401      F1022T = F19C2T
0402      F1032T = GAM8*F1022T
0403      F19C2T = D21
0404      F1022T = F19C2T
0405      BB8C2T = F1032T
0406      F1C2T = A1*BB8C2T
0407      AC2TCG = -F1C2T*F1A1I
0408      YC2TCG = Y1A1*AC2TCG
0409      TC2C2T = ALP2*F37I
0410      T2C2CG = TC2A1*AC2TCG + TC2Y1*YC2TCG + TC2C2T
0411      T3C2CG = TC3Y1*YC2TCG
0412      T4C2CG = TC4Y1*YC2TCG
0413      T5C2CG = TC5Y1*YC2TCG
0414      F3102T = T2C2CG + T3C2CG + T4C2CG + T5C2CG
0415      F3112T = Y1*F3102T + F310*YC2TCG
0416      F3C2T = F3112T
0417      C1C2TG = -F3C2T*DF3C1I
0418      A1C2TG = AC2TCG + A1C1*C1C2TG
0419      Y1C2TG = YC2TCG +DY1C1*C1C2TG

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0420      T2C2TG = T2C2CG+DTC2C1*C1C2TG
0421      T3C2TG = T3C2CG+DTC3C1*C1C2TG
0422      T4C2TG = T4C2CG+DTC4C1*C1C2TG
0423      T5C2TG = T5C2CG+DTC5C1*C1C2TG
0424      C2C2TG = C2C1*C1C2TG + C2TC2*T2C2TG
0425      C3C2TG = C3C1*C1C2TG + C3TC3*T3C2TG
0426      C4C2TG = C4C1*C1C2TG + C4TC4*T4C2TG
0427      C5C2TG = C5C1*C1C2TG + C5TC5*T5C2TG
0428      U1C2TG = 2.0*(C1C2TG + C2C2TG + A1C2TG)
0429      U2C2TG = .5*(C3C2TG + C4C2TG + C5C2TG)
0430      U3C2TG = U1C2TG + U2C2TG
0431      UC2TG = UP5*U3C2TG
0432      U5C2TG = U5U5*UC2TG
0433      U6C2TG = TEMX * U5C2TG
0434      U4C2TG = U*U6C2TG + UC2TG * U6
0435      EX2UDG = =EXPU*U4C2TG
0436      F4C2TG = =EX2UDG
0437      GAMC2T = =F4C2TG*DF4GI
0438      IF(IGAM.EQ.1) GAMC2T = 0.0
0439      DC1C2T = C1C2TG + DC1G*GAMC2T
0440      DA1C2T = A1C2TG + DA1G*GAMC2T
0441      DY1C2T = Y1C2TG + DY1G*GAMC2T
0442      DC2C2T = C2C2TG + DC2G*GAMC2T
0443      DC3C2T = C3C2TG + DC3G*GAMC2T
0444      DC4C2T = C4C2TG + DC4G*GAMC2T
0445      DC5C2T = C5C2TG + DC5G*GAMC2T
0446      DA2C2T = 0.0
0447      DA3C2T = 0.0
0448      DCCS(K1) = DC1C2T
0449      DCCS(K2) = DC2C2T
0450      DCCS(K3) = DC3C2T
0451      DCCS(K4) = DC4C2T
0452      DCCS(K5) = DC5C2T
0453      DCCS(K6) = DA2C2T
0454      DCCS(K7) = DA3C2T
0455      DCCS(K8) = DA1C2T
0456      DG(JKK) = GAMC2T
0457      DG8(JKK) = GAM78*GAMC2T
0458      C(IKK) = C2

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0459      K1 = 17
0460      K2 = 18
0461      K3 = 19
0462      K4 = 20
0463      K5 = 21
0464      K6 = 22
0465      K7 = 23
0466      K8 = 24
0467      JKK = JKK+1
0468      KKK = JKK
0469      IKK = IKK+1
0470      7001 CONTINUE
0471      IF(NMONCA.EQ.0) GO TO 7002
0472      TC3C3T = ALP3*F38I
0473      T3C3CG = TC3C3T
0474      F3103T = T3C3CG
0475      F3113T = Y1*F3103T
0476      F3C3T = F3113T
0477      C1C3TG = -F3C3T*DF3C1I
0478      A1C3TG = A1C1*C1C3TG
0479      Y1C3TG = DY1C1*C1C3TG
0480      T2C3TG =          DTC2C1*C1C3TG
0481      T3C3TG = T3C3CG+DTC3C1*C1C3TG
0482      T4C3TG =          DTC4C1*C1C3TG
0483      T5C3TG =          DTC5C1*C1C3TG
0484      C2C3TG = C2C1*C1C3TG + C2TC2*T2C3TG
0485      C3C3TG = C3C1*C1C3TG + C3TC3*T3C3TG
0486      C4C3TG = C4C1*C1C3TG + C4TC4*T4C3TG
0487      C5C3TG = C5C1*C1C3TG + C5TC5*T5C3TG
0488      U1C3TG = 2.*(C1C3TG + C2C3TG + A1C3TG)
0489      U2C3TG = .5*(C3C3TG + C4C3TG + C5C3TG)
0490      U3C3TG = U1C3TG + U2C3TG
0491      UC3TG = UP5*U3C3TG
0492      U5C3TG = U5U5*UC3TG
0493      U6C3TG = TEMX * U5C3TG
0494      U4C3TG = U*U6C3TG + UC3TG*U6
0495      EX3UDG = -EXPU*U4C3TG
0496      F4C3TG = -EX3UDG
0497      GAMC3T = -F4C3TG*DF4GI

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0498      IF (IGAM.EQ.1) GAMC3T = 0.0
0499      DC1C3T = C1C3TG + DC1G*GAMC3T
0500      DA1C3T = A1C3TG + DA1G*GAMC3T
0501      DY1C3T = Y1C3TG + DY1G*GAMC3T
0502      DC2C3T = C2C3TG + DC2G*GAMC3T
0503      DC3C3T = C3C3TG + DC3G*GAMC3T
0504      DC4C3T = C4C3TG + DC4G*GAMC3T
0505      DC5C3T = C5C3TG + DC5G*GAMC3T
0506      DA2C3T = 0.0
0507      DA3C3T = 0.0
0508      DCCS(K1) = DC1C3T
0509      DCCS(K2) = DC2C3T
0510      DCCS(K3) = DC3C3T
0511      DCCS(K4) = DC4C3T
0512      DCCS(K5) = DC5C3T
0513      DCCS(K6) = DA2C3T
0514      DCCS(K7) = DA3C3T
0515      DCCS(K8) = DA1C3T
0516      DG(JKK) = GAMC3T
0517      DG8(JKK) = GAM78*GAMC3T
0518      C(IKK) = C3
0519      K1 = K8+1
0520      K2 = K1+1
0521      K3 = K2+1
0522      K4 = K3+1
0523      K5 = K4+1
0524      K6 = K5+1
0525      K7 = K6+1
0526      K8 = K7+1
0527      KK1 = KK1+1
0528      IKK = IKK+1
0529      IF(NMONCA.EQ.1) GO TO 7002
0530      TC4C4T = ALP4*F39I
0531      T4C4CG = TC4C4T
0532      F3104T = T4C4CG
0533      F3114T = Y1*F3104T
0534      F3C4T = F3114T
0535      C1C4TG = -F3C4T*DF3C1I
0536      A1C4TG = A1C1 * C1C4TG

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0537      Y1C4TG =DY1C1*C1C4TG
0538      T2C4TG =          DTC2C1*C1C4TG
0539      T3C4TG =          DTC3C1*C1C4TG
0540      T4C4TG = T4C4CG+DTC4C1*C1C4TG
0541      T5C4TG =          DTC5C1*C1C4TG
0542      C2C4TG = C2C1*C1C4TG + C2TC2*T2C4TG
0543      C3C4TG = C3C1*C1C4TG + C3TC3*T3C4TG
0544      C4C4TG = C4C1*C1C4TG + C4TC4*T4C4TG
0545      C5C4TG = C5C1*C1C4TG + C5TC5*T5C4TG
0546      U1C4TG = 2.*(C1C4TG + C2C4TG + A1C4TG)
0547      U2C4TG = .5*(C3C4TG + C4C4TG + C5C4TG)
0548      U3C4TG = U1C4TG + U2C4TG
0549      UC4TG = UP5*U3C4TG
0550      U5C4TG = U5U5*UC4TG
0551      U6C4TG = TEMX * U5C4TG
0552      U4C4TG = U*U6C4TG + UC4TG*U6
0553      EX4UDG = -EXPU*U4C4TG
0554      F4C4TG = -EX4UDG
0555      GAMC4T = -F4C4TG*DF4GI
0556      IF(IGAM.EQ.1) GAMC4T = 0.0
0557      DC1C4T = C1C4TG + DC1G * GAMC4T
0558      DA1C4T = A1C4TG + DA1G*GAMC4T
0559      DY1C4T = Y1C4TG + DY1G*GAMC4T
0560      DC2C4T = C2C4TG + DC2G*GAMC4T
0561      DC3C4T = C3C4TG + DC3G*GAMC4T
0562      DC4C4T = C4C4TG + DC4G*GAMC4T
0563      DC5C4T = C5C4TG + DC5G*GAMC4T
0564      DA2C4T = 0.0
0565      DA3C4T = 0.0
0566      DCCS(K1) = DC1C4T
0567      DCCS(K2) = DC2C4T
0568      DCCS(K3) = DC3C4T
0569      DCCS(K4) = DC4C4T
0570      DCCS(K5) = DC5C4T
0571      DCCS(K6) = DA2C4T
0572      DCCS(K7) = DA3C4T
0573      DCCS(K8) = DA1C4T
0574      DG(KK1) = GAMC4T
0575      DGB(KK1) = GAM7B*GAMC4T

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0576      C(IKK) = C4
0577      K1 = K8+1
0578      K2 = K1+1
0579      K3 = K2+1
0580      K4 = K3+1
0581      K5 = K4+1
0582      K6 = K5+1
0583      K7 = K6+1
0584      K8 = K7+1
0585      KK1 = KK1+1
0586      IKK = IKK+1
0587      IF(NMONCA.EQ.2) GO TO 7002

C
0588      TC5C5T = ALP5*F3011
0589      T5C5CG = TC5C5T
0590      F3105T = T5C5CG
0591      F3115T = Y1*F3105T
0592      F3C5T = F3115T
0593      C1C5TG = -F3C5T*DF3C11
0594      A1C5TG = A1C1 * C1C5TG
0595      Y1C5TG = DY1C1*C1C5TG
0596      T2C5TG =          DTC2C1*C1C5TG
0597      T3C5TG =          DTC3C1*C1C5TG
0598      T4C5TG =          DTC4C1*C1C5TG
0599      T5C5TG = T5C5CG+DTC5C1*C1C5TG
0600      C2C5TG = C2C1*C1C5TG + C2TC2*T2C5TG
0601      C3C5TG = C3C1*C1C5TG + C3TC3*T3C5TG
0602      C4C5TG = C4C1*C1C5TG + C4TC4*T4C5TG
0603      C5C5TG = C5C1*C1C5TG + C5TC5*T5C5TG
0604      U1C5TG = 2.*(C1C5TG + C2C5TG + A1C5TG)
0605      U2C5TG = .5*(C3C5TG + C4C5TG + C5C5TG)
0606      U3C5TG = U1C5TG + U2C5TG
0607      UC5TG = UP5*U3C5TG
0608      U5C5TG = U5U5*UC5TG
0609      U6C5TG = TEMX * U5C5TG
0610      U4C5TG = U*U6C5TG + UC5TG*U6
0611      EX5UDG = -EXPU*U4C5TG
0612      F4C5TG = - EX5UDG
0613      GAMC5T = -F4C5TG*DF4G1

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0614      IF (IGAM.EQ.1) GAMC5T = 0.0
0615      DC1C5T = C1C5TG + DC1G * GAMC5T
0616      DA1C5T = A1C5TG + DA1G * GAMC5T
0617      DY1C5T = DY1G * GAMC5T + Y1C5TG
0618      DC2C5T = C2C5TG + DC2G * GAMC5T
0619      DC3C5T = C3C5TG + DC3G * GAMC5T
0620      DC4C5T = C4C5TG + DC4G * GAMC5T
0621      DC5C5T = C5C5TG + DC5G * GAMC5T
0622      DA2C5T = 0.0
0623      DA3C5T = 0.0
0624      DCCS(K1) = DC1C5T
0625      DCCS(K2) = DC2C5T
0626      DCCS(K2) = DC2C5T
0627      DCCS(K3) = DC3C5T
0628      DCCS(K4) = DC4C5T
0629      DCCS(K5) = DC5C5T
0630      DCCS(K6) = DA2C5T
0631      DCCS(K7) = DA3C5T
0632      DCCS(K8) = DA1C5T
0633      DG(KK1) = GAMC5T
0634      DGB(KK1) = GAM78 * GAMC5T
0635      C(IKK) = C5
0636      K1 = K8+1
0637      K2 = K1+1
0638      K3 = K2+1
0639      K4 = K3+1
0640      K5 = K4+1
0641      K6 = K5+1
0642      K7 = K6+1
0643      K8 = K7+1
0644      KK1 = KK1+1
0645      IKK = IKK+1
0646      700? CONTINUE
0647      IF (NMONAN.EQ.0) GO TO 7005
0648      U2A2TG = .5
0649      U3A2TG = U2A2TG
0650      UA2TG = UP5 * U3A2TG
0651      U5A2TG = U5U5 * UA2TG
0652      U6A2TG = TENX * U5A2TG

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0653      U4A2TG = U6*UA2TG + U * U6A2TG
0654      EXA2TG = -EXPU*U4A2TG
0655      F4A2TG = - EXA2TG
0656      GAMA2T = -F4A2TG*DF4GI
0657      IF(IGAM.EQ.1) GAMA2T = 0.0
0658      DC1A2T = DC1G * GAMA2T
0659      DC2A2T = DC2G*GAMA2T
0660      DC3A2T = DC3G*GAMA2T
0661      DC4A2T = DC4G*GAMA2T
0662      DC5A2T = DC5G*GAMA2T
0663      DA1A2T = DA1G*GAMA2T
0664      DY1A2T = DY1G*GAMA2T
0665      DA2A2T = 1.0
0666      DA3A2T = 0.0
0667      DCCS(K1) = DC1A2T
0668      DCCS(K2) = DC2A2T
0669      DCCS(K3) = DC3A2T
0670      DCCS(K4) = DC4A2T
0671      DCCS(K5) = DC5A2T
0672      DCCS(K6) = DA2A2T
0673      DCCS(K7) = DA3A2T
0674      DCCS(K8) = DA1A2T
0675      DG(KK1) = GAMA2T
0676      DGB(KK1) = GAM7B*GAMA2T
0677      C(IKK) = A2T
0678      KI = K8+1
0679      KK1 = KK1+1
0680      IKK = IKK+1
0681      K1 = K8+1
0682      K2 = K1+1
0683      K3 = K2+1
0684      K4 = K3+1
0685      K5 = K4+1
0686      K6 = K5+1
0687      K7 = K6+1
0688      K8 = K7+1
0689      IF(NMONAN.EQ.1) GO TO 7005
0690      U2A3TG = .5
0691      U3A3TG = U2A3TG

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0692      UA3TG = UP5*U3A3TG
0693      U5A3TG = U5U5*UA3TG
0694      U6A3TG = TEMX * U5A3TG
0695      U4A3TG = U6*UA3TG + U * U6A3TG
0696      EXA3TG = -EXPU*U4A3TG
0697      F4A3TG = - EXA3TG
0698      GAMA3T = -F4A3TG*DF4GI
0699      IF(IGAM.EQ.1) GAMA3T = 0.0
0700      DC1A3T = DC1G*GAMA3T
0701      DC2A3T = DC2G*GAMA3T
0702      DC3A3T = DC3G*GAMA3T
0703      DC4A3T = DC4G*GAMA3T
0704      DC5A3T = DC5G*GAMA3T
0705      DA1A3T = DA1G*GAMA3T
0706      DY1A3T = DY1G*GAMA3T
0707      DA2A3T = 0.0
0708      DA3A3T = 1.0
0709      DCCS(K1) = DC1A3T
0710      DCCS(K2) = DC2A3T
0711      DCCS(K3) = DC3A3T
0712      DCCS(K4) = DC4A3T
0713      DCCS(K5) = DC5A3T
0714      DCCS(K6) = DA2A3T
0715      DCCS(K7) = DA3A3T
0716      DCCS(K8) = DA1A3T
0717      DG(KK1) = GAMA3T
0718      DG8(KK1) = GAM78*GAMA3T
0719      C(IKK) = A3T
0720      K1 = K8+1
0721      K2 = K1+1
0722      K3 = K2+1
0723      K4 = K3+1
0724      K5 = K4+1
0725      K6 = K5+1
0726      K7 = K6+1
0727      K8 = K7+1
0728      KK1 = KK1+1
0729      IKK = 1KK+1
0730      7005 CONTINUE

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0731      IF(NSULF.EQ.0) GO TO 7006
0732      F1A1T = -F18-F105*A1
0733      A1A1T = -F1A1T*F1A1I
0734      AA1TCG = A1A1T
0735      YA1TCG = Y1A1 * AA1TCG
0736      T2A1CG = TC2A1*AA1TCG + TC2Y1*YA1TCG
0737      T3A1CG =      TC3Y1*YA1TCG
0738      T4A1CG =      TC4Y1*YA1TCG
0739      T5A1CG =      TC5Y1*YA1TCG
0740      T1SMCG = T2A1CG + T3A1CG + T4A1CG + T5A1CG
0741      T1SYCG = Y1 * T1SMCG + F310 * YA1TCG
0742      F3A1CG = T1SYCG
0743      C1A1TG = -F3A1CG*DF3C1I
0744      A1A1TG = AA1TCG + A1C1*C1A1TG
0745      Y1A1TG = YA1TCG +DY1C1*C1A1TG
0746      TC2A1G = T2A1CG+DTC2C1*C1A1TG
0747      TC3A1G = T3A1CG+DTC3C1*C1A1TG
0748      TC4A1G = T4A1CG+DTC4C1*C1A1TG
0749      TC5A1G = T5A1CG+DTC5C1*C1A1TG
0750      C2A1TG = C2C1*C1A1TG + C2TC2*TC2A1G
0751      C3A1TG = C3C1*C1A1TG + C3TC3*TC3A1G
0752      C4A1TG = C4C1*C1A1TG + C4TC4*TC4A1G
0753      C5A1TG = C5C1*C1A1TG + C5TC5*TC5A1G
0754      U1A1TG = 2.0 * (C1A1TG + C2A1TG + A1A1TG)
0755      U2A1TG = .5* (C3A1TG + C4A1TG + C5A1TG)
0756      U3A1TG = U1A1TG + U2A1TG
0757      UA1TG = UP5*U3A1TG
0758      U5A1TG = U5U5*UA1TG
0759      U6A1TG = TEMX * U5A1TG
0760      U4A1TG = U6*UA1TG + U * U6A1TG
0761      EXA1TG = -EXPU*U4A1TG
0762      F4A1TG = - EXA1TG
0763      GAMA1T = -F4A1TG*DF4GI
0764      IF(IGAM.EQ.1) GAMA1T = 0.0
0765      DC1A1T = DC1G*GAMA1T + C1A1TG
0766      DC2A1T = DC2G*GAMA1T + C2A1TG
0767      DC3A1T = DC3G*GAMA1T + C3A1TG
0768      DC4A1T = DC4G*GAMA1T + C4A1TG
0769      DC5A1T = DC5G*GAMA1T + C5A1TG

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0770      DA1A1T = A1A1TG + DA1G*GAMA1T
0771      DY1A1T = V1A1TG + DY1G*GAMA1T
0772      DA2A1T = 0.0
0773      DA3A1T = 0.0
0774      DCCS(K1) = DC1A1T
0775      DCCS(K2) = DC2A1T
0776      DCCS(K3) = DC3A1T
0777      DCCS(K4) = DC4A1T
0778      DCCS(K5) = DC5A1T
0779      DCCS(K6) = DA2A1T
0780      DCCS(K7) = DA3A1T
0781      DCCS(K8) = DA1A1T
0782      C(IKK) = A1
0783      DG(KK1) = GAMA1T
0784      DGB(KK1) = GAM78*GAMA1T
0785      K1 = K8+1
0786      K2 = K1+1
0787      K3 = K2+1
0788      K4 = K3+1
0789      K5 = K4+1
0790      K6 = K5+1
0791      K7 = K6+1
0792      K8 = K7+1
0793      KK1 = KK1+1
0794      7006 CONTINUE
0795      IF(ITHET.EQ.0) GO TO 7007
0796      T1TH = 1./RHOB
0797      ALP1TH = 200.*T1TH
0798      ALP2TH = ALP1TH
0799      ALP3TH = 100.*T1TH
0800      ALP4TH = ALP3TH
0801      ALP5TH = ALP3TH
0802      F302TH = C2T*ALP2TH
0803      F303TH = C3T*ALP3TH
0804      F304TH = C4T*ALP4TH
0805      F305TH = C5T*ALP5TH
0806      FC21TH = -(FC21/ALP2)*ALP2TH
0807      FC31TH = -(FC31/ALP3)*ALP3TH
0808      FC41TH = -(FC41/ALP4)*ALP4TH

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0809      FC51TH = -(FC51/ALP5)*ALP5TH
0810      TC2TH = F37I*F302TH
0811      TC3TH = F303TH*F38I
0812      TC4TH = F39I*F304TH
0813      TC5TH = F301I*F305TH
0814      F310TH = ALP1TH+TC2TH+TC3TH+TC4TH+TC5TH
0815      F311TH = Y1*F310TH
0816      F3TH = F311TH
0817      C1THG = -F3TH*DF3C1I
0818      A1THG = DA1C1*C1THG
0819      Y1THG = DY1C1*C1THG
0820      TC2THG = TC2TH+DTC2C1*C1THG
0821      TC3THG = TC3TH+DTC3C1*C1THG
0822      TC4THG = TC4TH+DTC4C1*C1THG
0823      TC5THG = TC5TH+DTC5C1*C1THG
0824      GAC1TG = GAMRTC*C1THG
0825      FC22TG = C1*FC21TH+FC21*C1THG
0826      FC32TG = GAC1*FC31TH+FC31*GAC1TG
0827      FC42TG = GAC1*FC41TH+FC41*GAC1TG
0828      FC52TG = GAC1*FC51TH+FC51*GAC1TG
0829      C2THG = TC2*FC22TG+FC22*TC2THG
0830      C3THG = TC3*FC32TG+FC32*TC3THG
0831      C4THG = TC4*FC42TG+FC42*TC4THG
0832      C5THG = TC5*FC52TG+FC52*TC5THG
0833      U1THG = 2.*(C1THG+C2THG+A1THG)
0834      U2THG = 0.5*(C3THG+C4THG+C5THG)
0835      L3THG = U1THG+U2THG
0836      UTHG = UP5*U3THG
0837      U5THG = U5U5*UTHG
0838      U6THG = TEMX * U5THG
0839      U4THG = U*U6THG+U6*UTHG
0840      EXTHG = -EXPU*U4THG
0841      F4THG = -EXTHG
0842      GAMTH = -F4THG*DF4GI
0843      IF(IGAM,EQ.1) GAMTH = 0.0
0844      DC1TH = C1T-G+DC1G*GAMTH
0845      DA1TH = A1THG+DA1G*GAMTH
0846      DC2TH = C2THG+DC2G*GAMTH
0847      DC3TH = C3THG+DC3G*GAMTH

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0848      DC4TH = C4THG+DC4G*GAMTH
0849      DC5TH = C5THG+DC5G*GAMTH
0850      DA2TH = 0.0
0851      DA3TH = 0.0
0852      DCCS(K1) = DC1TH
0853      DCCS(K2) = DC2TH
0854      DCCS(K3) = DC3TH
0855      DCCS(K4) = DC4TH
0856      DCCS(K5) = DC5TH
0857      DCCS(K6) = DA2TH
0858      DCCS(K7) = DA3TH
0859      DCCS(K8) = DA1TH
0860      DG(KK1) = GAMTH
0861      DGB(KK1) = GAM78*GAMTH
0862      7007 CONTINUE
0863      KIJ = KON*NDER
0864      KIJS = KIJ
0865      KKK = 1
0866      JIK = KKK-8
0867      DO 4001 II = 1, NDER
0868      KIJ = KIJ+1
0869      JIK = JIK + 8
0870      4001 DCC(KIJ) = DCCS(JIK)
0871      KIJS = KIJS+NDER
0872      KIJ = KIJS
0873      IF(INDICAT.EQ.1) GO TO 6002
0874      KKK = 2
0875      JIK = KKK-8
0876      DO 4002 II=1, NDER
0877      KIJ = KIJ+1
0878      JIK = JIK + 8
0879      4002 DCC(KIJ) = DCCS(JIK)
0880      KIJS = KIJS+NDER
0881      KIJ = KIJS
0882      6002 IF(NMCNCA.EQ.0) GO TO 6005
0883      KKK = 3
0884      DO 4010 III = 1, NMONCA
0885      JIK = KKK-8
0886      DO 4003 II=1, NDER

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0887         KIJ = KIJ+1
0888         JIK = JIK + 8
0889     4003 DCC(KIJ) = DCCS(JIK)
0890         KIJS = KIJS+NDER
0891         KIJ = KIJS
0892     4010 KKK = KKK+1
0893     6005 IF(NMONAN.EQ.0) GO TO 6007
0894         KKK = 6
0895         DO 4020 II=1,NMONAN
0896             JIK = KKK=8
0897             DO 4004 III=1,NDER
0898                 KIJ = KIJ+1
0899                 JIK = JIK + 8
0900     4004 DCC(KIJ) = DCCS(JIK)
0901         KIJS = KIJS+NDER
0902         KIJ = KIJS
0903     4020 KKK = KKK+1
0904     6007 IF(NSULF.EQ.0) GO TO 6008
0905         KKK = 8
0906         JIK = KKK=8
0907         DO 4005 III=1,NDER
0908             KIJ = KIJ+1
0909             JIK = JIK + 8
0910     4005 DCC(KIJ) = DCCS(JIK)
0911     6008 CONTINUE
0912         Y11(K) = Y1
0913         GAMA(K) = GAM1
0914         GAMA8(K) = GAM8
0915     5001 CONTINUE
0916         RETURN

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APPENDIX M

USERS GUIDE TO THE MODEL

The purpose of this appendix is to provide the user of the paddy model with instructions for operation. A list of the required input variables is provided in Table M-1. The organization of the input data is shown in Table M-2 where the data is divided into sets, with each data set corresponding to a FORTRAN READ statement in the computer program. Also shown in Table M-2 are the units where applicable, data type, the number of cards in each data set, and the displacement of the important input data on each card.

A brief summary of the calculations in the important program is given so the logic can be traced.

TABLE M-1. INPUT VARIABLES

M	= ND. Grid Points	Profile depth = $(M-3/2)*DELZ$ cm	→ Bdy Cond at $z = (M-3/2)*DELZ$:
DELZ	= Grid Spacing (cm)		$C_{iM} = C_{iM-1} + \frac{\partial C_i}{\partial z} \Big _{z=}$ = 0
NDICAT	= no. divalent cations (=2 for $Ca^{++} + Mg^{++}$) (max = 2) (min = 1)		
NMONCA	= no. monovalent cations (max = 3) (min = 0)		
NSULF	= 1 if SO_4 present = 0 if not		
NMONAN	= no. monovalent anions (0 - 2)		
ITHET	= 1 if changes in H_2O content are accounted for either in soil or paddy water. This includes changes in H for paddy H_2O .		
IGAM	= 1 if GAMA (activity coef) \equiv 1 = 0 if GAMA calculated in EQUIL		
ML2	= 1 if changes in surface concentration are calculated = 2 if concentrations at surface constant for the run		
ICHG	= 0 if diffusion to chg gradients are calculated = 1 if diffusion to chg gradients are ignored		
VALI(I)	= valence of ion I ($2 \leq I \leq NION = NDICAT + NMONCA + NSULF + NMONAN$)		
DIFUS(I)	= soil diffusion coefficient for ion i		
DIFX1	= diffusion coefficient for $CaSO_4^0$, $MgSO_4^0$		
DIFX2	= diffusion coefficient for $CaSO_4^0$, $MgSO_4^0$		

(continued)

TABLE M-1. (Continued)

DIFEDE	= apparent diffusion coefficient for ion i = $.6*0*DIFUS(I)+0*DIFCOF*(q/\theta)**DIFEXP$
DIFEXP	= apparent diffusion coefficient for ion i = $.6*0*DIFUS(I)+0*DIFCOF*(q/\theta)**DIFEXP$
TIMAX	= length of run in subroutine SOIL before return to MAIN, in this case TIMAX = 1440 min = no. min in a day
TPRIN	= no. days run before printout
IF TPRIN = 3	= printout occurs at end of day 3 = beginning of day 4
D_{11}, D_{21}	= inverse of dissociation constants for $CaSO_4^0$ and $MgSO_4^0$, respectively.
DELT	= time step size for SUBROUTINE SOIL
$E_{12}, E_{13}, E_{14}, E_{15}$	= exchange coefficient for exchange between cation 1 and cations 2, 3, 4, 5, respectively; must not = 0.
CEC(K)	= cation exchange capacity (in center at $z - (K-1)*DELZ$)
RHOB(K)	= bulk density
THETAI(K)	= H_2O content
CT(IK)	= initial total ion concentrations ($mmoles/cm^3$) at H_2O content THETAI(K)
NDAYS	= no. days for run
NOPT if = 1,	= irrigation occurs to 10 cm depth when the paddy H_2O depth falls to or below 4 cm - occurs only at start of new day
DAYLNG	= no. daylight hours/day

(continued)

TABLE M-1. (Continued)

RIONRT(I)	= mg/cm^3 ion uptake coefficient
WMOL(I)	= molecular weight of ion i
IPERC(K)	= percentage of total trans. taken up from layer K
IRDEP	= depth (units of 1 cm) of irrigation on a given day
IPREC	= rainfall (units of 1 cm)
IDRAIN	= deep percolation (.1 cm) total for day
IEVAP	= evaporation (.1 cm) total for day
ITRANS	= transpiration (.1 cm) total for day
IFERT(I)	= fertilizer application (kg/ha) of ion i
IRCONC(I)	= concentration (mg/l) of ion i in irrigation H_2O

TABLE M-2. INPUT DATA DECK

Card #	Variable	Columns	Format	Definition	Units
1	M	1-3	I3	number of grid points	
1	NDICAT	4-6	I2	number of divalent cations	
1	NMONCA	7-9	I2	number of monovalent cations	
1	NSULF	10-12	I3	0 if sulfate absent; 1 if sulfate present	
1	NMONAN	13-15	I3	number of monovalent anions	
1	ITHET	16-18	I3	0 for steady flow; 1 if water contents vary with time at any grid point	
2	IGAM	1-3	I3	0 for concentration-dependent activity coefficient 1 if not concentration-de- pendent	
2	ML2	4-6	I3	1 for unit activity coefficient	
2	ICHG	7-9	I3	1 if change-induced lfux is ignored; 0 otherwise	
3	VALI(I), (I=1)	1-16	E16.4	valence of ion I*	
3	VALI(I), (I=2)	17-32	E16.4	valence of ion I	
3	VALI(I), (I=3)	33-48	E16.4	valence of ion I	
3	VALI(I), (I=4)	49-64	E16.4	valence of ion I	
3	VALI(I), (I=5)	65-80	E16.4	valence of ion I	
4	VALI(I), (I=6)	1-16	E16.4	valence of ion I	
4	VALI(I), (I=7)	17-32	E16.4	valence of ion I	
4	VALI(I), (I=8)	33-48	E16.4	valence of ion I	
5	DIFUS(I), (I=1)	1-16	E16.4	diffusion coefficient of ion I	cm ² min ⁻¹
5	DIFUS(I), (I=2)	17-32	E16.4	diffusion coefficient of ion I	cm ² min ⁻¹
5	DIFUS(I), (I=3)	33-48	E16.4	diffusion coefficient of ion I	cm ² min ⁻¹
5	DIFUS(I), (I=4)	49-64	E16.4	diffusion coefficient of ion I	cm ² min ⁻¹
6	DIFUS(I), (I=5)	65-80	E16.5	diffusion coefficient of ion I	cm ² min ⁻¹
6	DIFUS(I), (I=6)	1-15	E16.4	diffusion coefficient of ion I	cm ² min ⁻¹

* Ions are as follows: calcium, magnesium, potassium, ammonium, chloride, bicarbonate, sulfate, sodium.

(continued)

TABLE M-2. (Continued)

Card #	Variable	Columns	Format	Definition	Units
6	DIFUS(I), (I=7)	17-32	(E16.4)	diffusion coefficient of ion I	$\text{cm}^2 \text{min}^{-1}$
6	DIFUS(I), (I=8)	33-48	(E16.4)	diffusion coefficient of ion I	$\text{cm}^2 \text{min}^{-1}$
7	DIFX1	1-16	(E16.4)	diffusion coefficient for CaSO_4	$\text{cm}^2 \text{min}^{-1}$
7	DIFX2	17-32	(E16.4)	diffusion coefficient for MgSO_4	$\text{cm}^2 \text{min}^{-1}$
8	DIFCOF	1-16	(E16.4)	parameter used in calculation of hydrodynamic dispersion	
8	DIFEXP	17-32	(E16.4)	parameter used in calculation of hydrodynamic dispersion	
8	TIMAX	33-48	(E16.4)	total simulated time	min
8	TPRIN	49-64	(E16.4)	successive print-outs of con- centrations	days
9	D11	1-16	(E16.4)	inverse of diffusion coeffi- cient for Ca SO_4	1 mol^{-1}
9	D21	17-32	(E16.4)	inverse of diffusion coeffi- cient for MgSO_4	1 mol^{-1}
10	DELT	1-16	(E16.4)	time step size	min
10	DELZ	33-48	(E16.4)	grid spacing	cm
11	E12	1-16	(E16.4)	Exchange coefficient for mass-action relationship	
11	E13	17-32	(E16.4)	Exchange coefficient for Gapon relationship	$(\text{mol l}^{-2})^{1/2}$
11	E14	33-48	(E16.4)	exchange coefficient for Gapon relationship	$(\text{mol l}^{-2})^{1/2}$
11	E15	49-64	(E16.4)	exchange coefficient for Gapon relationship	$(\text{mol l}^{-2})^{1/2}$
12	CEC(K), (K=1)	1-10	(F10.4)	cation exchange coefficient at grid point K	$\text{meq}(100\text{g})^{-1}$
12	CEC(K), (K=2)	11-20	(F10.4)	cation exchange coefficient at grid point K	$\text{meq}(100\text{g})^{-1}$
12	CEC(K), (K=3)	21-30	(F10.4)	cation exchange coefficient at grid point K	$\text{meq}(100\text{g})^{-1}$
12	CEC(K), (K=4)	31-40	(F10.4)	cation exchange coefficient at grid point K	$\text{meq}(100\text{g})^{-1}$
12	CEC(K), (K=5)	41-50	(F10.4)	cation exchange coefficient at grid point K	$\text{meq}(100\text{g})^{-1}$
12	CEC(K), (K=6)	51-60	(F10.4)	cation exchange coefficient at grid point K	$\text{meq}(100\text{g})^{-1}$

(continued)

TABLE M-2. (Continued)

Card #	Variable	Columns	Format	Definition	Units
12	CEC(K), (K=7)	61-70	(F10.4)	cation exchange coefficient at grid point K	meq(100g) ⁻¹
12	CEC(K), (K=8)	71-80			
13	CEC(K), (K=9)	1-10			
13	CEC(K), (K=10)	11-20			
13	CEC(K), (K=11)	21-30			
13	CEC(K), (K=12)	31-40			
13	CEC(K), (K=13)	41-50			
13	CEC(K), (K=14)	51-60			
13	CEC(K), (K=15)	61-70			
13	CEC(K), (K=16)	71-80			
14	CEC(K), (K=17)	1-10			
14	CEC(K), (K=18)	11-20			
14	CEC(K), (K=19)	21-30			
14	CEC(K), (K=20)	31-40			
14	CEC(K), (K=21)	41-50			
14	CEC(K), (K=22)	51-60			
14	CEC(K), (K=23)	61-70			
14	CEC(K), (K=24)	71-80			
15	RHOB(K), (K=1)	1-10	(F10.4)	bulk density at grid pt. K	gm cm ⁻³
15	RHOB(K), (K=2)	11-20			
15	RHOB(K), (K=3)	21-30			
15	RHOB(K), (K=4)	31-40			
15	RHOB(K), (K=5)	41-50			
15	RHOB(K), (K=6)	51-60			
15	RHOB(K), (K=7)	61-70			
15	RHOB(K), (K=8)	71-80			

(continued)

TABLE M-2. (Continued)

Card #	Variable	Columns	Format	Definition	Units
16	RHOB(K), (K=9)	1-10	(F10.4)	bulk density at grid pt. K	gm cm ⁻³
16	RHOB(K), (K=10)	11-20			
16	RHOB(K), (K=11)	21-30			
16	RHOB(K), (K=12)	31-40			
16	RHOB(K), (K=13)	41-50			
16	RHOB(K), (K=14)	51-60			
16	RHOB(K), (K=15)	61-70			
16	RHOB(K), (K=16)	71-80			
17	RHOB(K), (K=17)	1-10			
17	RHOB(K), (K=18)	11-20			
17	RHOB(K), (K=19)	21-30			
17	RHOB(K), (K=20)	31-40			
17	RHOB(K), (K=21)	41-50			
17	RHOB(K), (K=22)	51-60			
17	RHOB(K), (K=23)	61-70			
17	RHOB(K), (K=24)	71-80			
18	THETA1(K), (K=1)	1-10	(F10.4)	water content at grid point K	cm ³ cm ⁻³
18	THETA1(K), (K=2)	11-20			
18	THETA1(K), (K=3)	21-30			
18	THETA1(K), (K=4)	31-40			
18	THETA1(K), (K=5)	41-50			
18	THETA1(K), (K=6)	51-60			
18	THETA1(K), (K=7)	61-70			
18	THETA1(K), (K=8)	71-80			
19	THETA1(K), (K=9)	1-10			

(continued)

TABLE M-2. (Continued)

Card #	Variable	Columns	Format	Definition	Units
19	THETA1(K), 11-20 (K=10)		(F10.4)	water content at grid point K	cm ³ cm ⁻³
19	THETA1(K), 21-30 (K=11)				
19	THETA1(K), 31-40 (K=12)				
19	THETA1(K), 41-50 (K=13)				
19	THETA1(K), 51-60 (K=14)				
19	THETA1(K), 61-70 (K=15)				
19	THETA1(K), 71-80 (K=16)				
20	THETA1(K), 1-10 (K=17)				
20	THETA1(K), 11-20 (K=18)				
20	THETA1(K), 21-30 (K=19)				
20	THETA1(K), 31-40 (K=20)				
20	THETA1(K), 41-50 (K=21)				
20	THETA1(K), 51-60 (K=22)				
20	THETA1(K), 61-70 (K=23)				
20	THETA1(K), 71-80 (K=24)				
21	CT(IK), 1-16 (IK=1)		(E16.4)	total concentration of ion IK at grid point K	mole l ⁻¹
21	CT(IK), 17-32 (IK=2)				
21	CT(IK), 33-48 (IK=3)				
21	CT(IK), 49-64 (IK=4)				
21	CT(IK), 65-80 (IK=5)				
22	CT(IK), 1-16 (IK=6)				
22	CT(IK), 17-32 (IK=7)				
22	CT(IK), 33-48 (IK=8)				

(continued)

TABLE M-2. (Continued)

Card #	Variable	Columns	Format	Defination	Units
69	NDAYS	1-3	(I3)	number of day bar simulation	days
69	NOPT	4-6	(I3)	number of options	
70	RIONRT(I), (I=1)	1-16	(E16.4)	factor bar ion (I) uptake by roots (ion)	mg cm ⁻³ (H ₂ O)
70	RIONRT(I), 17-32 (I=2)		↓	↓	↓
70	RIONRT(I), 33-48 (I=3)		↓	↓	↓
70	RIONRT(I), 49-64 (I=4)		↓	↓	↓
70	RIONRT(I), 65-80 (I=5)		↓	↓	↓
71	RIONRT(I), 1-16 (I=6)		↓	↓	↓
71	RIONRT(I), 17-32 (I=7)		↓	↓	↓
71	RIONRT(I), 33-48 (I=8)		↓	↓	↓
72	WTMOL(I), 1-16 (I=1)		(E16.4)	gram mol. wt. of ion (I) per mol of ion (I)	gm mole ⁻¹
72	WTMOL(I), 17-32 (I=2)		↓	↓	↓
72	WTMOL(I), 33-48 (I=3)		↓	↓	↓
72	WTMOL(I), 49-64 (I=4)		↓	↓	↓
72	WTMOL(I), 65-80 (I=5)		↓	↓	↓
73	WTMOL(I), 1-16 (I=6)		↓	↓	↓
73	WTMOL(I), 17-32 (I=7)		↓	↓	↓
73	WTMOL(I), 33-48 (I=8)		↓	↓	↓
74	SUNTIM	1-16	(E16.4)	sun up time	hours
74	DAYLNG	17-32	(E16.4)	length of daylight period	hours
75	IPERC(K), (K=1)	1-4	(I4)	percentage of total transpira- tion taken up from layer K	
75	IPERC(K), 5-8 (K=2)		↓	↓	
75	IPERC(K), 9-12 (K=3)		↓	↓	
75	IPERC(K), 13-16 (K=4)		↓	↓	
75	IPERC(K), 17-20 (K=5)		↓	↓	

(continued)

TABLE M-2. (Continued)

Card #	Variable	Columns	Format	Definition	Units
75	IPERC(K), (K=6)	21-24	(I4)	percentage of total transpiration taken up from layer K	
75	IPERC(K), (K=7)	25-28			
75	IPERC(K), (K=8)	29-32			
75	IPERC(K), (K=9)	33-36			
75	IPERC(K), (K=10)	37-40			
75	IPERC(K), (K=11)	41-44			
75	IPERC(K), (K=12)	45-48			
75	IPERC(K), (K=13)	49-52			
75	IPERC(K), (K=14)	53-56			
75	IPERC(K), (K=15)	57-60			
75	IPERC(K), (K=16)	61-64			
75	IPERC(K), (K=17)	65-68			
75	IPERC(K), (K=18)	69-72			
75	IPERC(K), (K=19)	73-76			
75	IPERC(K), (K=20)	77-80			
75	IPERC(K), (K=21)	1-4			
75	IPERC(K), (K=22)	5-8			
75	IPERC(K), (K=23)	9-12			
75	IPERC(K), (K=24)	13-16			
77	IRDEP	4-6	(I3)	depth of irrigation	mm day ⁻¹
77	IPREC	7-9	(I3)	precipitation rate	mm day ⁻¹
77	IDRAIN	10-12	(I3)	drainage rate	mm day ⁻¹
77	IEVAP	13-15	(I3)	evaporation rate	mm day ⁻¹
77	ITRANS	16-18	(I3)	transpiration rate	mm day ⁻¹
77	IFERT(I1) (I1=1)	19-21	(I3)	amount of fertilizer ion (I1) added to grid point 1	kg ha ⁻¹ day ⁻¹
77	IFERT(I1) (I1=2)	22-24	(I3)	amount of fertilizer ion (I1) added to grid point 1	kg ha ⁻¹ day ⁻¹

(continued)

TABLE M-2. (Continued)

Card #	Variable	Columns	Format	Definition	Units
77	IFERT(I1), 25-27 (I1=3)		(I3)	amount of fertilizer ion (I1) added to grid point 1	kg ha ⁻¹ day ⁻¹
77	IFERT(I1), 28-30 (I1=4)				
77	IFERT(I1), 31-33 (I1=5)				
77	IFERT(I1), 34-36 (I1=6)				
77	IFERT(I1), 37-39 (I1=7)				
77	IFERT(I1), 40-43 (I1=8)		↓		↓
77	IRCONC(I1), 43-45 (I1=1)		(I3)	concentration of ion (I1) in ir- rigation water	mg l ⁻¹
77	IRCONC(I1), 46-48 (I1=2)				
77	IRCONC(I1), 49-51 (I1=3)				
77	IRCONC(I1), 52-54 (I1=3)				
77	IRCONC(I1), 55-57 (I1=4)				
77	IRCONC(I1), 58-60 (I1=5)				
77	IRCONC(I1), 61-63 (I1=6)				
77	IRCONC(I1), 64-66 (I1=7)		↓		↓
78	ISOL(I), 4-6 (I=1)		(I3)	amount of fertilizer ion (I) added to grid point 2	kg ha ⁻¹
78	ISOL(I), 7-9 (I=2)				
78	ISOL(I), 10-12 (I=3)				
78	ISOL(I), 13-15 (I=4)				
78	ISOL(I), 16-18 (I=5)				
78	ISOL(I), 19-21 (I=6)				
78	ISOL(I), 22-24 (I=7)				
78	ISOL(I), 25-27 (I=8)		↓		↓
79	IRUNOF	1-4	(I4)	amount of runoff	mm day ⁻¹

**

** Cards #74-79 (6 cards) are within a do loop; each set of 6 cards are read after the program runs for that day and progresses to the next day (by one day) and then reads the data set (next 6 cards) for the next day.

APPENDIX N

FINITE-DIFFERENCE VERIFICATION OF PARTIAL DERIVATIONS

The computational procedure used to solve the system of chemical equilibrium equations requires the calculation of a number of partial derivatives. In addition, the numerical scheme used to solve the transport equations also requires the calculation of the derivatives of certain functions with respect to the ion totals C_{iT} , $i = 1, 2, \dots, 8$. For transient flow conditions the derivatives of these functions with respect to θ are required.

To insure that the computational procedure had been programmed correctly, these partial derivatives were evaluated using the programmed procedure and then compared with finite-difference approximations to the corresponding derivatives. Favorable comparison, after some corrections were made, indicated consistency between calculated function values and calculated values for the partial derivatives.

In order to carry out these comparisons, values were first assigned to each of the parameters and soil-and moisture-dependent variables in both SUBROUTINE SOIL and SUBROUTINE EQUIL and to each of the independent variables C_{1Tk} , C_{2Tk} , \dots , C_{5Tk} , A_{1Tk} , \dots , A_{3Tk} , for $k = 1, 2, \dots, 5$. The value of each function for which a test was desired, for example G'_{13} , was calculated in terms of the assigned values of the parameters and total concentrations. If a test of the derivatives with respect to C_{2Tk} was desired, then the derivatives of each function with respect to C_{2Tk} were also evaluated. Then only the value of C_{2Tk} was changed by a small amount, ΔC_{2Tk} , while the remaining independent variables retained their original values. The functions and their corresponding derivatives were again evaluated in terms of $C_{2Tk} + \Delta C_{2Tk}$, and finally, finite-difference approximations to each of the partial derivatives were calculated. For example,

$$[G'_{13}(C_{2Tk} + \Delta C_{2Tk}) - G'_{13}(C_{2Tk})]/\Delta C_{2Tk}$$

was the finite-difference approximation calculated for $\partial G'_{13}/\partial C_{2Tk}$. For a sufficiently small change in the independent variable (in this example, ΔC_{2Tk}), the finite-difference approximation would be expected to be in reasonable agreement with the calculated values of the partial derivatives at the end-points (e.g. C_{2Tk} and $C_{2Tk} + \Delta C_{2Tk}$). That this is the case can be seen from Tables N-1 through N-6. The first column in each table corresponds to the calculated value of the derivative of the indicated function at the left end-point and the third column corresponds to derivative values at the right end-point. The center column contains values of the finite-difference approximations.

Although each of the functions of the total concentrations was checked individually, Tables N-1 through N-6 contain only derivatives of the G'_{ik} functions. In all cases, it can be seen that the calculated finite-difference lies numerically between the values of the derivatives calculated for the end-points.

TABLE N-1. DERIVATIVE OF G_{ik} WITH RESPECT TO CATION 1 AT THIRD GRID POINT

i =	Derivative		
	$C_{1T} = 0.11$	F.D. Check	$C_{1T} = 0.12$
1	-1.158×10^{-3}	-1.153×10^{-3}	-1.145×10^{-3}
2	-1.452×10^{-4}	-1.328×10^{-4}	-1.123×10^{-4}
3	1.010×10^{-4}	1.119×10^{-4}	1.209×10^{-4}
4	1.010×10^{-4}	1.119×10^{-4}	1.209×10^{-4}
5	1.010×10^{-4}	1.119×10^{-4}	1.209×10^{-4}
6	-2.229×10^{-4}	-2.033×10^{-4}	-1.853×10^{-4}
7	-7.356×10^{-4}	-7.124×10^{-4}	-6.887×10^{-4}
8	-7.356×10^{-4}	-7.124×10^{-4}	-6.887×10^{-4}

TABLE N-2. DERIVATIVE OF G_{ik} WITH RESPECT TO CATION 2 AT THIRD GRID POINT

i =	Derivative		
	$C_{2T} = 0.05$	F.D. Check	$C_{2T} = 0.06$
1	-2.750×10^{-4}	-2.349×10^{-4}	-1.065×10^{-4}
2	-9.170×10^{-4}	-9.393×10^{-4}	-9.582×10^{-4}
3	2.104×10^{-5}	3.676×10^{-5}	5.068×10^{-5}
4	2.104×10^{-5}	3.676×10^{-5}	5.068×10^{-5}
5	2.104×10^{-5}	3.676×10^{-5}	5.068×10^{-5}
6	-2.229×10^{-4}	-2.047×10^{-4}	-1.879×10^{-4}
7	-7.356×10^{-4}	-7.124×10^{-4}	-6.888×10^{-4}
8	-7.356×10^{-4}	-7.124×10^{-4}	-6.888×10^{-4}

TABLE N-3. DERIVATIVE OF G_{ik} WITH RESPECT TO CATION 3, 4* OR 5* AT THIRD GRID POINT

i =

	Derivative		
	$C_{3T} = 0.05$	F.D. Check	$C_{3T} = 0.06$
1	1.253×10^{-5}	1.659×10^{-5}	2.063×10^{-5}
2	7.384×10^{-6}	9.196×10^{-6}	1.095×10^{-5}
3	-1.358×10^{-3}	-1.357×10^{-3}	-1.355×10^{-3}
4	7.903×10^{-5}	7.970×10^{-5}	8.031×10^{-5}
5	7.903×10^{-5}	7.970×10^{-5}	8.031×10^{-5}
6	-1.114×10^{-4}	-1.090×10^{-4}	-1.067×10^{-4}
7	-3.678×10^{-4}	-3.628×10^{-4}	-3.579×10^{-4}
8	-3.678×10^{-4}	-3.628×10^{-4}	-3.579×10^{-4}
*	For cation 4, rows 3 and 4 should be interchanged. For cation 5, rows 3 and 5 should be interchanged.		

TABLE N-4. DERIVATIVE OF G_{ik} WITH RESPECT TO ANION 1 AT THIRD GRID POINT

i =	Derivative		
	$A_{1T} = 0.03$	F.D. Check	$A_{1T} = 0.04$
1	-5.755×10^{-4}	-5.448×10^{-4}	-5.147×10^{-4}
2	-2.247×10^{-4}	-2.141×10^{-4}	-2.036×10^{-4}
3	-1.626×10^{-4}	-1.591×10^{-4}	-1.553×10^{-4}
4	-1.626×10^{-4}	-1.591×10^{-4}	-1.553×10^{-4}
5	-1.626×10^{-4}	-1.591×10^{-4}	-1.553×10^{-4}
6	-1.982×10^{-3}	-1.933×10^{-3}	-1.881×10^{-3}
7	7.356×10^{-4}	7.329×10^{-4}	7.276×10^{-4}
8	7.356×10^{-4}	7.329×10^{-4}	7.276×10^{-4}

TABLE N-5. DERIVATIVE OF G_{ik} WITH RESPECT TO ANION 2 OR 3* AT THIRD GRID POINT

i =	Derivative		
	$A_{2T} = 0.075$	F.D. Check	$A_{2T} = 0.085$
1	-2.018×10^{-4}	-1.995×10^{-4}	-1.972×10^{-4}
2	-9.423×10^{-5}	-9.314×10^{-5}	-9.205×10^{-5}
3	-1.507×10^{-4}	-1.488×10^{-4}	-1.469×10^{-4}
4	-1.507×10^{-4}	-1.488×10^{-4}	-1.469×10^{-4}
5	-1.507×10^{-4}	-1.488×10^{-4}	-1.469×10^{-4}
6	1.114×10^{-4}	1.103×10^{-4}	1.092×10^{-3}
7	-1.837×10^{-3}	-1.817×10^{-3}	-1.798×10^{-3}
8	3.678×10^{-4}	3.631×10^{-4}	3.585×10^{-4}
* For anion 3, rows 7 and 8 should be interchanged.			

TABLE N-6. DERIVATIVE OF G_{ik} WITH RESPECT TO θ AT THIRD GRID POINT

i =	Derivative		
	$\theta = 0.49$	F.D. Check	$\theta = 0.50$
1	-1.722×10^{-4}	-1.677×10^{-4}	-1.632×10^{-4}
2	-7.687×10^{-5}	-7.493×10^{-5}	-7.302×10^{-5}
3	-2.483×10^{-5}	-2.308×10^{-5}	-2.144×10^{-5}
4	-2.483×10^{-5}	-2.308×10^{-5}	-2.144×10^{-5}
5	-2.483×10^{-5}	-2.308×10^{-5}	-2.144×10^{-5}
6	-6.817×10^{-5}	-6.522×10^{-5}	-6.241×10^{-5}
7	-2.182×10^{-5}	-2.120×10^{-5}	-2.059×10^{-5}
8	-2.182×10^{-5}	-2.120×10^{-5}	-2.059×10^{-5}

Appendix O

Analysis of Covariance
for Adsorbed and Solution
Cation Concentrations

TABLE O-1. ANALYSIS OF COVARIANCE OF ADSORBED AND SOLUTION CONCENTRATIONS
OF IONS IN SOIL SAMPLE 1

Analysis of Covariance of Equilibrium Data								
Source of Variation	df	x,x	Sum of Products x,y	y,y	df	y Adjusted for x SS	MS	F
Total	51	51,394.22	960.42	1732.89				
Cations	3	5,361.28	-99.86	1674.48				
Treatments	12	12,144.51	162.67	7.69				
Error	36	33,888.43	897.61	50.72	35	26.94	.77	
<hr/>								
Treatment and Error	48	46,032.94	1060.28	58.41	47	33.99		
<hr/>								
Treatments Adjusted					12	7.05	.59	.76

TABLE O-2. ANALYSIS OF COVARIANCE OF ADSORBED AND SOLUTION CONCENTRATIONS OF IONS IN SOIL SAMPLE 2

Analysis of Covariance of Equilibrium Data								
Source of Variation	df	$\sum X_1 X$	Sum of Products $\sum X_1 Y$	$\sum Y_1 Y$	df	Y Adjusted for X SS	MS	F
Total	67	44,929.86	7,036.26	8,643.76				
Ions	3	9,711.9	6,688.66	8,364.09	2			
Treatments	16	17,211.21	141.52	6.02	15			
Error	48	18,006.76	206.08	273.65	47	271.30	5.77	
Treatments and Error	64	35,217.97	347.60	279.67	63	276.24		
Treatments Adjusted					16	4.94	.31	NS

$$E_{yy} - \frac{E(xy)^2}{E_{xx}} = 271.30 - \frac{(206.08)^2}{18,006.76}$$

$$S_{yy} - \frac{E(xy)^2}{S_{xx}} = 276.24 - \frac{(347.6)^2}{35,217.97}$$

F Table 16, 47 df = 2.40

There was no real difference on the cation adsorbed at the different treatments when adjusted for Y on X.

TECHNICAL REPORT DATA		
Please read Instructions on the reverse before completing		
1. REPORT NO. EPA-600/2-78-082	2.	3. RECIPIENT'S ACCESSION NO.
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16. ABSTRACT A three year field and laboratory study was conducted to determine the influence of management practices on the quantity and quality of irrigation return flow from rice paddies. Continuous and intermittent irrigation techniques were used on replanted field plots which received either recommended or excessive applications of fertilizer and four selected pesticides. Water quality was evaluated with respect to fertilizer amendments, pesticides, pH and total salt load. Pesticides monitored included propanil, molinate, carbofuran, carbaryl and their respective metabolites. Present water management practices result in large return flow volumes. Occasionally concentrations of NH_4 exceeded drinking water standards. Losses as nitrate were below such limits and the total nitrogen losses were a small fraction of the fertilizer applied. A model was developed to simulate the ionic constituency of the return flow. Propanil was washed from the foliage into the flood water and dissipated within 24 hours. Evidence is given that carbaryl is washed from the leaves by rainfall, thus providing available source to contaminate return flow. As long as 8 days were required to dissipate residue resulting from recommended applications. Retention times to assure low concentrations in the irrigation return flow for carbofuran are of the order of 16 days. Granular applied molinate necessitates a retention time of 4 days to assure concentrations are within 10% of the TLM to fish. It is suggested that through improved water management and knowledge of dissipation rates, the quantity of irrigation return flow can be reduced and the quality improved.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Irrigation Pesticides Water Quality Water Pollution Agronomy Soil Water	Irrigation Return Flow, Rice irrigation, Pesticide residue, Propanil, Carbofuran, Molinate, Carbaryl, Salt balance	98/C 98/D
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