This is to certify that the

dissertation entitled

"Simulation and Measurement of Atrazine and Nitrate Losses as Influenced by Water Table Management"

presented by

Argyrios Gerakis

has been accepted towards fulfillment
of the requirements for

Doctors degree in **Philosophy**

Joe T. Ritchie
Major professor

Date **April 8, 1994**

SIMULATION AND MEASUREMENT OF ATRAZINE AND NITRATE LOSSES AS INFLUENCED BY WATER TABLE MANAGEMENT

By

Argyrios Gerakis

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Resource Development

1994

ABSTRACT

SIMULATION AND MEASUREMENT OF ATRAZINE AND NITRATE LOSSES AS INFLUENCED BY WATER TABLE MANAGEMENT

By

Argyrios Gerakis

Subirrigation/drainage systems have been introduced in areas of Michigan. Until now, there was little information on how water table management affects chemical losses. The objective of this study was to measure and simulate atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) and NO_3-N losses from subsurface tile drains. The study has three parts. In the first part, the effect of duration and timing of flooding was observed in five lysimeters with independently controlled water table. The lysimeters were planted with corn (*Zea mays* L.). Shorter flooding was associated with higher atrazine and NO_3-N peak concentrations during water table drawdown. Shorter flooding was associated with more total NO_3-N in drainage. Flooding duration did not affect total atrazine loss. Early inundation was associated with higher atrazine and NO_3-N peak concentrations during water table drawdown, and more total atrazine and NO_3-N in drainage. All flooding had at least some negative impact on yield, especially the prolonged, early flooding. In the second part of the study, CERES, a soil-crop-atmosphere model, was modified to simulate pesticide fate with the presence of a water table. Given the uncertainty of field measurements, the model successfully simulated drainage, atrazine and NO_3-N concentrations, and total leaching for the limited period following drawdown. In the third part of the study, two flow tracers (Br and

Rhodamine WT) were applied on a field lysimeter followed by intense irrigation. Pronounced by-pass flow occurred.

To my parents and sister

ACKNOWLEDGMENTS

Thanks to the USDA Soil Conservation Service and the Saginaw Bay, Michigan Subirrigation/Drainage Project for sponsoring a significant part of this project.

Thanks to Joe Ritchie, my major professor, for his excellent academic guidance, friendship, and substantial financial support throughout my studies. Thanks to my committee members, Bud Belcher, Eckhart Dersch and Karen Renner for their guidance throughout this research.

The following offered me financial support during my studies and should be acknowledged: Maxine Ferris and the Department of Outreach Communications; Carl Ramm and the Departments of Fisheries and Wildlife, Forestry, Parks and Recreation Resources, and Resource Development; Ger Schultink and the CRIES project; Baxter Vieux and the GEM project.

Sharon Anderson and Fran Pierce loaned analytical equipment essential to this study. Special thanks to Mike Kenney for offering a fluorometer for dye analysis.

My Nowlin Chair colleagues offered me support and friendship. Special thanks to: Brian Baer, my basement-mate and computer Grand Master, who can program like there's no tomorrow; Jon Lizaso, who built and tested the facility I used in this project; Val Snow, for her research advice. Thanks to my colleagues from Resource Development, Eric Fitch and Sashi Nair, who helped me get a clue during my early years in the Department.

Last but not least, I would like to thank Anastasia Analyti for her programming help, her company and for being there.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I
INTRODUCTION

BACKGROUND AND SETTING

Nutrient and pesticide leaching from farmlands contributes to groundwater pollution in rural Michigan. In one of the first surveys of rural groundwater quality in the state, Ervin and Kittleson (1988) report concentrations from 38 wells in Hillsdale, Kalamazoo, and St. Joseph counties. During 1987, eight wells consistently exceeded the health advisory level of 10 mg/L NO_3-N; 16 wells did so occasionally. Eleven wells showed atrazine above the health advisory level of 3 µg/L at least once during the season. A follow-up of contaminated wells during 1988 confirmed high NO_3-N levels. Overall atrazine levels were lower in 1988, possibly because of the severe drought. Results in 1987 represent groundwater quality under "worst-case" conditions, because the counties selected for sampling were known for intensive use of agricultural chemicals and vulnerable aquifers. Results in 1988 represent "best-case" scenarios for these areas, because of the drought. Overall, sampling was not frequent enough to fully characterize seasonal trends in contamination. Yet, this study raised doubts about the quality of groundwater in sensitive areas of Michigan.

Nitrogen and atrazine are two of the most important inputs in corn production in Michigan. The following statistics are from the Michigan Department of Agriculture (1992). In 1991, 97% of the corn acreage received N fertilizer, more than any other nutrient. The average application rate was 139

kg/ha. For comparison, K, the second most frequently applied nutrient, was applied on 90% of the corn acreage at an average application rate of 106 kg/ha. In the same year, 74% of the corn acreage received atrazine, more than any other herbicide or insecticide. The average rate applied was 1.5 kg/ha. For comparison, metolachlor, the second most frequently applied herbicide or insecticide, was applied on 38% of the corn acreage at an average application rate of 2 kg/ha.

High doses of NO_3 may cause methemoglobinemia, a blood disorder, in infants. Atrazine's toxic effects include: Skin irritation, lung/respiratory effects, central nervous system disorders, blood cell disorders, embryotoxicity (U.S. Congress, Office of Technology Assessment, 1984). Yet, mutagenicity has caused the most concern. USEPA classifies atrazine as a possible human carcinogen (Rubio et al., 1991). Another risk from atrazine is damage to submerged aquatic vegetation in estuaries and streams (Glotfelty et al., 1984; Baker et al., 1981, both cited in Leonard, 1990).

Water transports water soluble chemicals through the soil. Nitrate is highly soluble and non-adsorptive, therefore it has high leaching potential. Once in groundwater, it is persistent. Atrazine has high leaching potential compared to other pesticides (Renner and Kells, 1994), though its behavior varies with pH. Once in groundwater, it is persistent (Klint et al., 1993). In soils atrazine may be persistent enough to damage sensitive rotational crops (Weed Science Society of America, 1983). The method, amount, and timing of irrigation and drainage can affect the fate of both chemicals. It is important to study the effect of these factors in areas where farmers consider innovative approaches to irrigation, such as subirrigation in some areas of Michigan.

The 1982 USDA Soil Conservation Service National Resources Inventory cites Michigan as having over 1.21 Mha cropland that could be drained to be more productive. Much of that cropland could potentially

benefit from a subirrigation/drainage combination (Belcher, 1988). LeCureux (1991) shows the feasibility and profitability of subirrigation systems on appropriate soils with proper operation. Still, there are knowledge gaps regarding the effects of water table management on chemical loading of groundwater.

In a subirrigation/drainage system the water table may be shallow to provide water to the roots. Because of high antecedent water content, the infiltration capacity of the soil during a storm may be exceeded. This may result in runoff, which can carry dissolved and suspended chemicals to surface waters (Leonard, 1990). When the drains are opened, saturated conditions may enhance macropore flow and chemical leaching through the drains (White, 1985).

More empirical evidence is needed as well as decision-making tools to address productivity and water quality issues. Integrated soil-crop-atmosphere simulation models might be a valuable tool to plan management tactics. Protasiewicz et al. (1988), after reviewing the most popular U.S. water quality models, found none that would model both a shallow water table and water quality.

PROBLEM STATEMENT

In areas of Michigan, intensive agriculture over vulnerable aquifers threatens groundwater with contamination from agricultural chemicals. Nitrate and atrazine were selected for this study because of widespread use, high mobility in soil, and reports of contamination. There is a knowledge gap about the fate of these chemicals as influenced by subirrigation/drainage. Research is needed to collect experimental data, to understand and to model the fate of NO_3 and atrazine with water table management.

RESEARCH OBJECTIVES

1. Measure atrazine and NO_3-N losses from field lysimeters as affected by water table management.

2. Adapt an existing soil-crop-atmosphere simulation model to predict the influence of water table management on atrazine and NO_3-N losses.

3. Observe the distribution in soil of a chemical tracer pulse leached under conditions conducive to preferential flow.

The above objectives define the organization of this study into chapters. The first two objectives complement each other, as the data collected in the field were used to test the model. The last objective is related to the other two because preferential flow is suspected by many (e.g., White, 1985) to affect chemical leaching.

LIMITATIONS OF THE STUDY

The data were collected from a research subirrigation/drainage facility at Michigan State University. Conclusions from this study apply only to that location. Another limitation is the amount of testing possible for the simulation model. The model was based on the CERES crop-soil-atmosphere model (Jones and Kiniry, 1986). Scientists worldwide have successfully tested the whole or parts of CERES under many combinations of climate, soil, and management. Yet, most testing has been on yield and fertilizer response, not on drainage and leaching. The adapted model will be tested only with data from this study.

SUMMARY

Nitrate and atrazine have been detected in vulnerable aquifers underlying farmland in Michigan. Subirrigation is a relatively new practice that might affect the leaching of these two chemicals. Data collection, interpretation, and the development of the appropriate decision support tools are part of the response to these issues.

CHAPTER II

MEASUREMENT OF ATRAZINE AND NITRATE LOSSES AS INFLUENCED BY WATER TABLE MANAGEMENT

PROBLEM STATEMENT

The objective of subirrigation is to supply adequate water to the roots by raising the water table. During early crop development stages, the root system is shallow, so the water table should be close to the soil surface (e.g., at 38 to 51 cm for corn [J. LeCureux, undated, "Production of corn with subirrigation," Huron County Cooperative Extension Service, MI]). A storm may exceed the limited infiltration capacity of the soil and result in runoff. Runoff may carry dissolved and suspended agricultural chemicals to surface waters. When the drains are opened, saturated conditions may promote macropore flow and increase the risk of chemical leaching. The leachate may end up in surface waters or groundwater. Besides potential water contamination, any losses of chemicals would reduce their efficacy and cause financial losses.

The objective of this chapter is to describe and discuss the effect, if any, of water table management strategies on atrazine and NO_3 leaching.

REVIEW OF THE LITERATURE

The objective of this section is to review past work regarding the effect of water table management on atrazine and NO_3 leaching. The relevant

findings are summarized and critiqued. Drawbacks, if any, are noted, as well as suggestions for improving the usefulness of the research.

Besides the obvious benefit of meeting transpiration demand, subirrigation may have other agronomic benefits. Kaspar et al. (1989) show that drying of the fertilized soil layer reduces soybean (*Glycine max* L.) shoot growth and accumulation of applied P and K fertilizers, though water was available at greater depths (45 cm) through subirrigation. Specifically, drying of the fertilized zone reduced shoot dry weight by 14 to 17%, shoot P uptake by 17 to 25%, and shoot K uptake by 14 to 18%. The lowest in each pair of figures is for drying starting at an earlier stage, though the differences between early and late stage drying were not significant. This paper suggests that sufficient moisture is needed above 45 cm for optimum growth and nutrient use efficiency.

LeCureux and Booms (1988b) report NO_3-N concentrations in the water table of subirrigated corn. Nitrogen was applied at three rates, 213, 247, and 280 kg/ha of N. These rates could potentially result in overfertilization if they coincided with any area of high residual N.[1] There are problems with the reporting of the data. Concentrations are reported from "low" and "high" N application areas. This implies only two fertilization treatments, though there were three N rates. The highest NO_3-N concentrations came from the low N application site. This is hard to interpret if the rates cannot be assessed.

---

[1]The yield goals were 10034, 11288, and 12542 kg/ha. According to LeCureux (undated, "Production of corn with subirrigation," Huron County Cooperative Extension Service, MI) yield goals of 10974 to 11288 kg/ha are realistic for that area. One kg of corn grain requires about 0.03 kg N (Hartmann, 1988). Then, the yield goals require 301, 339, and 376 kg/ha N. The soil test indicated 115 to 151 kg/ha residual N, with a mean of 135 kg/ha. In the above calculations and throughout this writing, 1 bushel/acre equals 62.71 kg/ha (ASA, CSSA, and SSSA, 1988).

Sampling at the high and low N application sites stopped before the field was put in drainage mode at the end of the season. This precludes the assessment of the possible effect of the water table drop on NO_3-N concentrations.

LeCureux and Booms (1988a) report NO_3-N concentrations in the drainage effluent from two adjacent corn fields; one subirrigated and the other not. Nitrogen was applied at 269 kg/ha. This rate could result in overfertilization if residual soil N was high.[2] A reference exists in the text to a table with residual N. Yet, this table does not exist. Apart from subirrigation the two fields were treated the same. Ten effluent samples were collected during the season, six from the subirrigated field, and four from the non-irrigated. On the dates both fields were sampled, the subirrigated field had equal or higher NO_3-N levels to the non-irrigated. In eight out of the 10 samples, NO_3-N exceeded 10 mg/L. There seems to have been no effect of water table management on NO_3-N concentration. This was possibly because there was no sampling on any date that the water table level had changed. This paper would be more relevant if cumulative NO_3-N losses in the tile effluent could be determined. Nitrate-N concentrations are needed for critical dates such as when the water table level changed or when rain fell.

LeCureux and Booms (1988c) report NO_3-N concentrations in the drainage effluent from subirrigated sugar beets (*Beta vulgaris* L.). Two tile spacings were tested, 18 m ("wide") and 9 m ("narrow"). Two N rates were tested, 107 and 151 kg/ha. The N rate recommended by the soil testing lab ("Terra Analytics") was 123 kg/ha. The irrigation water was an additional source of N, varying from 8.1 mg/L (at the onset of subirrigation) to 2.9 mg/L (at the end of subirrigation). Total subirrigation was 12.2 cm. At 8.1 mg/L of

---

[2]The potential of that soil for corn is reported as 8152 kg/ha. Following the calculations in Footnote 1, this yield requires 245 kg/ha N.

NO_3-N, irrigation would add 10 Kg/ha N. At 2.9 mg/L of NO_3-N, irrigation would add 4 Kg/ha N. Early in the season NO_3-N concentrations exceeded 10 mg/L at the control stand (19 April to 25 May), at the high N treatment with wide spacing (13 to 29 June), and at the high N treatment with narrow spacing (3 June). Data for the low N treatment with narrow spacing are not reported until 29 June, and on that date it had lower NO_3-N levels than any of the high N treatments. The high N rate with wide spacing consistently had higher NO_3-N levels than any other treatment. It is not clear why this happened; the water table level at the wide spacing was only 4 cm lower on the average than at the narrow spacing. A possible explanation is lower N plant uptake at the wide spacing; at the wide spacing, yield was 5928 kg/ha or 9.8% lower than the yield at the narrow spacing. This implies that better N utilization by the crop may result in less N available for leaching. Unfortunately, sampling from all treatments stopped before the field was drained, so the effect of drainage on NO_3-N concentrations cannot be assessed.

Protasiewicz et al. (1988) compared nutrient and pesticide loading from two treatments; one with subirrigation and one with subsurface drainage. The treatments were planted with corn. Nitrogen was applied at 7 kg/ha as a starter, at 30 kg/ha as sidedress, and at approximately 1 kg/ha after harvest. This rate was below standard recommendations.[3] Atrazine was

---

[3]A realistic yield goal for subirrigated corn in Michigan's "Thumb" area is 10974 to 11288 kg/ha (LeCureux, undated, "Production of corn with subirrigation," Huron County Cooperative Extension Service, MI). The location of the field was at Banister, close to Saginaw, one of the "Thumb" counties. Assuming a yield goal of 10974 to 11288 kg/ha, and following the calculations of Footnote 1, 329 to 339 kg/ha of N would be required. Residual soil N is unreported.

applied at an unreported time at a rate of 0.68 kg/ha. This rate was lower than recommended for mineral soils (0.84 to 1.12 kg/ha [Renner and Kells, 1994]). By the end of April of the following year, the subirrigated treatment had released 21 cm of effluent, 12 kg/ha NO_3-N (32% of N applied), and 2.8 g/ha (0.4% of amount applied) of atrazine. The drainage-only treatment had released 27 cm of effluent, 21 kg/ha of NO_3-N (55% of N applied), and 1.3 g/ha (0.2% of amount applied) of atrazine. Months of high NO_3-N and atrazine leaching were associated either with unusually high precipitation or a sudden drop in the water table. Nitrate-N concentrations were generally well under 10 mg/L in both treatments, possibly due to the conservative fertilizer application. It is not clear why the subirrigated treatment leached less NO_3-N but more atrazine. For NO_3-N, authors speculate higher denitrification due to anaerobic conditions, higher plant N uptake, and higher runoff from the subirrigated plot. The denitrification argument is reasonable, due to anoxic conditions prevalent with a high water table. The higher plant uptake argument also is reasonable, given the higher yields from the subirrigated plots. The higher runoff argument is plausible, though runoff was not measured. For atrazine, the authors speculate it may have diffused into solution in the subirrigated plot during the winter months. Another explanation is that microbial degradation of atrazine is very limited under anaerobic conditions, though atrazine can decompose chemically without microorganisms (Kaufman and Kearney, 1970).

The possibility that a shallow water table helps reduce NO_3-N losses in drainage is also supported by Gilliam et al. (1979). They compared the concentrations and amount of NO_3-N lost from conventional drainage with those lost from controlled drainage. Two soils were tested; moderately well drained and poorly drained. The rest of this paragraph refers to the moderately well drained soil. The controlled drainage treatment lost less

NO_3-N through the tiles than the uncontrolled drainage. Concentrations were similar, therefore the difference in leachate mass was probably due to flow volume difference. In the controlled drainage treatment, the researchers could not maintain the water table above 0.5 m for more than 1-3 d at a time. For significant drainage to occur, the water table had to rise above 0.3 m depth, which may explain why little tile flow occurred. There was no evidence that denitrification helped reduce NO_3-N losses.

In the poorly drained soils, controlling the water table was easier. The authors report no effect of water table control on the NO_3-N concentrations from any particular field. Yet, the graph that accompanies the text shows otherwise. Maximum winter concentrations from one field varied from about 16 mg/L in a controlled drainage year to about 8 mg/L in an uncontrolled drainage year. Therefore, the authors' claim that NO_3-N losses from each treatment were only dependent on the flow volume is not necessarily true. Cumulative NO_3-N loss could be calculated but concentration and flow would have to be estimated from graphs. Another problem is that drainage flow volumes are compared among years with very different precipitation (27, 31, and 42 cm), which tends to obscure the effect of drainage control on NO_3-N losses. There were indications for denitrification below 1.2 m depth in both treatments (lack of O_2, low oxidation-reduction potentials, low NO_3-N concentrations relative to surface and subsurface discharge). Overall, this work suggests that in moderately well drained soils, drainage control reduces NO_3-N losses through tiles by reducing total flow volume. In poorly drained soils, denitrification may reduce NO_3-N losses through the tile lines, but there seems to be no difference between controlled drainage and conventional drainage.

The effect of soil profile characteristics on NO_3-N fate in soils was examined by Devitt et al. (1976). All soils had tile drainage but different

texture. In uniformly coarse-textured profiles, NO_3-N losses in tile drainage were high (24 to 177% of N applied). The losses were attributed to a downward hydraulic gradient and/or conditions unfavorable for denitrification (high measured redox potential, supported by low Mn concentrations). In coarse-textured profiles with a clay layer at approximately 76 to 100 cm, the NO_3-N lost in tile drainage was only 13 to 21% of N applied. One exception was a soil with high clay content that had recently been brought into cultivation. It lost 53% of applied N through the tiles but this was interpreted as the result of N stored within the profile. The authors attribute reduced NO_3-N losses in soils with a clay layer to conditions favoring denitrification (high water table and/or low measured redox potential, supported by increasing Mn concentrations with depth). The denitrification hypothesis is further supported by soil solution samples taken with porous cup samplers from different depths. The soils with the clay layer had much lower NO_3-N concentrations at 183 cm depth than the uniformly coarse-textured ones. This suggests that a clay layer restricting water movement tends to promote conditions suitable for denitrification.

Kalita and Kanwar (1990) measured pesticide concentrations in field lysimeters and in a subirrigated field. Sampling was done with solute suction tubes and piezometers that were installed in each lysimeter and in the subirrigated field at fixed depths. The plots and the field were planted with corn. Atrazine and alachlor were both applied at 2.2 kg/ha 1 d prior to sowing. The atrazine rate was higher than the recommended (0.84 to 1.12 kg/ha for mineral soil [Renner and Kells, 1994]). At planting, the water table level was below 1.5 m. Fifty-seven d after planting the water table was raised and maintained constant until 30 d after harvest. Three water table depths were tested; 30, 60, and 90 cm. The authors did not find a clear relationship between water table depths and atrazine mobility. They attribute that to

limited data from only one season. Yet, this is not necessarily the case. Though it is always helpful to have data spanning more than one season, more likely causes were raising the water table late (57 d after atrazine application), infrequent sampling (every 15 d) and ignoring the concentrations in the drainage effluent. Each time the water table rose above its prescribed depth for any reason, including precipitation, a sump pump would automatically pump out enough water to compensate for the rise. The volume and concentration of this effluent is not reported, yet it could contain significant atrazine.

Muir and Baker (1976) observed flow volumes and atrazine concentrations in tile drain discharge from a corn field. The drains were continuously open. Atrazine was applied post-emergence, at an unreported date, at a rate of 2.8 kg/ha, higher than recommended for mineral soils. Flow volumes and atrazine concentrations from this paper are plotted in Figure 1. Sampling was not frequent enough to calculate meaningful cumulative losses.

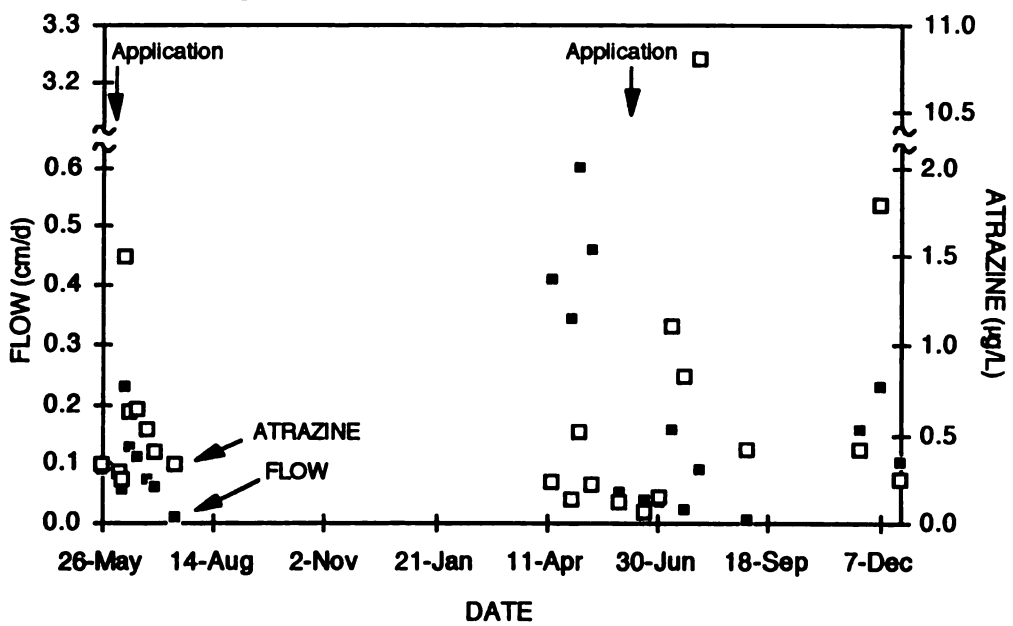

Figure 1. Flow and atrazine concentrations (data from Muir and Baker, 1976).

This graph shows that daily flow volumes are somewhat related to atrazine concentrations. The general trend in atrazine concentrations is to decline with time since application. Relatively higher flows sometimes are accompanied by relatively higher atrazine concentrations. Though the water table was not controlled in this study, the results may be relevant to controlled water table systems. It is probably safe to assume that the volume of water collected through the drains is related to the amount of water moving through the soil. Events that increase the time rate of downward flow, such as drainage of a subirrigated field, could increase atrazine concentrations in the tile outflow.

Milburn et al. (1990) designed an observation similar to Muir and Baker's, but with more frequent sampling. They measured drainage volume, NO_3-N concentrations and total NO_3-N in the tile discharge from a potato field. The drains were continuously open. They sampled every 1 h for flow volume and every 4 h for NO_3-N. Plots of the data show a relationship between drainage rates and NO_3-N concentrations. The relationship changes with time after fertilizer application. During the first drainage event after fertilizer application, NO_3-N concentrations increase with flow rates, peak at about the same time, and decline as flow rates decline. In later drainage events, NO_3-N concentrations decrease as flow rates increase, and increase as the flow rates decrease. The authors attribute both trends to preferential flow; shortly after fertilizer addition, NO_3 is on the outside of the soil structural units and subject to rapid leaching by water flowing around the peds. Later in the season, NO_3 has relocated within the peds, and it is less accessible to water flowing around the peds. Eventually NO_3 diffuses slowly back into the interaggregate pore space, which explains why NO_3-N concentrations increase afeter the drainage peak.

Smettem et al. (1983) monitored NO_3-N concentration and drainage from a wheat crop for approximately three months. Nitrate-N concentrations and drainage rates plotted against time show a very strong relationship;

concentrations and flows rate rise, peak and fall at the same time. The authors attribute this relationship to preferential flow through structural voids that leached the recently applied (13 d old) fertilizer. They report that the second and third drainage events were not as efficient in leaching NO_3-N because NO_3-N had relocated within the peds. Unlike Milburn et al. (1990), Smettem et al. do not support their hypothesis with plots of concentrations and flow during the later drainage events. Their evidence of by-pass flow during the second and third drainage events is that the ratio of NO_3-N load (mg/s) to water discharge volume (dm^3/s) dropped from about 6 to 0.5. Yet, this evidence by itself does not necessarily support the by-pass flow hypothesis; Nitrogen may be lost to leaching, decay, and uptake between flow events, as well as being relocated within soil peds.

Ervin and Kittleson (1988) analyzed effluent collected from the bottom of two lysimeters. The variable tested was irrigation scheduling. In the first lysimeter (Research Plot), the irrigation amount was based on evaporation losses, and it was triggered by visible crop stress. In the second lysimeter (Farmer's Plot), timing and amount of irrigation were left at the judgment of the farmer. Atrazine was applied to the entire field where the lysimeters were installed 12 and 13 d after sowing at a rate of 3.5 L/ha. A common atrazine formulation weighs 0.48 kg/L (K. Renner, 1994, personal communication). The rate applied would be 1.68 kg/ha, somewhat higher than recommended. In both lysimeters, atrazine concentrations followed the same trend; they increased following application, reached a maximum about 50 d after application and then started to dwindle until they reached pre-application level, about 152 d after application. The Farmer's Plot received and drained a lot more water during the growing season, and yielded slightly higher atrazine concentrations. Yet, the dates when concentrations from the Farmer's Plot exceeded the concentrations of the Research Plot were not necessarily the dates of higher water inputs. There

was no obvious correlation between daily water input and atrazine concentration in the effluent. Drainage volume could be a better predictor of atrazine concentrations, but daily drainage volumes are not reported.

LeCureux (1991) reports results from a subirrigation/drainage study concurrently undertaken in plots of sugar beets, corn, and navy beans (*Phaseolus* sp.). The tile effluent from all plots was screened for NO_3-N and triazines (atrazine, cyanazine, and simazine) among other chemicals. The sugar beet and corn plots were parts of the same field but not the navy bean plots. In the sugar beet and corn plots two tile spacings were tested, 9 and 18 m, and there was a non-subirrigated zone. The navy bean field had 8 m tile spacing, though the figure referenced in the text shows two different tile spacings. In the sugar beet field, N was applied at 129 kg/ha, and residual NO_3-N in the soil was 45 kg/ha. The corn field was fertilized with 213 kg/ha of N and residual NO_3-N was 34 kg/ha. The application probably was less than standard.[4] The N rate for navy beans was 56 kg/ha. Application rates of the triazines are not reported. The water sampling methodology in all of the three crops is not clearly presented. Some samples were taken when the drains were opened after heavy precipitation. Yet, other samples were taken when the system was in closed (subirrigated) mode. Whether the drains were opened for this sampling is not clear. Presentation of the results makes comparisons among treatments and among crops difficult. Concentrations from each tile spacing treatment, from the water source, from the non-irrigated treatments and composite samples of several plots are all

---

[4]The yield goal was 11601 kg/ha. Applying the calculations in Footnote 1, this yield goal requires 348 kg/ha N. The N fertilizer plus the residual N would be about 100 kg/ha short of this requirement.

interspersed in one table per crop. Comparisons are even harder because all plots were not sampled concurrently.

In all plots, NO_3-N levels were below 10 mg/L for most of the season, possibly due to conservative application rates. High levels were measured from the sugar beet plots and from the corn plots when water had to be released after heavy precipitation. Detection limits for atrazine, cyanazine, and simazine were 0.05, 1.0, and 0.05 µg/L. Yet, why some reported concentrations were below these limits is not clear. Triazine concentrations from all plots were low, less than 2 µg/L. This result cannot be interpreted because the application rate is unreported. This paper indicates that high NO_3-N concentrations in drainage discharge are associated with a drop in the water table after precipitation. The study could be more useful if the sampling methodology and the triazine application rates were known, if cumulative leachate was estimated (there are no flow volume data), and if results were presented in a logical order.

Ritchie and Lizaso (1991) observed the effect of timing and duration of flooding in field lysimeters, each drained with a tile. The water table could be independently controlled in each lysimeter. The treatments were two flooding durations (4 and 8 d) at two different times (19 and 38 d after atrazine application). At the end of the flooding the plots were drained and effluent samples were collected for 2 d after the onset of drainage. Atrazine was not measured for the late, short duration flooding. Atrazine was applied at 1.12 kg/ha pre-emergence. Results suggest higher peak atrazine concentrations in the tile effluent when flooding was applied early in the season (48 µg/L) versus late (6.6 µg/L). This result is expected because later in the season less atrazine is available after decomposition, leaching and plant uptake. Another finding is that higher peak concentrations were associated with the longer inundation (48 µg/L) than with the short (17 µg/L). It is possible that the

longer inundation allowed atrazine sorbed within the soil aggregates to diffuse into the interaggregate solution. A better interpretation would be made if total leachate could be estimated (there are no flow volume data).

The above study was the motivation to further explore the relationship between the duration and the timing of the flooding and atrazine losses through drainage. The experimental design described later in this chapter was based in part on the Ritchie and Lizaso study.

Important conclusions that seem to emerge from the literature are:

1. Drying of the soil surface seems to limit growth and nutrient use. A high water table is beneficial because it supplies water for transpiration and increases nutrient use efficiency.
2. Chemical concentrations in tile effluent often relate to flow rates. However, the relationship is not straightforward; Concentrations may initially increase or decrease with flow rate depending on whether the chemicals have relocated within the soil structural units.
3. Excesses of N fertilizer lead to high NO_3-N concentrations in the tile effluent. Fertilization should be combined with realistic yield goals so that N is efficiently used by the crop. This is true of all water regimes, not just high water table.
4. Nitrate and atrazine persist over the winter, so management decisions should span more than one season. Reduced NO_3-N losses in drainage discharge may be a benefit of maintaining a high water table throughout the year. The suspected cause is denitrification favored by anoxic conditions.

RESEARCH OBJECTIVES AND GENERAL APPROACH

The objective of this study was to measure and compare concentrations, flow volumes, and plant growth among different water table management treatments. Concentrations were selected as a common measure of environmental impact. Some environmental regulation centers around permissible concentrations in groundwater. Flow volumes were selected because, combined with concentration, they yield the total leachate escaping the drains. Boll et al. (1992) recommend the use of tile lines for field scale experiments as "the only method that yields integrated groundwater-loading samples (both concentration and flow is measured), although time resolution is poor." Time resolution was maintained in this study by increasing sampling frequency when the experimental plots were drained. Water table depth was measured as part of the water table management operations. Measurements of water table depth, soil water content, precipitation, initial soil NO_3-N and atrazine, and other soil properties were collected as inputs to the simulation model, discussed in the next chapter. Plant measurements were taken, if they were easily obtainable; plant growth was not the main focus of this research.

Because natural precipitation is unpredictable, conditions of intense rainfall and flooding had to be artificially recreated. Flooding events were created at two different times during the growing season and for two different durations.

MATERIALS AND METHODS

Site Selection

The study was done at the Michigan State University Box Farm. The soil is Capac loam (Aeric Ochraqualfs; fine-loamy, mixed, mesic). The series consists of somewhat poorly drained, moderately and moderately slowly permeable soils on till plains and moraines. It has a seasonal high water table within 30 to 61 cm of the surface in winter and spring. The major limitation in this cropland is the excess water, which often delays planting and harvesting. Tile and surface drains are needed (Soil Conservation Service, 1979). A more detailed description of the soil series is in Appendix A.

The controlled subirrigation/drainage facility was designed, constructed, and tested by Lizaso (1993). The facility is shown in Figure 2, drawn approximately to scale. It has five lysimeters in a row each measuring 1.9 by 2.1 m. Each lysimeter is encased by a vertical 0.15 m thick, 1.35 m deep reinforced concrete wall that penetrates into the flow restricting layer. The top end is 0.15 m above the ground to form a basin around each plot. The facility runs in an east to west direction. A corrugated plastic tile, 0.1 m in diameter, is buried at 1.1 m depth in each lysimeter. The north side of the facility is bounded by an excavated working area. Valves in the working area control the outflow from each lysimeter. A vertical PVC cylinder, 0.15 m in diameter, is found at the corner of each lysimeter (Figure 3). The PVC cylinder is used to elevate the water table as follows: Water from a tap raises the water level inside the cylinder to a height determined by the length of a controlling rod. When that level is reached the tap automatically shuts off. The bottom end of the vertical cylinder is connected to one end of the drainage tile. The other end of the drainage tile is capped. Therefore, water

that flows into the cylinder is forced by gravity to exit through the tile and thus raises the water table in the lysimeter. Observation tubes for monitoring water table depth and neutron probe access tubes were installed, one per plot. More details on the construction of the facility are given by Lizaso (1993).

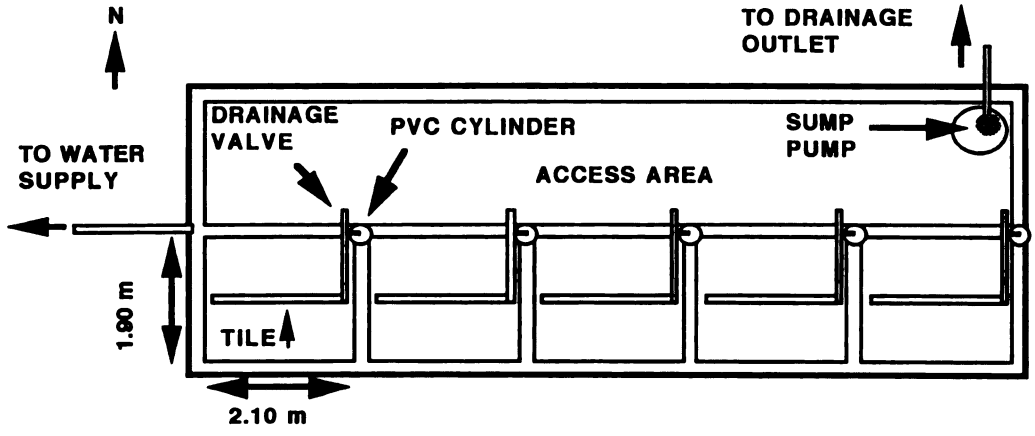

Figure 2. Layout of the experimental facility (plan view).

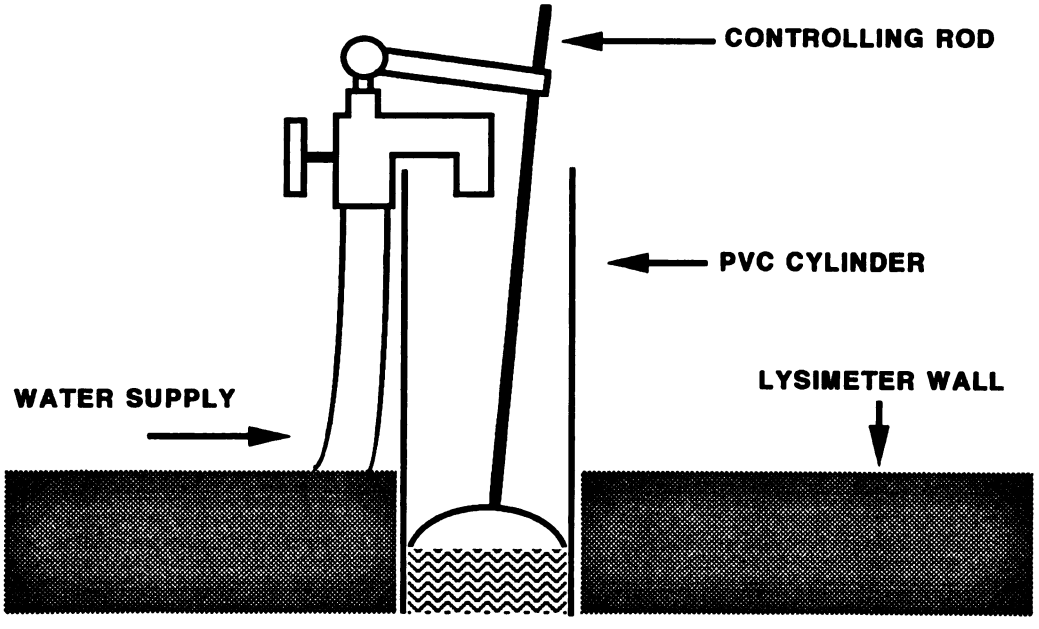

Figure 3. Detail of the water intake (side view).

Lizaso (1993) tested the facility and showed that the water table can be independently controlled in each lysimeter.

Site Preparation

On 28 Apr. 1992, the access area was drained and cleaned. The water table level in the lysimeters was allowed to drop to permit spring field operations. Between 13 and 20 May soil cores were taken to establish the initial conditions for NO_3-N and atrazine, soil water content, bulk density, organic matter, and pH. The sampling procedure is described in "Soil Sampling and Measurements."

On 21 May, the plots were prepared for sowing. The soil was turned with a shovel and leveled with a rake, approximately simulating mechanized cultivation. Corn ('Pioneer 3573') was sown at a population of 6 plants/m^2. Corn was also sown outside the facility, at least 10 rows along each side, to approximate the environment in the middle of a typical corn field.

Atrazine was applied on the same day at 1.121 kg/ha of active ingredient. The rate was based on Michigan Cooperative Extension Service guidelines for a mineral soil (Renner and Kells, 1994). The rate was achieved as follows: Forty-five hundredths of 1 L of atrazine product (Atrazine 4L [Shell], 42.2% active ingredient) were diluted in 9.46 L of water. The solution was applied with a backpack sprayer. A boom with four nozzles (Teejet® 730308) spaced 0.60 m apart delivered the solution at 450 kPa. At that pressure each nozzle could deliver 47.9 mL/s. The operator walked at 1.4 m/s.

Nitrogen fertilizer was incorporated at the time of sowing at a rate of 152 kg/ha of N (diammonium and monoammonium phosphate, with a percentage of urea undisclosed by the manufacturer). This rate could be

efficiently used by the crop based on experience by J. Lizaso (1992, personal communication) and E. Martin (1992, personal communication).

Flooding Treatments

Five treatments were randomly assigned to the five lysimeters:

1. An instant inundation starting at the appearance of the 8th leaf.
2. A 14 d inundation starting at the appearance of the 8th leaf.
3. An instant inundation starting 1 wk after silking.
4. A 14 d inundation starting 1 wk after silking.
5. The fifth lysimeter was used as a control and received no flooding. It was subirrigated so that the water table was close to the roots, based on past experience at the same facility by J. Lizaso (1992, personal communication).

The shorthand notation used from now on for the five treatments is Early-Short, Early-Long, Late-Short, Late-Long, and Control.

The time of the floodings was chosen to coincide with two distinct plant development stages: One of rapid vegetative growth, and one of slow vegetative growth, near grain filling. The duration of the floodings was chosen to simulate two cases: The first would be a well-managed field where the water table would rise to the surface but would promptly drain. The second would be a field that would remain ponded for several days due to poor management or because of a local depression that would not drain as fast as the rest of the field. Such a depression existed in the surrounding field, and it held water for most of the season.

On 21 June the water table in all plots was raised from 80 cm to 20 cm through subirrigation. On 26 June the first flooding (Early-Short) started. The water table was raised at first by sprinkling water on the plot. Three cm

of water were added at a mean time rate of 1.6 cm/h to simulate rainfall. However, infiltration was slow, possibly due to surface sealing. To complete the flooding and subsequent sampling in a day, approximately 1.1 cm of water had to be added through subirrigation. After raising the water table, the lysimeter was promptly drained.

On 14 August, treatment Late-Short started. The water table was deeper initially (81 cm), so 8.8 cm of surface irrigation were added at a mean time rate of 0.6 cm/h to bring the water table to the surface. The lysimeter was promptly drained.

Treatments Early-Long and Late-Long started on 26 June and 14 August. The water table was raised through surface irrigation and sustained about 5 cm above the soil surface for 14 d with surface additions of 8.4 cm/d.

Water Table Measurements

During construction of the lysimeters, plastic observation tubes had been installed, one per plot. To measure the water table depth, a thin, flexible plastic tube was inserted in the observation tube while blowing air. The sound of bubbles coming from the end of the flexible tube signaled the surface of the water table. The depth of the water table was determined by the depth marks imprinted on the flexible tube.

Soil Water Content Measurements

Before drainage and at each measurement interval, soil water content was measured with a neutron meter (Hydroprobe®, CPN Corp., 2830 Howe Rd., Martinez, CA 94553) at 13, 26, 42, 67, and 89 cm depths. Thirteen cm was selected as the shallowest depth to obtain a reliable measurement; the

neutron meter averages neutron counts from a sphere of approximately that radius. The exact radius depends on the water content. Eighty-nine cm was the deepest measured point permitted by the depth of the access tubes. The other depths were selected to match the standard soil layer depths used in the DSSAT family of crop models (IBSNAT, 1986), because water contents were to be used for simulation model testing (Chapter 3). The neutron meter had been previously calibrated by J. Lizaso (1992, personal communication). There was one access hole for the neutron probe per plot.

Soil Sampling and Measurements

Soil cores at 3.2 and 9.6 cm depth were taken on 13 and 14 May. A 2 cm diameter metal probe was used to sample at three points diagonally across each plot. More cores were taken between 18 and 20 May, from 17.5 to 137.5 cm depth at 10 cm intervals. For these later samples, one hole was drilled in every lysimeter except the middle one, later to be Early-Long. The middle lysimeter was not sampled because a rock impeded drilling. The cores were taken from the bottom of holes drilled with an auger, about 10 cm in diameter. The cores were taken with a cylindrical metal probe (6.8 cm height, 3.3 cm diameter) attached to the end of an iron pole about 2 m long. Before the probe was inserted, the bottom of the holes were lightly tapped with an iron cylinder to ensure a flat surface. Care was taken to minimize sample disturbance. The auger holes were refilled and packed with the excavated soil. All soil samples were temporarily stored and transported in an ice cooler. Later on the same day they were moved to storage at –20°C where they remained until analysis. The samples were analyzed for soil water content, organic matter, pH, NO_3-N, and atrazine.

The samples were thawed prior to analysis. For organic matter, pH, NO_3-N, and atrazine analysis they were air-dried, ground with mortar and pestle, mixed, and passed through a sieve with 3 mm opening. Soil water content was determined gravimetrically. Bulk density was taken from Lizaso (1993). Organic matter was measured by the loss on ignition procedure by the Soil Testing Lab at Michigan State University. A glass-calomel combination electrode (model No. 476 530, Corning) and a Hach meter (Hach Company, P.O. Box 389, Loveland, CO 80539) were used to measure pH in a 0.01M $CaCl_2$ solution. The soil to solution ratio was 1:1. The details of the method are given in Mc Lean (1982).

Nitrate-N was measured with an ion-specific electrode model 44430 (ISE, Hach Company) and volt meter (Hach Company). The analyses were done according to Keeney and Nelson (1982), and the instruction manuals of the electrode and meter (Hach Company, 1992). Standard NO_3 solutions were prepared to encompass the range of concentrations expected in each batch. Each sample was analyzed as follows: Ten g of air-dried, sieved soil, 25 mL of de-ionized water, and 0.75 g of ionic strength adjuster prepared by Hach Co. were added to a 50 mL beaker. The mixture was stirred vigorously for 30 s. A small amount of electrolyte was dispensed through the electrolyte dispenser built into the meter. The reading was taken once the meter display stabilized. Each reading was multiplied by a dilution factor of 2.5.

Atrazine was measured with a technique called enzyme-linked immunosorbent assay or ELISA (Thurman et al., 1990; Van Emon et al., 1989), or enzyme immunoassay analysis (Stearman, 1992). From now on the technique will be called immunoassay. Though immunoassay has been used in the clinical sciences for a long time, only recently it began to establish itself in pesticide residue analysis. Van Emon et al. (1989) and Rubio at al. (1991)

discuss the scientific and sociological reasons for this delay. In this study, immunoassay was selected for the following reasons:

1. It offers adequate precision and accuracy for the intended purpose with little investment in equipment and materials.
2. It requires a small sample size. The kit used in this study required 0.2 mL per sample per replicate.
3. Aqueous samples require little or no preparation.
4. Results can be obtained in 2 to 3 h for a batch of 25 aqueous samples in duplicate. The actual time and output depends on the apparatus available.

Atrazine immunoassay cross-reacts to varying degrees with related compounds, such as other triazine herbicides and atrazine transformation products. Cross-reactivity may be an advantage or a disadvantage, depending on the purpose of the study. In this study it is a potential disadvantage, because the objective is quantitative recovery of atrazine. But other triazine herbicides had not been applied at the facility for at least two years prior to the study, and the cross-reactivity with most atrazine transformation products is low; according to Ohmicron Corp. (undated, "RaPID Assays®: Atrazine") the least detectable concentrations of deethylatrazine, deisopropylatrazine, and hydroxyatrazine are 1.3, 17, and 24 times higher than for atrazine. Another study reports that the least detectable concentrations of deethylatrazine and hydroxyatrazine are 4 and 10 times higher than for atrazine (Bushway et al., 1988). The concentration that causes 50% inhibition or IC_{50} (i.e., a sample with half the optical density of the zero standard) is another measure of cross-reactivity. Thurman et al. (1990) found that the IC_{50} for deethylatrazine, deisopropylatrazine, and hydroxyatrazine are 75, 75, and 70 times higher than for atrazine. Bushway et al. (1988) report that the IC_{50} for deethylatrazine and hydroxyatrazine are 25 and 70 times higher than for atrazine.

Van Emon et al. (1989) cite literature to support the immunoassay method for analysis of pesticides other than atrazine. Rubio at al. (1991) show the suitability of immunoassay for atrazine measurement in water samples. Immunoassay performed well in the areas of precision, recovery, interference from NO_3, metal cations and pH, and correlated well to gas chromatography/mass spectrometry (GS/MS) for concentrations up to 14 µg/L. Thurman et al. (1990) compared immunoassay to GS/MS for analysis of triazines (including atrazine) and their metabolites in surface water and groundwater. Recoveries by both methods were comparable in the range tested (0.2 to 2 µg/L). Good correlation between the two methods was observed in the above range. Bushway et al. (1988) compared immunoassay to high-performance liquid chromatography (HPLC) for analysis of atrazine in water samples and in soils. Water samples from various sources were fortified with atrazine in the range 0 to 100 µg/L. Immunoassay gave better recovery in 7 samples, worse recovery in 12 samples, and equally good recovery in 11 samples. In soil samples the initial concentrations were unknown. In 10 out of 18 soils, the two methods agreed within 50% of the smallest of the two values. The Bushway et al. study could be better if the difference in optical density between the sample and the zero standard was normalized by the optical density of the zero standard, as in standard practice (Thurman et al., 1990; Rubio at al., 1991).

Soil samples were prepared according to the Ohmicron (375 Pheasant Run, Newtown, PA 18940) recommended protocol (Ohmicron Corp., undated, "Detection of atrazine, alachlor, cyanazine and metolachlor in soil"). Ten g of the air-dried, sieved soil were added to a bottle with 30 mL of a 3:1 methanol-to-water mixture. The bottle was shaken vigorously at 200 cycles/min for 30 min. The sample was allowed to settle for 18 h, was shaken again for 30 min, and was allowed to settle again for 15 min. One-half of 1

mL of the extract was diluted 1:50 with sample diluent (Ohmicron) and analyzed according to the enclosed assay instructions (Ohmicron Corp., undated, "RaPID Assays®: Atrazine"), also published by Rubio et al. (1991).

The basic reaction of an immunoassay is the linking of the antigen (in this case atrazine) with the antibody, a protein produced in response to the antigen. Antibodies possess binding sites that are specific to an area of the molecule of the antigen called an epitope or antigenic determinant. Antibody specificity for that area of the antigen and the resulting immune complex is what determines the specificity of the immunoassay (Van Emon et al., 1989). After the linking of the antigen to the antibody, the rest of the assay procedure isolates the complex and induces a chromogenic reaction. The intensity of the color is inversely related to the concentration of the analyte. Color intensity was measured in this study with the RPAIII Photometer (Ohmicron).

The least detectable concentration of the RaPID Assays® kit is estimated at 0.05 µg/L. This is within the National Primary Drinking Water Regulation Maximum Contaminant Level Goal (MCLG) of 3 µg/L, Practical Quantitation Level (PQL) of 1 µg/L, and Method Detection Limit (MDL) of 0.1 µg/L (USEPA 1991 [cited in Rubio et al., 1991]).

Effluent Sampling and Measurements

After each flooding treatment, water was released through the drainage valves. No measurements were taken for the first 30 s, the time for the water inside the intake cylinder to empty. Measurements were then taken at 3 and 5 min after drainage, then at 5 min intervals for the 1st h, every 15 min for the 2nd h, and subsequently every 1 h until dark. Measurements continued once a day for the next 15 d. Flow volume after each interval was measured

with a graduated cylinder. Drainage grab samples were taken after each interval for NO_3-N and atrazine analysis. Grab samples were temporarily stored and transported in an ice cooler. Later in the day they were moved to storage at –20°C until analysis.

Nitrate-N in drainage samples was measured with the same method and equipment as for soil extracts. No sample preparation or dilution was necessary except the addition of a 0.75 g pillow of powdered ionic strength adjuster, prepared by Hach Co. Atrazine in drainage samples was measured with the same method and equipment as for soil extracts. No sample preparation or dilution was necessary.

Samples of irrigation water were also analyzed. Nitrate-N was measured on 15 and 26 June, and 14 Aug. Atrazine was measured on 15 and 26 June.

Plant Sampling and Measurements

Two representative plants were taken from Early-Long and Control on the day Early-Long was drained (10 July) for dry mass comparison. Root mass was from a volume of soil approximately 20 cm in diameter around the base of the stem of each plant. Other treatments were not compared because of the small number of plants per plot.

To observe the effect of flooding on ear elongation rate, ear lengths of the treatment Late-Long were measured on 15, 18, 22, 25, and 28 August, and 5 September. The rate of grain filling would have been a better measure of the economic effect of flooding, but it would require destructive measurements. Ear lengths of treatment Control were measured for comparison.

After the growing season, the above ground parts were cut and separated into stems, leaves, cobs and grain. All parts were dried and weighed.

RESULTS AND DISCUSSION

Water Table Measurements

Figure 4 presents the water table depth since the beginning of water table management. The dotted line is the target depth. The criterion for the target depth was to provide adequate moisture to the roots without causing O_2 stress. As the roots grew deeper, the water table was lowered. The method was based on past experience at the same site (J. Lizaso, 1992, personal communication).

When Early-Short was drained, the water table would remain around 70 cm for several days, though the drains were at 105 cm. To eliminate the possibility that lateral flow from the adjacent lysimeter (Late-Short) hindered drainage in Early-Short, subirrigation in the adjacent lysimeter was temporarily interrupted.

Precipitation is in Figure 5. After heavy rainfall, some water would be released from all lysimeters to compensate for the rise in the water table. After the lysimeters were put in a drainage-only mode (28 August), the water table would rise for short periods due to precipitation. These peaks were not observed in Early-Long, apparently due to its higher hydraulic conductivity. This shows the variability in hydraulic properties to be expected in the field, even within very short distances.

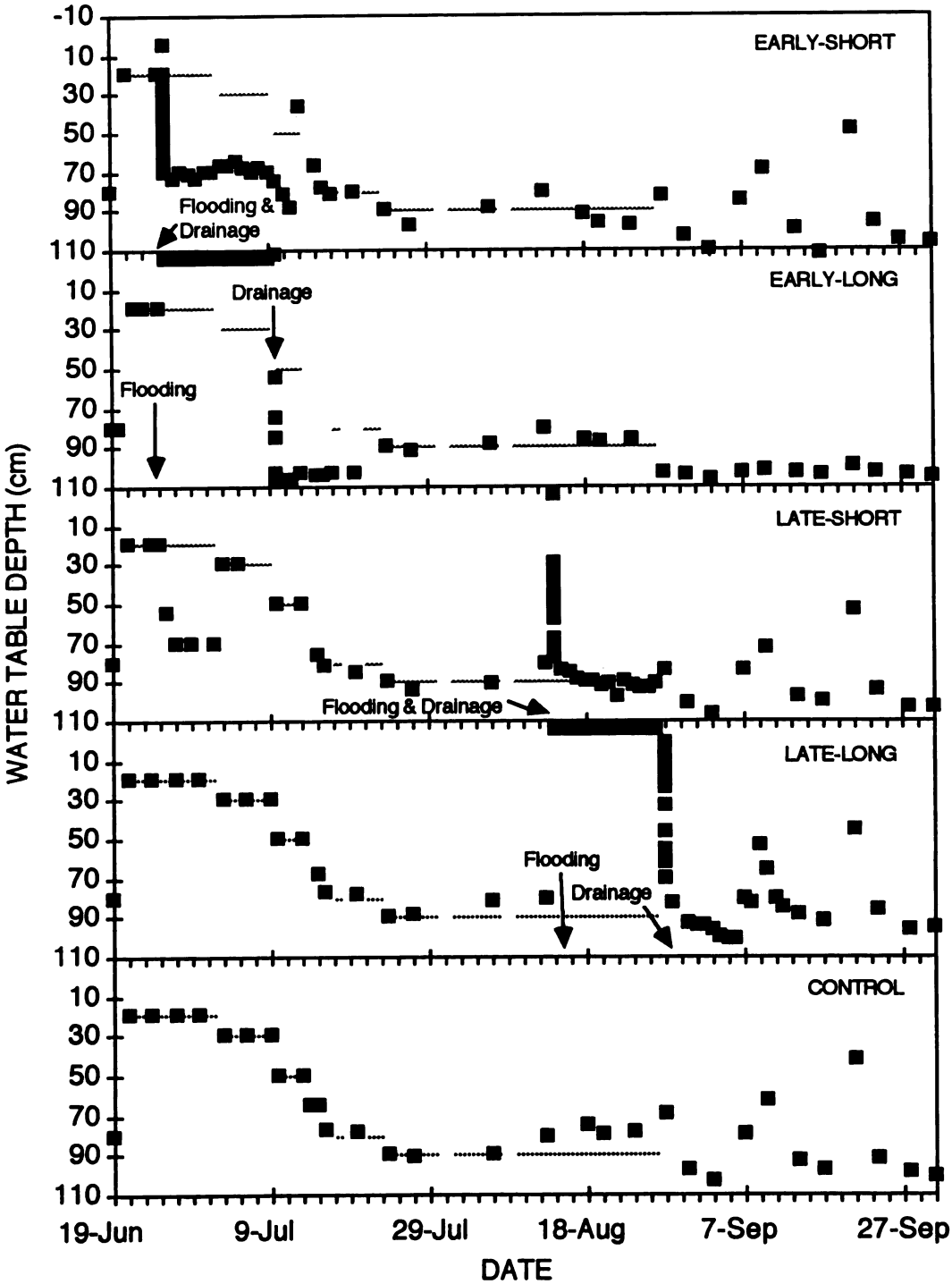

Figure 4. Water table depths during the season. The dotted line is the target depth.

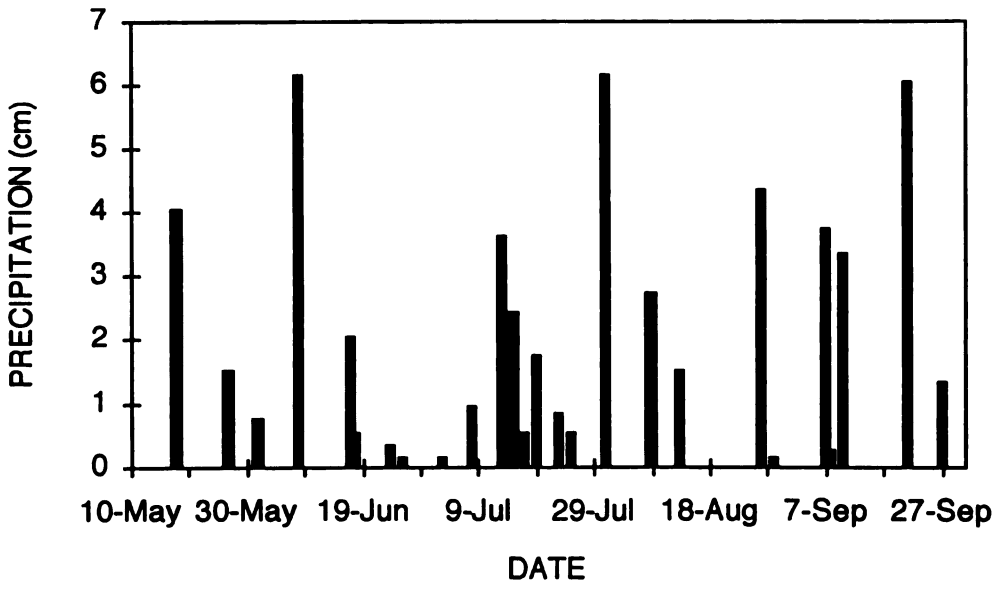

Figure 5. Precipitation during the 1992 season.

To maintain a shallow pond in the two long-flooding treatments, 8.4 cm of surface irrigation was added daily. Part of this amount was to replenish evaporation, and part was unaccounted for. To find how much was unaccounted for, a total water balance was calculated using the following equation:

Unaccounted = (Precipitation) + (Surface Irrigation) + (Subirrigation) - (Tile Drainage) - (Soil Evaporation) - (Plant Evaporation)

For the period of flooding, subirrigation and tile drainage were zero. Potential evaporation was used instead of soil and plant evaporation. Potential evaporation was estimated using the CERES simulation model (Jones and Kiniry, 1986). For the periods of flooding, potential evaporation estimates ranged from 0.1 to 0.7 cm/d. Thus, in days with no precipitation, 7.7 to 8.3 cm/d was unaccounted for. This amount most likely escaped through the bottom of the lysimeter. If this assumption is correct, then the

bottom of the lysimeter was a lot more permeable than expected given the bulk density and the soil survey description (Appendix A). On the other hand, sometimes even clayey soils have high permeabilities. Childs et al. (1957) were surprised to find that some clayey soils approach the permeability of gravel. They attribute that to fissures in clay.

Soil Water Measurements

Figure 5 shows volumetric water content (cm^3/cm^3). Water content at 89 cm for treatment Late-Short was not measured because water had seeped into the neutron probe access tube. It is not recommended that the neutron source be submersed in water.

In the two early flooding treatments, water extraction below 13 cm seems limited compared with the Control. This implies that flooding at an early stage disrupts root growth and reduces the subsequent water uptake capability of the crop. Lizaso (1993) found that a 4 or 8 d inundation in corn beginning at the 6th leaf tip severely reduces total plant root length and root density at 15 and 40 cm depth. He observed very little root growth near 90 cm, the deepest water table level that he maintained. This explains why water content changes so little at 89 cm.

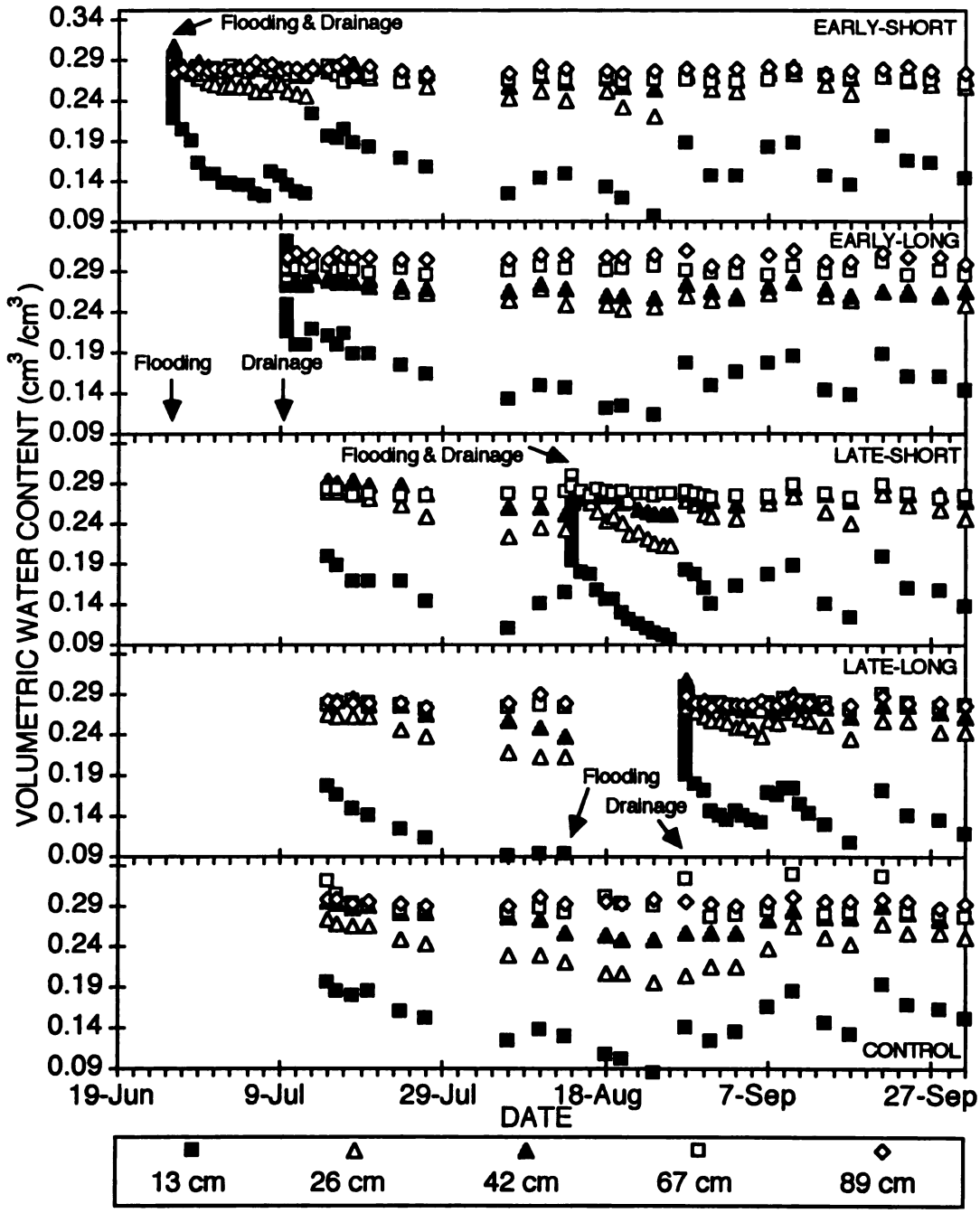

Figure 5. Volumetric water content at five depths during the season.

Soil Sampling and Measurements

Figure 6 and Table 1 show bulk density with depth (data from J. Lizaso, 1992, personal communication). These samples were taken from three holes outside the lysimeters, along the south edge of the facility and at approximately 2 m from it.

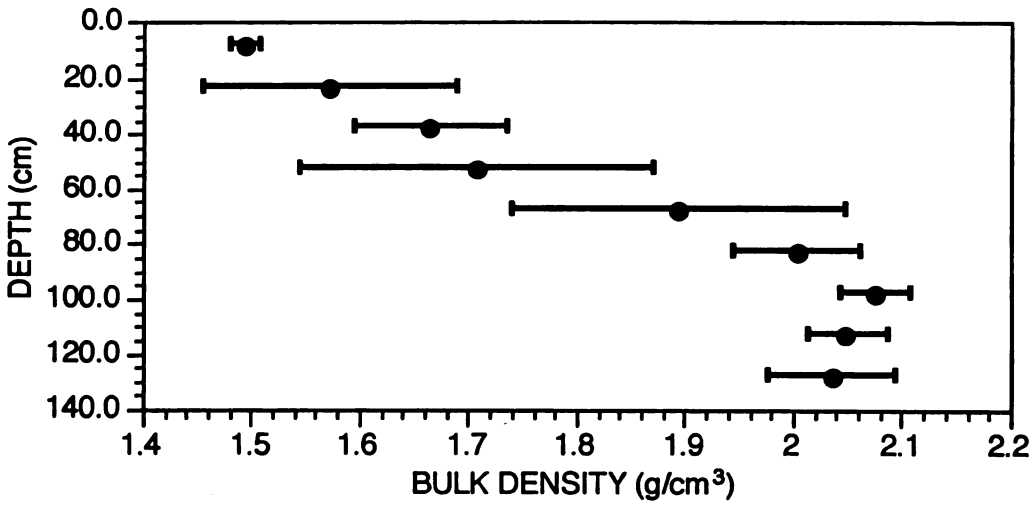

Figure 6. Soil bulk density (data from J. Lizaso, 1992, personal communication). Horizontal bars represent ±1 SD.

Table 1. Soil bulk density (data from J. Lizaso, 1992, personal communication).

Depth (cm)	Hole 1 (g/cm^3)	Hole 2 (g/cm^3)	Hole 3 (g/cm^3)	$\bar{x}$ (g/cm^3)	SD
7.5	1.48	1.49	1.51	1.50	0.01
22.5	1.69	1.46	1.56	1.57	0.12
37.5	1.75	1.62	1.64	1.67	0.07
52.5	1.85	1.74	1.53	1.71	0.16
67.5	2.04	1.90	1.74	1.89	0.15
82.5	2.07	1.99	1.95	2.00	0.06
97.5	2.11	2.05	2.06	2.08	0.03
112.5	2.07	2.07	2.01	2.05	0.04
127.5	2.08	2.06	1.97	2.04	0.06

Bulk density below 60 cm is unusually high and suggests a very impermeable soil. Yet, this is not necessarily so. Childs et al. (1957) found that fissures exist even in wet clay, and may cause clayey soils to be highly permeable.

Table 2 shows soil organic C content and pH. One sample was used from each of four plots. The same samples were used in both measurements. In the pesticide modeling literature, organic matter commonly is expressed as organic C content. Because one of the objectives of this study was to develop a simulation model, data are displayed as organic C. The conversion assumes 1.73 g organic matter for each g organic C (Taylor and Spencer, 1990).

Table 2. Soil organic C content and pH. The same samples were used in both measurements. Samples were taken 13 to 20 May.

Depth (cm)	Organic C (% of dry soil)			pH	
	n	$\bar{x}$	SD	$\bar{x}$	SD
3.2	4	2.0	0.07	7.6	0.09
9.6	4	1.9	0.09	7.7	0.10
57.5	4	1.1	0.10	7.8	0.26

Table 3 shows pre-fertilizer NO_3-N concentrations in soil. Table 4 shows pre-application atrazine concentrations in soil. The samples are separated by treatments to come. Some values are missing because the drilling of the auger hole was impeded by a rock, others because the soil sample was used for another analysis. The last column is the mean mass of the chemical expressed as percent of mass applied. Application rates were 152 kg/ha N and 1.121 kg/ha of atrazine active ingredient. The mass of a chemical is the product of soil volume, bulk density, and concentration. Bulk densities and concentrations were interpolated between sample points and extrapolated outside sample points. Each sample point represents half of the soil volume between that point and each of the adjacent points. The deepest sample point represents a layer with thickness equal to the distance from the point above it.

Table 3. Initial soil NO_3-N. Concentrations are mg/kg. The last column is mean mass as percent of fertilizer N applied. For the first two depths, n = 3 per plot, otherwise n = 1. Samples were taken 13 to 20 May.

Depth (cm)	Early-Short	Late-Short	Early-Long	Control	Late-Long	$\bar{x}$ (mg/kg)	SD	Mass (% app.)
3.2	18.4	14.2	12.2	13.3	12.7	14.2	2.5	8.8
9.6	18.8	18.6	12.3	11.8	15.0	15.3	3.3	10.9
17.5	34.6	20.0		17.1		23.9	9.4	21.7
27.5	6.2	14.7		14.4	13.2	12.1	4.0	12.8
37.5	2.1			2.2	1.9	2.1	0.2	3.4
57.5	2.2	2.14		0.6		1.6	0.9	6.7
107.5	0.6	1.2		0.5		0.8	0.4	5.2
							Sum =	69.5

Table 4. Initial soil atrazine. Concentrations are µg/kg. The last column is mean mass as percent of active ingredient applied. For the first two depths, n = 3 per plot, otherwise n = 1. Samples were taken 13 to 20 May.

Depth (cm)	Early-Short	Late-Short	Early-Long	Control	Late-Long	$\bar{x}$ (µg/kg)	SD	Mass (% app.)
3.2	212.5	134.9	97	125.3	122.0	138.3	43.8	11.6
9.6	116.5	94.3	80.5	63.7	65.5	84.1	22.0	8.1
17.5	175.9	161		70.0	119.8	131.7	47.5	16.2
27.5	21.6	63.3		20.6		35.2	24.4	5.0
37.5	59.6			69.9	99.1	76.2	20.5	16.9
57.5	46.6	42.8		26.1	19.7	33.8	12.9	10.7
77.5	91.0	46.6		13.3		50.3	39.0	22.0
107.5	130.4	110.8		50.4		97.2	41.7	53.6
137.5	33.6	42.1		48.2		41.3	7.3	22.4
							Sum =	166.5

Initial NO_3-N concentrations followed a regular pattern with depth, increasing to a peak at 17.5 cm and then declining. On the other hand, initial atrazine followed a more irregular pattern. The highest peak was at 3.2 cm, a lower one at 17.5 cm. Below that depth the concentration generally decreased down to 57.5 cm, increased to a peak at 107.5 cm, and then decreased down to 137.5 cm. Because atrazine sorbs on organic matter, it should remain at shallow depths, where most of the organic matter is. The peak at 107.5 cm could mean that it slowly leaches to deeper layers (a year had passed since the last application). Troiano et al. (1993) detected similar patterns in the

distribution of atrazine, especially under furrow irrigation: A peak in the topsoil, suggesting a tightly bound fraction, and a second peak in the subsoil, suggesting a mobile fraction. Lower degradation rates in deeper layers may contribute to accumulation of atrazine. Lavy et al. (1973) report that the degradation rate of atrazine decreases with depth under either aerobic or anaerobic conditions.[5] Klint et al. (1993) found that atrazine does not degrade in groundwater.[6]

Effluent Sampling and Measurements

Nitrate-N and atrazine concentrations in tile outflow for the whole season are in Figures 7 and 8. Arrows point to the application date and the dates of flooding and drainage. After 21 June, effluent measurements were sporadic because the system was put in a closed (subirrigated) mode until 28 August. Any measurements during that period were taken when the flooding treatments were drained and when water had to be released after heavy rainfall. After the system was put in an open (drained) mode, measurements resumed at more regular intervals.

Nitrate-N and atrazine concentrations in tile outflow for the period following drainage of the flooded treatments are in Figures 9 and 10. The

---

[5]In one soil, atrazine-treated soil was phytotoxic even after a 41 mo incubation at 90 cm depth, but almost not phytotoxic at 40 or 15 cm depth. In another soil, the effect of depth was confused in part with the effect of the applied rate. Soil at 90 cm was less phytotoxic than at 40 cm, but it was treated with half the rate.

[6]Atrazine did not degrade 539 d after incubation in groundwater or 174 d after incubation in suspensions of groundwater and aquifer sediment taken from approximately 3 to 7 m depth. Atrazine did not degrade even after nutrients and primary substrates were added.

objective of these figures is to show possible relationships between outflow concentration and flow rate. To make small differences visible, the scale differs.

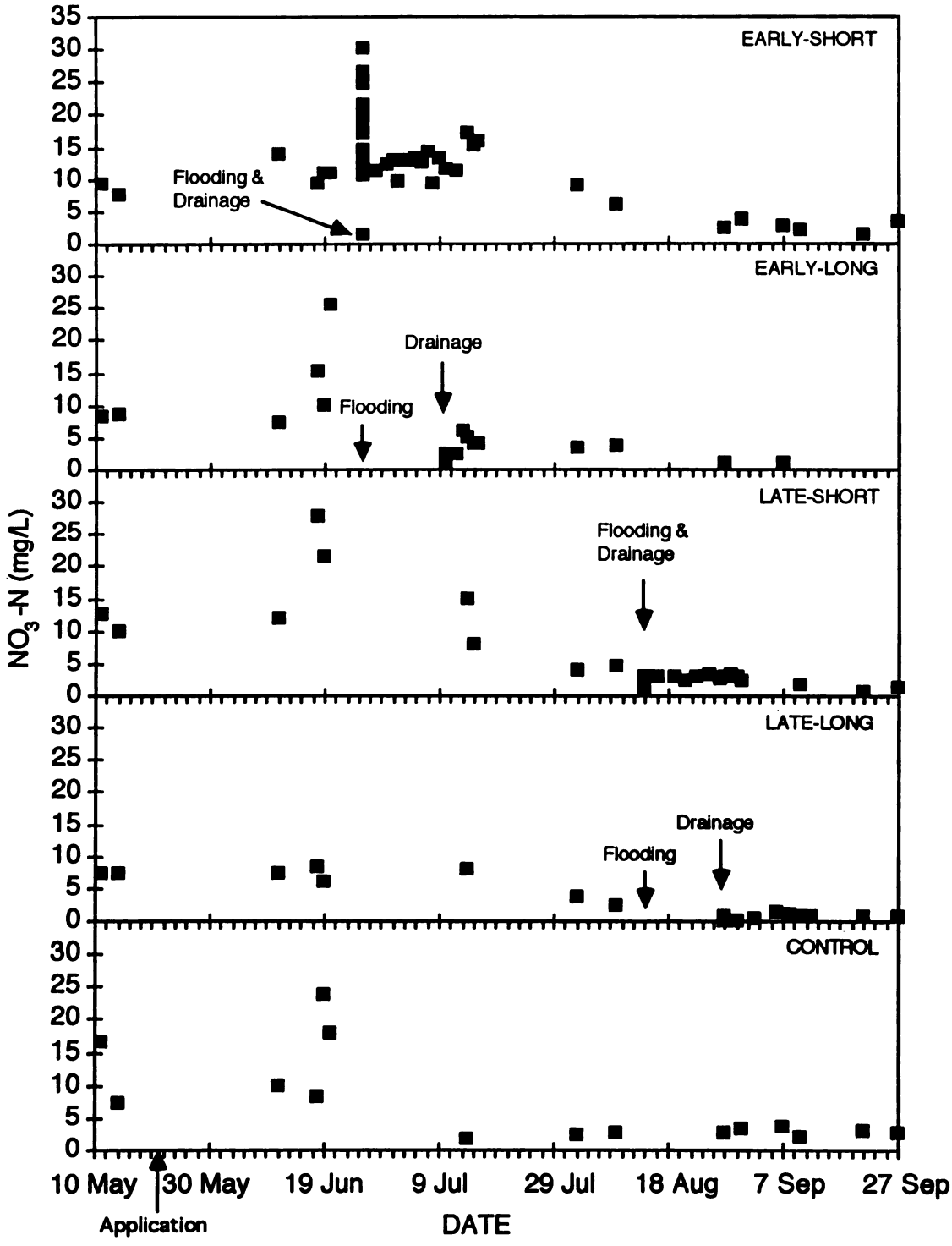

Figure 7. Nitrate-N concentrations in tile outflow for the whole season.

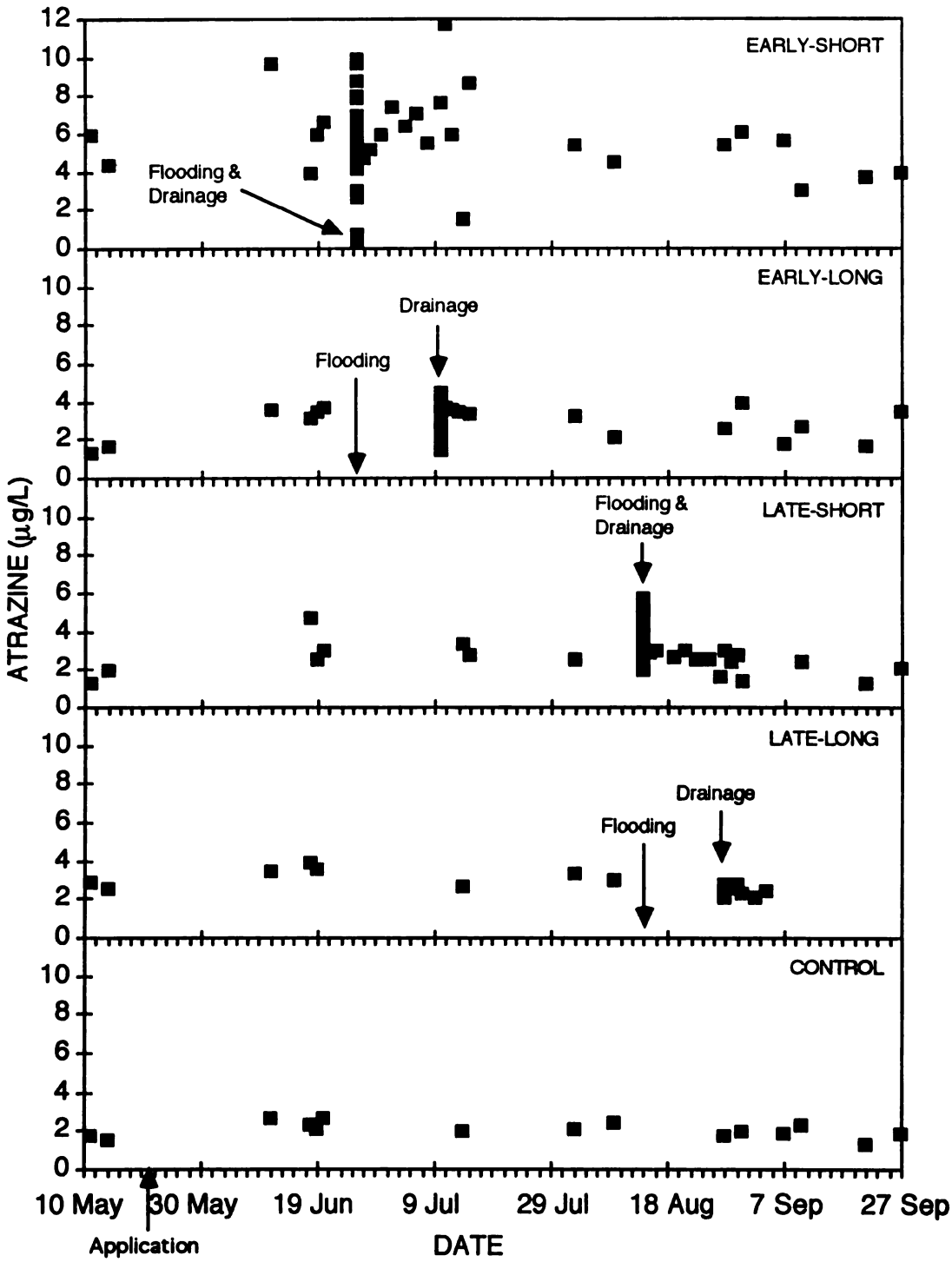

Figure 8. Atrazine concentrations in tile outflow for the whole season.

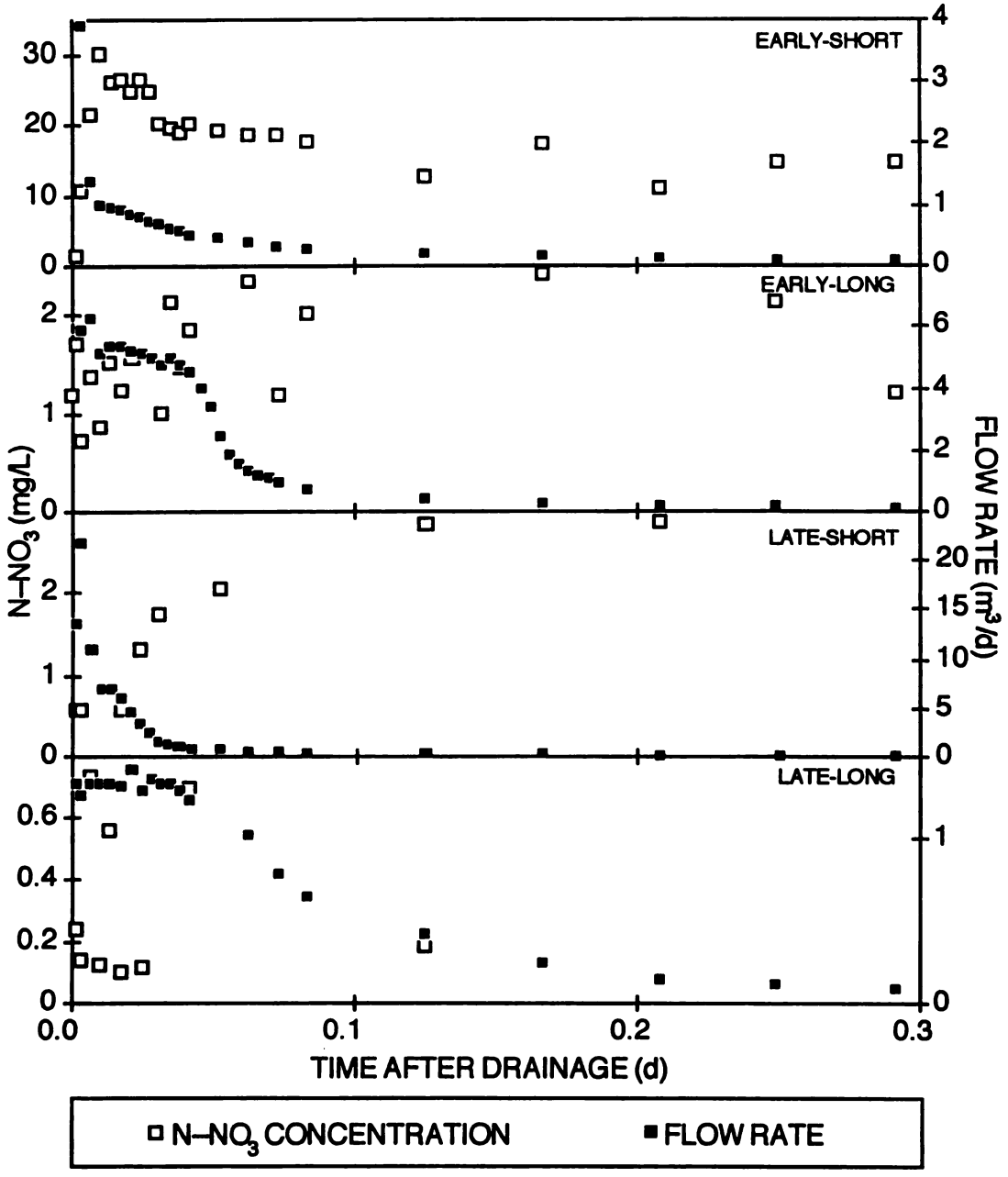

Figure 9. Nitrate-N concentrations in tile outflow for the period following drainage.

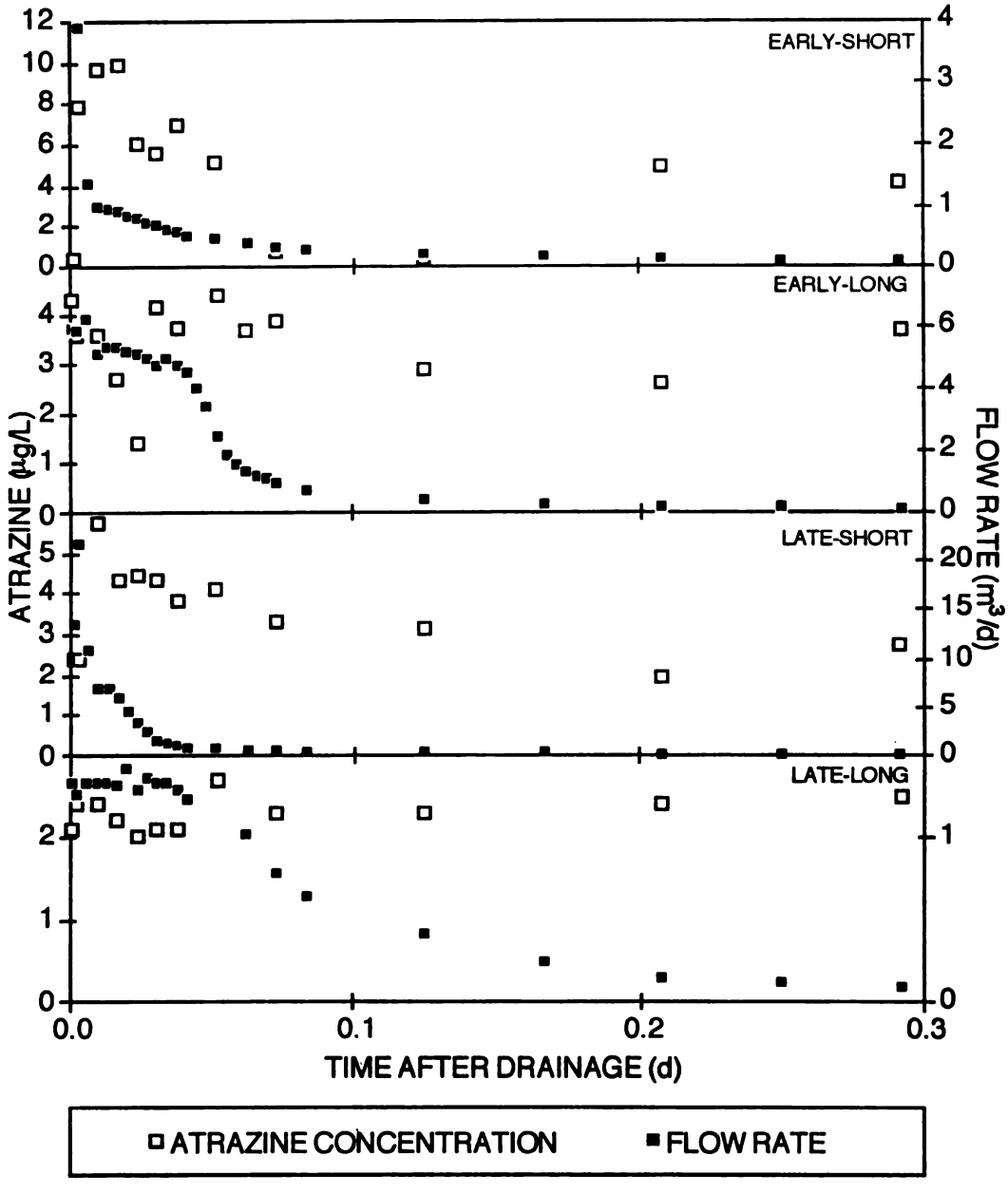

Figure 10. Atrazine concentrations in tile outflow for the period following drainage.

Nitrate-N concentrations increased after 18 June in three of the plots, possibly because of significant precipitation (2.5 cm) on the 17th and the 18th. Until then, all plots were treated the same. Pre-fertilizer soil N

concentrations were not necessarily identical, but fertilization should have smoothed out much of the difference. The fact that peaks were unequal shows that there is still variability to be expected in the field. It is also possible that concentrations from different plots peak at different times. For the rest of the season most concentrations were below 10 mg/L, except for Early-Short.

Treatment Early-Short had the highest peak NO_3-N concentrations on the day of drainage. This could be because the intensive water application leached down significant amounts of recently nitrified fertilizer from the topsoil. Near-saturated conditions during the initial stage of drainage guaranteed fast transport through a well-connected macropore network. Concentrations declined a few hours after the initial peak, as shown in Figure 9. It is probably not a coincidence that flow rates declined at the same time. As flow becomes unsaturated, macropores lose their continuity and their effectiveness as fast conduits of chemicals from the topsoil to the drains. It is also possible that as vertical flow rate decreases, the relative contribution of water moving laterally into the lysimeter from the surrounding field increases. The effect would be a dilution of the tile effluent.

Treatment Early-Long had much lower NO_3-N concentrations in the tile effluent when it was drained. Some NO_3-N could have leached, due to the daily water additions to maintain the water table. Some NO_3-N could have denitrified, due to anoxic conditions. On 13 July, heavy precipitation (3.6 cm) increased flow rate; in just 2.5 h, 0.6 cm had drained through the tiles, compared with a mean flow of 0.9 cm/d during the past two days. This high flow rate was accompanied by somewhat increased NO_3-N concentrations in both Early-Long and Early-Short, which again suggests that increased flow rate is associated with increased concentrations.

The two late flooding treatments had lower peak NO_3-N concentrations after drainage than the two early ones. By the time of the late flooding, significant N was likely to have leached, used up by the crop or degraded. At the time of the flooding, corn was 1 wk or more into silking but the ears had not yet attained full size. This corresponds to the R1 (first reproductive) stage, characterized by rapid N uptake (Iowa State University of Science and Technology, 1989). Some N in Late-Long must have leached during flooding, due to the daily water additions to maintain the water table. Nitrogen losses to denitrification probably were promoted by the anoxic soil environment.

Treatment Control was never inundated. Effluent was collected when water was drained after significant precipitation, and after the lysimeters were put in open (drained) mode. After 20 June, NO_3-N levels remained nearly constant.

Figure 9 shows drainage rates and concentrations during the short interval following drainage of the flooded treatments. Concentrations in Early-Short rise fast and then decrease with decreasing flow rate. It takes much longer in Early-Long and Late-Short for the concentrations to rise; concentrations keep increasing as drainage approaches zero. Especially in Late-Short, where the pattern is more clear, it seems that a significant fraction of NO_3 had moved within soil aggregates before the flooding. The rate of its subsequent release into the more mobile interaggregate water was controlled by diffusion, not convection. This is consistent with observations by Milburn et al. (1990). In Late-Long, NO_3-N concentrations after drainage follow an irregular pattern, but they are so low that this irregularity can be instrument noise.

Peak atrazine concentrations during the season were highest for Early-Short. Concentrations from this plot were higher even before inundation,

and they frequently were higher during the rest of the season. This contrasts with Ritchie and Lizaso (1991) who found that the early but longest inundation led to higher atrazine concentrations. This can be explained in part by different pre-application concentrations in the top soil layers of Early-Short. Also, the design of the Ritchie and Lizaso study was different; the flooding durations were 4 and 8 d, initiated at 19 and 38 d after atrazine application.

Atrazine concentrations in Early-Short seem related to flow rates. Unlike NO_3-N, atrazine concentrations started to rise again 2 d after drainage, and reached the highest value of the season 15 d after drainage. The reason for this increase is not clear. Drainage flows did not increase during the same period, and there was no significant precipitation. It is possible that a fraction of the atrazine was not flushed during the initial intense but short drainage event. Atrazine slowly diffused into the mobile interaggregate solution several days later. Atrazine is not as mobile as NO_3, so it took longer. Another explanation involves sorption non-singularity. Koskinen and Harper (1990) propose that there are "labile" and "restricted" soil surface sites. Sorption onto labile sites is easily reversible, but sorption onto restricted sites is not. If the rate of the reaction going from restricted to labile sites is slow compared with the rate of the reaction going from labile sites to solution, then sorption is hysteretic. The slow stage determines the overall desorption rate.

During drainage of Early-Long, high flow rates on the first day were associated with increased atrazine concentrations. Some fluctuation was observed very shortly after drainage (Figure 10) but, unlike Early-Short, an increase in concentrations was not observed in later days. This could be explained by better equilibrium between the intraaggregate and interaggregate solution, due to the long period of submersion.

During drainage of Late-Short, concentrations very soon reached a season maximum and then declined. There is no easy explanation why the NO_3-N peak was observed a few hours after the atrazine peak (Figures 9 and 10). Based on the relative mobilities of the two chemicals, the opposite would be expected.

In Late-Long, drainage did not result in an increase in concentrations. This was the last plot to drain, so plant uptake, leaching below the tile zone, and decomposition probably removed a lot of the "mobile" atrazine before the flooding. Levels of atrazine in drainage water were about the same as before application. According to Durand and Barceló (1992) atrazine forms "bound" residues with time.

Environmental impact depends on the total leachate that reaches a water body and not on the concentration at the point of discharge. Figure 11 shows cumulative NO_3-N leachate and cumulative atrazine leachate versus cumulative flow, for the period following drainage. Arrows point at the beginning of drainage and at the flow volume after 2 d. Nitrate-N and atrazine are shown as % and ‰ of amount applied. To show small differences, graph scales differ. Figure 12 is cumulative leaching plotted against time. Some graphs have fewer data points because a bucket overflow interrupted cumulative drainage measurements.

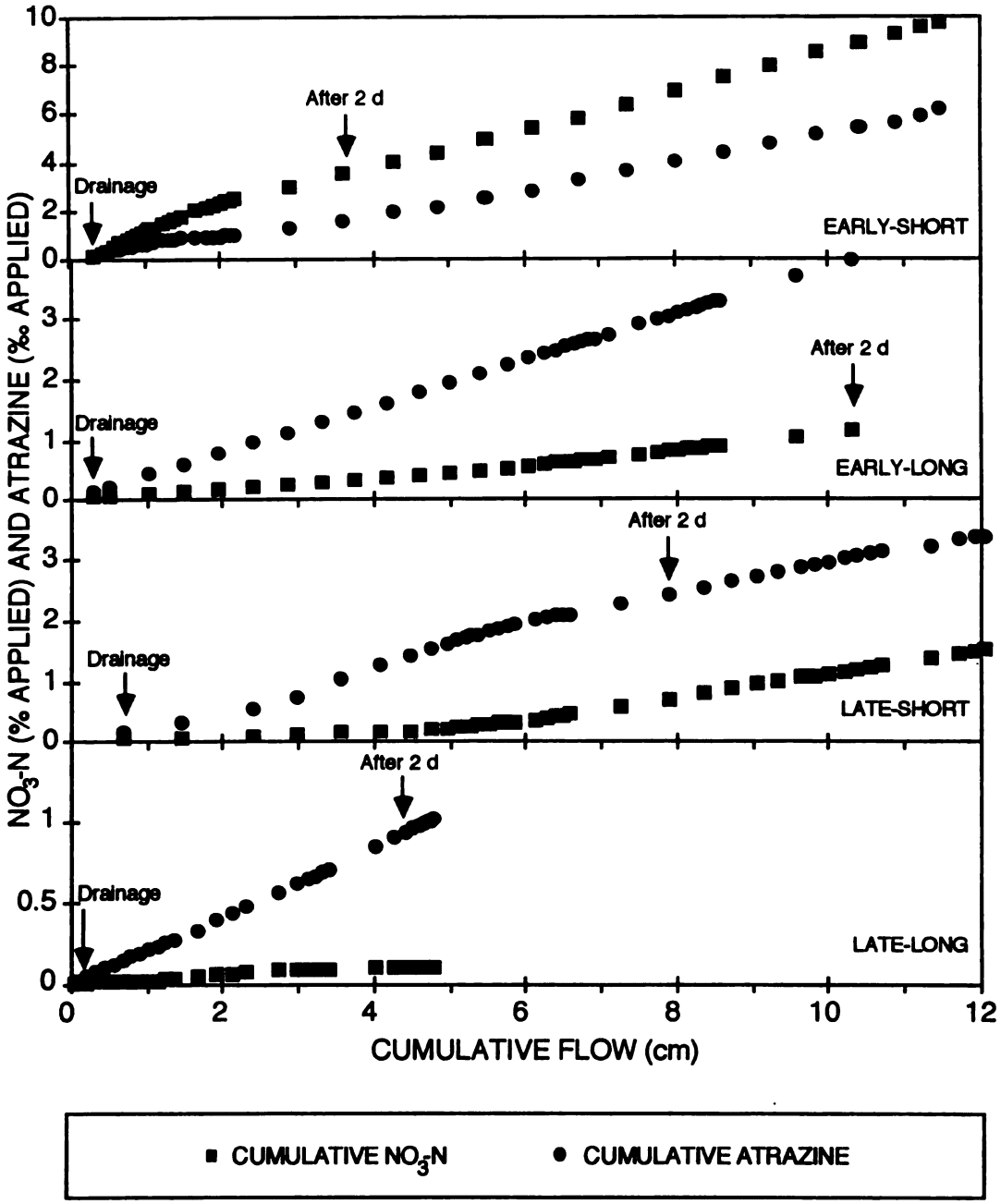

Figure 11. Cumulative NO_3-N and cumulative atrazine that escaped the drains during the period immediately following drainage of the four flooded treatments. Cumulative leaching is plotted against cumulative drainage.

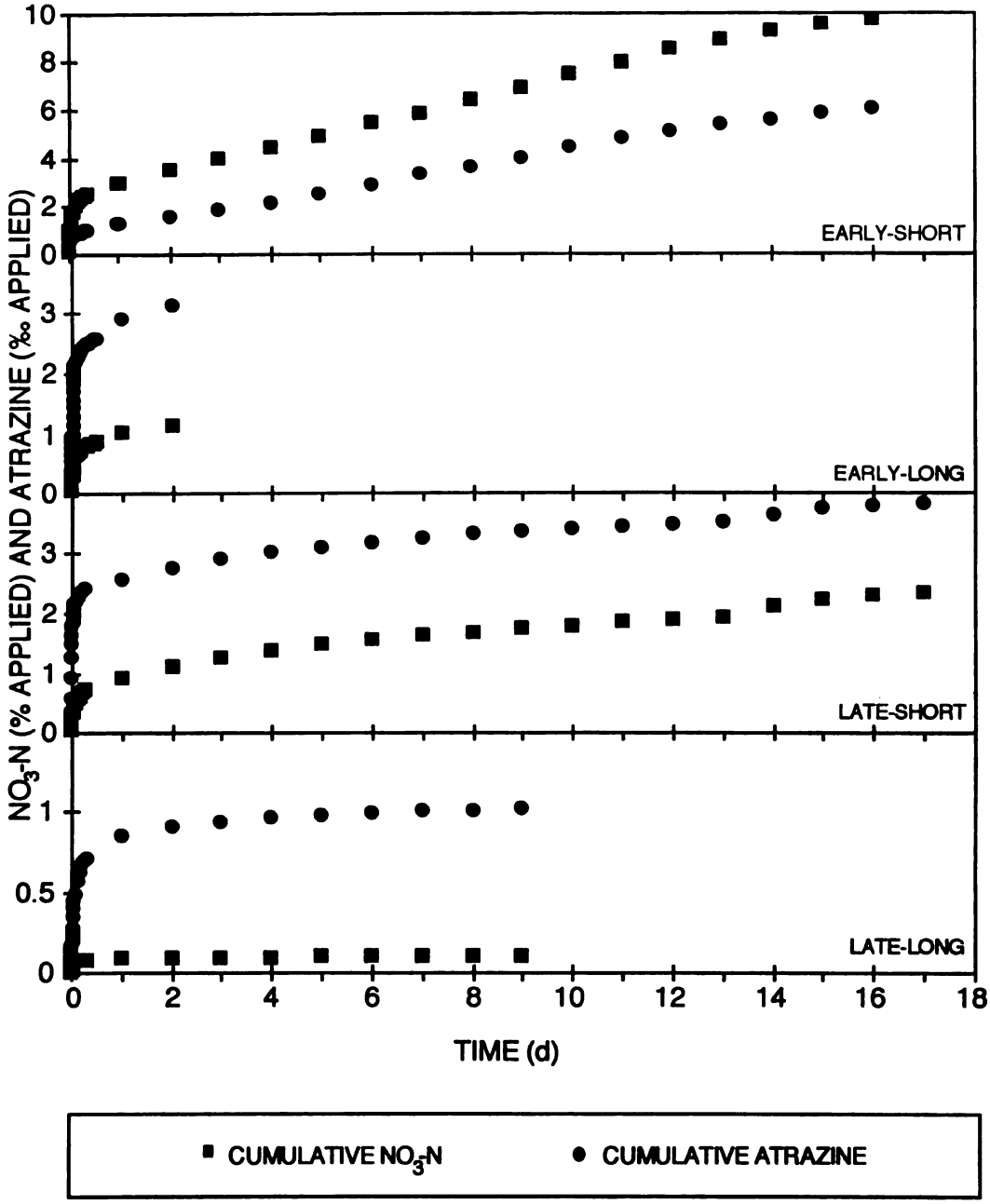

Figure 12. Cumulative NO_3-N and cumulative atrazine that escaped the drains during the period immediately following drainage of the four flooded treatments. Cumulative leaching is plotted against time.

For a fixed time (2 d, the longest period of uninterrupted measurements in all plots), Early-Short had the highest NO_3-N loss in tile drainage. In the same amount of time, Early-Long had the highest atrazine loss.

Differences in cumulative flow volume among treatments could reflect differences in water holding capacity, initial pond height, hydraulic conductivity, surrounding water table depth, and precipitation. To remove the effect of flow volume, cumulative leachate was also compared for a fixed volume of drainage; 4.8 cm, corresponding to the longest period of uninterrupted measurements in all plots. Early-Short produced the highest cumulative NO_3-N loss, because of higher concentrations overall. Cumulative atrazine was not very different among Early-Short, Early-Long, and Late-Short, despite the differences in peak concentrations. Cumulative atrazine was lowest for Late-Long.

The slopes of the cumulative leaching curves of Figure 11, multiplied by the application rate, represent the amount of chemical leached per unit volume of drainage. For treatments Early-Short, Early-Long, Late-Short, and Late-Long, the average slopes are, in that order: For NO_3-N, 1.3, 0.1, 0.2, and 0.03 kg cm^{-1} ha^{-1}; for atrazine, 0.6, 0.4, 0.3, and 0.2 g cm^{-1} ha^{-1}.

In addition to drainage effluent, irrigation water was periodically tested for NO_3-N and atrazine. Irrigation water may introduce bias in the results if it is contaminated with chemicals. Samples of irrigation water yielded the following NO_3-N concentrations: 0.9, 1.2, and 0.7 mg/L on 15 June, 26 June and 14 August. Atrazine was 0.1 and 0.2 µg/L on 15 June and 26 June. Most of the time, these concentrations were much lower than those in the drainage effluent. Late in the season, NO_3-N concentrations in the tile effluent approached those in the irrigation water, but by that time irrigation had ended.

Total N and pesticide balance were not calculated. A total mass balance would require measurement of daily flow volumes and concentrations throughout the season. It would also require plant tissue analysis. The expense of such measurements would exceed the resources of the project. Final soil concentrations could be measured, but it was decided that the lysimeters be left undisturbed for the preferential flow observation (Chapter 4).

Plant Measurements

The most obvious effect of flooding was in treatment Early-Long. Vegetative growth was severely retarded, lower leaves turned yellow, some with brown margin, and upper leaves turned light green. The appearance of reproductive organs was delayed 5 to 7 d compared with other treatments. Small, upward pointing roots emerged from the soil around the base of the stem. These roots died after the plot was drained.

Two representative plants were taken from Early-Long and Control on the day Early-Long was drained (10 July). Figure 13 shows the difference in dry mass. Root mass is from a volume of soil approximately 20 cm in diameter around the base of the stem of each plant. Other treatments were not compared because of the small number of plants per plot.

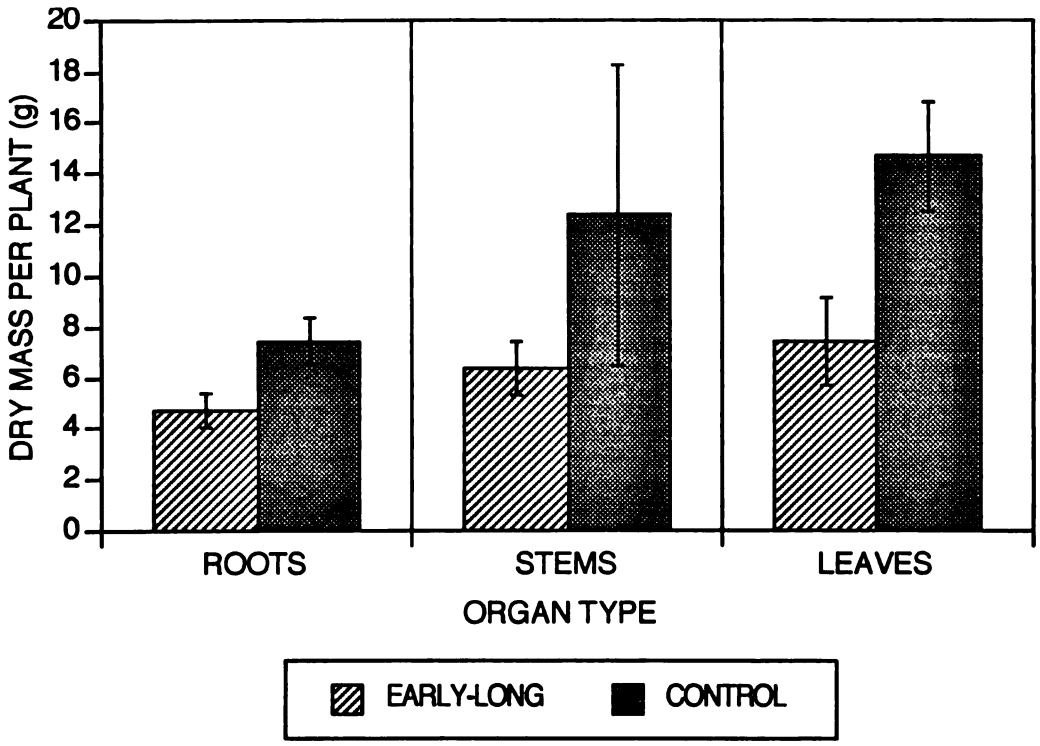

Figure 13. Dry mass for treatments Early-Long and Control. Thin vertical bars represent ±1 SD ($n = 2$).

Table 5 shows plant measurements at harvest. By harvest (3 October) the crop was not at physiological maturity due to cooler-than-normal temperatures during the season. The yield measures, therefore, are less than the potential of this variety. Due to the nature of the study measurements could not be replicated and therefore there was no analysis of statistical significance.

Table 5. Plant measurements at harvest.

	Treatment				
	Early-Short	Early-Long	Late-Short	Late-Long	Control
Kernels/m^2	2567	1014	2000	2484	3025
Kernel weight (g)	0 .24	0.22	0.25	0.24	0.25
Leaves (kg/ha)	2225	1193	2145	2368	3510
Stems (kg/ha)	3260	1138	3188	3235	1588
Cobs (kg/ha)	3500	963	2490	2563	3228
Grain yield(kg/ha)†	7317	2619	5905	6929	9080
Biomass (kg/ha)	15167	5507	12814	14021	15999

†Includes 15.5% moisture.

Figure 14 shows mean ear elongation rates of Late-Long during flooding. Ear elongation rates of Control are shown for comparison. The elongation rate is the mean daily increase from each measurement date shown to the next.

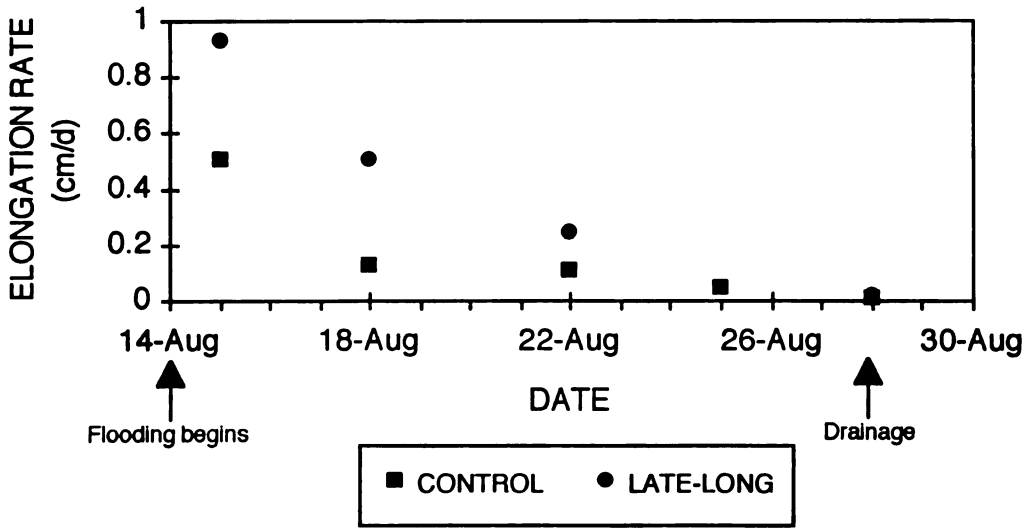

Figure 14. Mean ear elongation rate of treatment Late-Long during flooding.

All plants in Early-Long survived but never fully recovered from the flooding damage. All plant measures were affected. Root death due to lack of O_2 has been demonstrated by Lizaso (1993). Early depletion of soil N through leaching prevented the crop from recovering after the flooding.

Prolonged flooding did not cause as much plant damage late in the season as it did early in the season. Ears continued to elongate during flooding of Late-Long. The most visible effect in Late-Long was accelerated leaf senescence. Older leaves senesced first, possibly because as N became a limiting factor for growth it relocated from older to younger organs. Trought and Drew (1980) associate premature senescence of the first leaf of 11 d old, flooded wheat plants with net N movement out of that leaf. Lizaso (1993) observed premature leaf senescence as an immediate response of corn to flooding.

Yield of Late-Long was not as severely affected as that of Early-Long. Either photosynthesis did not stop, or the crop used reserve assimilates to

respond to O_2 stress. Under the second hypothesis, at the onset of flooding adequate carbohydrates were stored in the plant. The flow of assimilates to the grain continued during flooding, and it was sufficient to produce a reasonable yield. In treatment Early-Long, however, the plants were too young to have sufficient reserves.

Treatment Control had the highest yield and biomass. This implies that any amount of flooding has an adverse effect on yield and biomass. Root damage and N depletion through leaching are the likely causes. Root damage is more likely for the long flooding treatments than the short ones; interpolating data from Lizaso (1993) implies that 1 d of flooding would not seriously impact on total root length and root density. After 2 to 3 d differences show clearly.

Assuming that 1 kg of grain removes approximately 0.03 kg N (Hartmann, 1988), the five treatments removed the following amounts of N, expressed as % of N fertilizer applied: Early-Short, 122; Early-Long, 44; Late-Short, 98; Late-Long, 116; and Control, 151. Some N must have been provided from sources other than fertilizer, such as N stored in the soil from previous years, precipitation and irrigation.

CONCLUSIONS

Tile drainage sampling is an effective way to study the effects of water table management because it integrates flow and concentration over the study area. The NO_3 electrode and atrazine immunoassay are cost-effective ways to measure a moderate number of samples.

The duration of flooding affects peak concentrations of NO_3-N and atrazine after the water table is lowered. Shorter duration was associated with higher peaks. The duration of flooding possibly affects cumulative NO_3-N

losses for a fixed volume (4.8 cm) of tile drainage; early in the season, shorter duration was associated with more NO_3-N, but late in the season the difference was small. The duration of flooding did not affect cumulative atrazine losses in 4.8 cm of drainage.

The timing of flooding affects peak concentrations of NO_3-N and atrazine after the water table is lowered. Early inundation was associated with higher peaks. The timing of flooding possibly affects cumulative NO_3-N and atrazine losses in a fixed volume (4.8 cm) of tile drainage; earlier flooding was associated with more NO_3-N, though the difference between the long flooding treatments was small. Earlier flooding was also associated with more atrazine, though the difference between the short flooding treatments was small.

All flooding has some negative impact on yield. Plant damage is greatest for prolonged inundation at an early vegetative stage. Growth and development are retarded, and the final yield is poor. The same inundation has much less effect if applied at a later stage, probably because the plant uses N and carbohydrate reserves.

The above conclusions are subject to the limitations of the study, such as the lack of replication and the fact that the bottom of the lysimeters was much more permeable to water than a typical field with subirrigation/drainage.

Information from these measurements, supplemented with appropriate theory, can help develop decision support tools to predict the environmental impact of water table management. The development of a simulation model is the objective of the next chapter.

CHAPTER III

SIMULATION OF ATRAZINE AND NITRATE LOSSES AS INFLUENCED BY WATER TABLE MANAGEMENT

PROBLEM STATEMENT AND OVERVIEW

Much of Michigan cropland could potentially benefit from subirrigation (Belcher, 1988). Yet there are knowledge gaps regarding the effects of water table management on pesticide and nutrient losses. Long-term data collection is appropriate. Meanwhile, integrated crop-soil-atmosphere simulation models can help assess yield benefits and environmental risk. Though not a substitute for empirical data, a tested simulation model can evaluate a range of alternative management strategies that would be impractical to replicate in the real world. Simulation may guide data collection by revealing knowledge voids and posing new questions. Simulation can be a safe and inexpensive way to educate farmers and scientists about risks and benefits before costly investments are undertaken. Finally, once subirrigation systems are in place, it may help manage day to day operations such as irrigation scheduling and chemical applications.

Protasiewicz et al. (1988), after reviewing the most popular U.S. water quality models, found none that would model both a shallow water table and water quality. This study adapted CERES, a soil-crop-atmosphere model, to simulate both a shallow water table and NO_3-N and pesticide loading of drainage water. CERES also simulates crop growth and phenology, yield, and

water balance (evaporation, upward flow, drainage, soil water content). Until now, CERES could simulate surface irrigation but not subirrigation.

PRINCIPLES OF SOIL SYSTEMS SIMULATION

The Soil as a System

A system is a collection of material components or objects that work together as an entity. An outer boundary separates the system from its environment. Matter and energy flow within the system and across the boundary. A system is composed of subsystems, and most systems are components of larger systems.

The soil is a complex system with abiotic and biotic material components. Clay minerals, water, nutrients, and pesticide residues are some of the abiotic components. Roots, bacteria, and arthropods are some of the biotic components. There is a flow of energy (e.g., heat, light, chemical bond energy) across the boundary and among system components. Several subsystems can be identified (e.g., soil aggregates, pore water), and all soil is part of a larger system, the lithosphere.

Simulation Models

A simulation model is an analog of a real world system. Some components and functions of a model correspond one-to-one with some of the components and functions of the real system. A model imitates only the features of the system that are interesting to the modeler, therefore two models of a system may not be alike.

Simulation models may be physical analogs, mathematical abstractions, or computer models. Columns of repacked soil and lysimeters are simple physical analogs of soil profiles, useful in simulating processes such as leaching and sorption.

Mathematical models are the mathematical relations that describe the behavior of natural systems. Mathematical models may be deterministic relations or empirically derived, statistical relations. Deterministic relations, also called laws, have some universally recognized theoretical basis, and any deviation of the observations from this relation is considered experimental error (Bhattacharyya and Johnson, 1977). Laws are true. Statistical models, on the other hand, are relations derived by curve-fitting. They do not necessarily represent cause and effect. These relations are not necessarily backed by theory, and extrapolation is not possible.

Computer simulation has increased the usefulness of mathematical models. Analytical solutions often do not exist or are too time consuming to be practical. Numerical solutions are fast, and generally yield reasonable approximations. By delegating the tedious calculations to a computer, modelers can afford to create more detailed and realistic models of soil systems.

The Process of Simulation Modeling

Modeling is the art and science of conceiving, designing, constructing, implementing and evaluating models of systems. It requires sound knowledge of the subject matter, sound knowledge of system science principles, and creativity. The steps in a typical computer simulation problem are:

1. Conception: A research, training or management need often leads to the conception of a model.

2. Design: The modeler develops the outline of the system to be simulated (components and relations). The modeler makes a series of abstractions to include only the relevant features of the system. The mathematical models are selected.

3. Construction: The design is translated into a computer language.

4. Implementation: The model is tested until it performs without programming errors. Improbable outcomes and other gross anomalies should be detected at this stage.

5. Evaluation: The modeler fine-tunes the model using real data sets and intuition. Comparisons of observed versus simulated outcomes point to design weaknesses or the need for further data collection. There may be several iterations of steps 2 through 5.

Detailed model-building methodologies can be found in Manetsch and Park (1990), and Eisen (1988).

Types of Simulation Models

Deterministic vs. Stochastic. A deterministic model yields the same set of outputs for each unique set of inputs. It has no uncertainty. Relations are treated as physical laws.

Stochastic models, on the other hand, assume that inputs are random variables. As a result, model outputs usually are uncertain. Stochastic models are more realistic because they provide a measure of the variability expected of nature. However, they require a knowledge of the probability distribution of the input variables.

Deterministic models can be used stochastically, too. In Monte Carlo studies (Kennedy, 1989) the modeler generates inputs based on a suitable distribution. After several model runs, the modeler assesses the stochastic properties of the model (estimator) based on the distribution of the outputs (estimates). Carsel et al. (1987 [cited in Wagenet and Rao, 1990]) give an example of a deterministic model used in Monte Carlo mode to evaluate risk from pesticide leaching.

Mechanistic vs. Functional. Mechanistic models usually are based on dynamic rate concepts. They incorporate basic mechanisms of processes such as Darcy's or Fourier's law and the appropriate continuity equations for material and energy fluxes. Functional models usually are based on capacity factors. They treat processes more simply, reducing the inputs required. Functional models require less computing capacity, because they do not need the small time steps needed for the numerical solutions of mechanistic models (Ritchie and Johnson, 1990).

Mechanistic models are useful mainly as research tools, whereas functional models are useful mainly to evaluate management strategies. Both types use some level of empiricism to reduce the need for input information (Ritchie and Johnson, 1990).

Research, Management, Screening and Instructional Models. Addiscott and Wagenet (1985) distinguish solute simulation models into research, management, and screening. Research models provide good quantitative estimates but demand substantial data inputs. Management models need less data but at the cost of reduced precision. Screening models screen chemicals into broad behavioral classes under narrowly defined field conditions. Screening models need less data and are the least detailed. Wagenet and Rao (1990) propose an additional category called instructional

models. These models are characterized by interactive simulation suitable for teaching.

The distinction among different model types is not clear. As micro-computer capabilities improve, it becomes easier to use detailed research models for management and instruction.

PRINCIPLES OF NUTRIENT AND PESTICIDE SIMULATION

Agricultural chemicals do not remain unchanged in soil but participate in physical, chemical and biological processes. These processes collectively decide their fate. One way of thinking about the fate of chemicals is in terms of sources and sinks. Some processes depend on matter coming from a source and others deposit matter into a sink. Figure 15 shows the major sources and sinks of agricultural chemicals. Another way to think about chemicals is to focus on the processes. The major processes and the mathematical models that describe them are the purpose of this section.

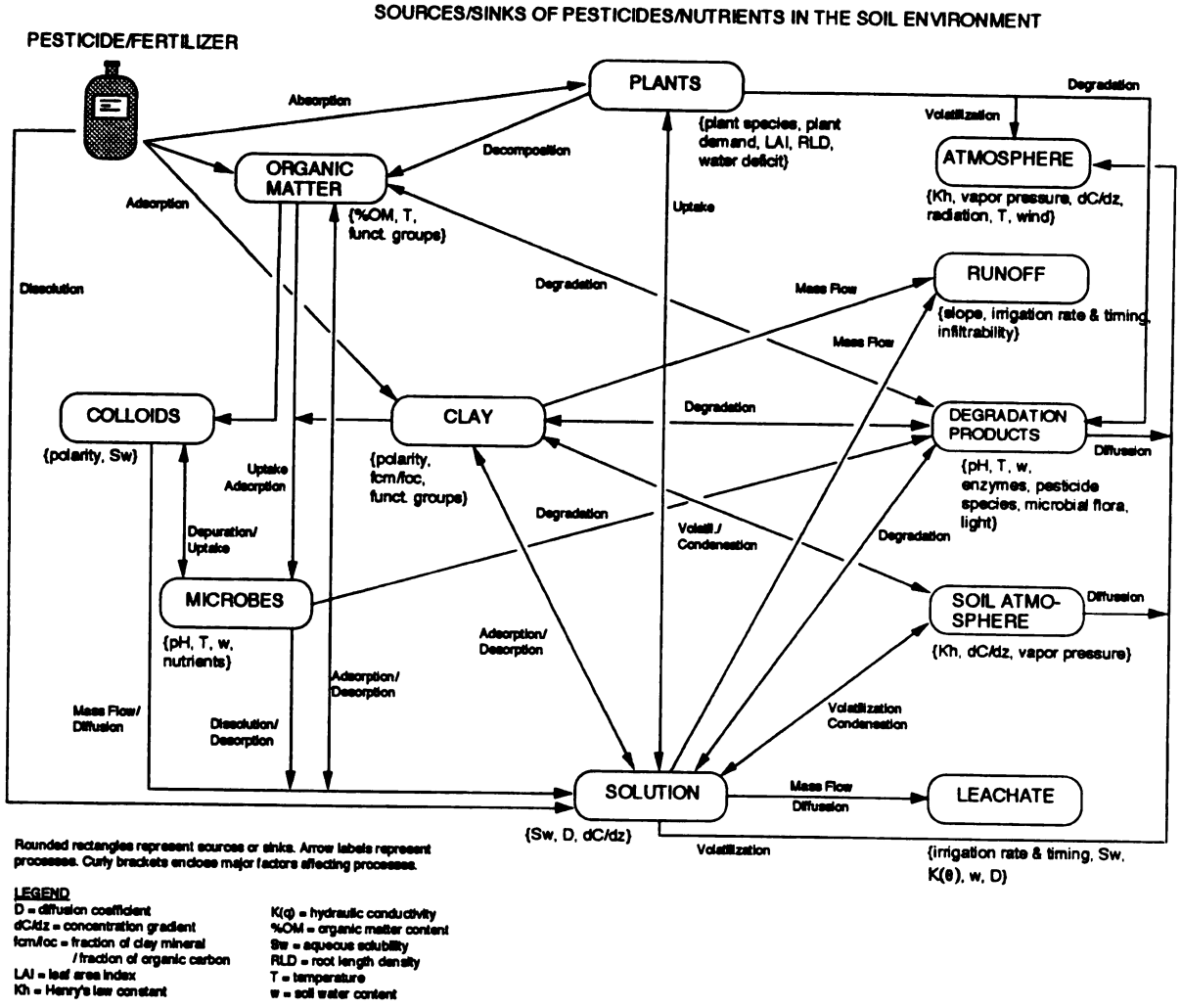

Figure 15. Major sources and sinks of agricultural chemicals.

Transport

Agricultural chemicals can be transported by convection or bulk flow of the solvent. Darcy's law governs one-dimensional, saturated flow. The volume of water passing through a unit area of the medium perpendicular to the direction of flow in unit time (flux density) is proportional to the gradient of hydraulic potential. The proportionality constant, K, is called hydraulic conductivity and depends on the soil (Marshall and Holmes, 1988):

$$v = Q/A = -K(d\phi/dx) \qquad [1]$$

where

v = discharge rate per unit area (flux density) [L/T]

Q = discharge rate through a cross-sectional area A [L^3/T]

K = hydraulic conductivity [L/T]

ϕ = hydraulic potential [L]

x = distance [L]

Darcy's law assumes that flow is laminar and accelerations are unimportant.

The law of the conservation of matter (Marshall and Holmes, 1988) dictates that:

$$\partial\theta/\partial t = -\partial v/\partial x + \text{sources} - \text{sinks} \qquad [2]$$

where

θ = volumetric water content [dimensionless]

t = time [T]

In other words, the rate of change of water content of an infinitesimal volume element is equal to the flux entering the volume minus that which exits the volume, plus or minus sources and sinks. Typically, the sink is plant uptake. For saturated soil, $\partial\theta/\partial t = 0$.

In the general case flow will be unsaturated and the hydraulic potential is given by:

$$\phi = \psi + z \qquad [3]$$

where

ψ = matric potential [L]

z = elevation above an arbitrary datum [L]

For vertical (along the z-axis) unsaturated flow, Eq. [1], [2] and [3] result in:

$$\frac{\partial \theta}{\partial t} = \frac{\partial (K(\theta)\, \partial \psi / \partial z)}{\partial z} + \frac{\partial K(\theta)}{\partial z} + \text{sources - sinks} \qquad [4]$$

where hydraulic conductivity now is a function of volumetric water content.

Experimental evidence suggests that $\psi = f[\theta(x)]$ (Marshall and Holmes, 1988). By the chain rule of differentiation:

$$\partial f[\theta(x)]/\partial x = [\partial f(t)/\partial t][\partial \theta(x)/\partial x]$$

and if soil water diffusivity D is defined as:

$$D = \frac{K(\theta)}{d\theta/d\psi}$$

then Eq. [4] becomes:

$$\frac{\partial \theta}{\partial t} = \frac{\partial (D\, \partial \theta / \partial z)}{\partial z} + \frac{\partial K(\theta)}{\partial z} + \text{sources - sinks} \qquad [5]$$

Eq. [4] and [5] are forms of the Richards equation (Hillel, 1982). Most mechanistic models of soil water flow solve Eq. [4].

Richards equation assumes that the soil is a rigid matrix and the air flow in the soil is unrestricted (Ross, 1990), and that the wetting front is stable (Beven, 1991). In field soils, these assumptions often are violated. Richards equation cannot model the fast movement of water on a macroscopic scale. During a heavy rainstorm or irrigation, water may move preferentially, by-passing the bulk of the soil matrix (Beven, 1991).

It would be an oversimplification to assume that solute transport depends on the mean water velocity. Water velocity varies locally in a porous medium depending on pore shape and diameter. The result is mechanical dispersion of the solute, also called hydrodynamic dispersion. The effect of mechanical dispersion often is combined with that of molecular diffusion in a single equation (Marshall and Holmes, 1988; Enfield and Yates, 1990; Wagenet and Rao, 1990). The convective flux of a solute with dispersion across a section normal to the positive x-direction of motion is:

$$q_s = \theta C \bar{v} - D\mathrm{d}(\theta C)/\mathrm{d}x$$

where

q_s = solute flux [$ML^{-2}T^{-1}$]

C = concentration [M/L^3]

$\bar{v}$ = mean velocity of solution in the pore space [L/T]

D = dispersion coefficient [L^2/T]

The dispersion coefficient is a function of the molecular diffusion coefficient of the solute in water, the tortuosity of the medium, volumetric water content, the darcian velocity, and an empirical constant called dispersivity. Various methods of estimating this coefficient are cited in Marshall and Holmes (1988), Enfield and Yates (1990), and Wagenet and Rao (1990).

Another mode of transport by mass flow is surface runoff. Some of the most popular U.S. runoff estimation models use the Soil Conservation Service curve number approach (Williams, 1991). Rather than a physical law, the curve number is an empirical constant that relates runoff volume with soil, land use, and management.

Sorbed contaminants may be transported by eroded particles in runoff. A common model of water erosion in the U.S. is the Universal Soil Loss Equation (USLE) and its modifications (Williams, 1991). USLE empirically

relates sediment yield to runoff, soil attributes, land use, and management. Leonard et al. (1979 [cited in Leonard, 1990]) found that runoff concentrations of atrazine and other pesticides strongly correlate to pesticide concentrations in the 0 to 1 cm surface layer of watershed soil. The concentration at this depth is used as a predictor of pesticide runoff in the CREAMS model (Knisel, 1980). Haith (1980, 1986) and Mulkey and Falco (1977 [cited in Rao and Davidson, 1980]) also developed models to estimate pesticide losses in runoff.

Wind erosion models are few. An approach similar to EPIC, considering crop, soil, and climate factors is used to model soil losses to wind erosion (Skidmore and Williams, 1991). It is possible to develop some empiricism to relate such a model to chemical losses.

Runoff and erosion models usually simulate water and soil losses, but not gains. Nations and Hallberg (1992) show that contaminants are carried by atmospheric precipitation. Precipitation and runoff are both spatially and temporally variable within a watershed. A comprehensive simulation of contaminant fate would eventually require watershed-scale models of these processes.

Gas phase convection is another process affecting transport of volatile chemicals. Soil gases move under changes in soil water content, barometric pressure, and temperature. In most simulation models, gas phase convection is ignored. Wagenet and Hutson (1990) propose that gas phase convection be modeled by increasing the gas diffusion coefficient, to be defined later. Several models reviewed by Taylor and Spencer (1990) simulate vapor transport as diffusion, but ignore convection (the term "convective flow" as used by the latter refers to gas transport by water flow).

Except for bulk flow, chemicals may be transported by molecular diffusion in the aqueous or gas phase. The combined influence of diffusion

and mechanical dispersion in solute transport has already been discussed. Diffusive flux alone is described by Fick's law (Marshall and Holmes, 1988):

$$q_S = -D_o(dC/dx)$$

where

q_s = quantity of solute diffused in unit time across unit cross-sectional area normal to the x-direction [$ML^{-2}T^{-1}$]

D_o= molecular diffusion coefficient in water [L^2/T]

C = concentration [M/L^3]

x = distance [L]

Fick's law states that the quantity of solute that is diffused in unit time across a unit cross-sectional area normal to the x-direction is proportional to the concentration gradient at the direction of diffusive flow. D_o depends on the properties of the diffusing molecules and the diffusion medium. In soil, diffusive flux in the liquid phase is limited to the wet fraction of the soil. Fick's law then becomes:

$$q_S = -D_p(dC/dx)$$

where $D_p = D_o b\theta$, where b is a tortuosity factor often allotted a value of about 0.6 (Marshall and Holmes, 1988).

Diffusion of gases or vapors in the gas phase follows Fick's law, just as diffusion in the liquid phase. The diffusion coefficient is called the vapor diffusion coefficient. Methods to estimate it are cited in Marshall and Holmes (1988), and Wagenet and Rao (1990).

Sorption

Sorption is one of the most important processes affecting the fate of organic compounds in porous media. The mobility of pesticides is inversely related to the extent of their adsorption (Hartley and Graham-Bryce, 1980).

Sorption directly or indirectly affects other processes such as abiotic transformations, and microbial uptake and decomposition (Pignatello, 1989).

Two mechanisms have been proposed for sorption: Surface adsorption and phase partitioning. Surface adsorption generally means a two-dimensional, net accumulation of a substance on clay mineral and organic matter surfaces. Phase partitioning generally means a solution-like phenomenon by which nonionic organic compounds transfer from one bulk solvent (usually water) into another (usually organic matter). Chiou (1979 [cited in Koskinen and Harper, 1990]) is the main advocate of partitioning. However, Mingelgrin and Gerstl (1983) find insufficient evidence for the general applicability of his theory. Instead, they accept a continuum of possible interactions starting with fixed site adsorption and ending with true partitioning. Pignatello (1989) also argues that the distinction between phase partitioning and surface adsorption blurs at some scale due to the complexity of the soil matrix.

Sorption can be viewed as either a thermodynamically or a kinetically controlled process. Thermodynamics is the study of the energy changes that accompany physical and chemical changes (Mortimer, 1986). It can tell whether a reaction can happen and its likely direction. It cannot predict the reaction rate or the path from the reactants to the final products, i.e., the kinetics. Thermodynamics of sorption has been studied better than kinetics, because of the ease in obtaining macroscopic, time-independent data. For this reason, most contaminant fate models simulate sorption as an instantaneous, reversible process (Koskinen and Harper, 1990). Typically, a Freundlich-type relation is used:

$$c_S = K_d\, c_L^{1/n}$$

where

c_S = mass of molecule sorbed per unit mass of soil [M/M]

K_d = distribution or sorption coefficient at equilibrium

c_L = concentration in solution [M/L^3]

$1/n$ = degree of equation, ≤ 1

The distribution coefficient K_d is determined by batch equilibrium studies (McCall et al., 1980). The distribution coefficient of a compound normalized for the organic C fraction of the soil (f_{oc}) is essentially independent of soil type. The relation is (Wagenet and Rao, 1990):

$$K_{oc} = (K_d / \%OC)\, 100$$

where

K_{oc} = sorption coefficient normalized for organic C

%OC = percent organic C in soil

A popular simulation model that uses a Freundlich-type isotherm to model sorption is LEACHM (Leaching Estimation And Chemistry Model) by Wagenet and Hutson (1986, 1990). Wagenet and Rao (1990) review other models with similar approach: BAM (Behavior Assessment Model), PRZM (Pesticide Root Zone Model), and CMLS (Chemical Movement in Layered Soil).

The weakness of this approach is that sorption equilibria are not established instantly, except perhaps for inorganic cations that adsorb on readily accessible surfaces. Wagenet and Hutson (1986 [cited in Wagenet and Rao, 1990]) admit that the assumption is not valid when water fluxes are high or when the geometry of the soil is such that ions need to diffuse toward sorption sites. In such cases, thermodynamics may result in overpredicting sorbed chemical.

Pignatello (1989) summarizes the inadequacies of the thermodynamics approach to organic chemical sorption:

1. The apparent non-singularity of sorption isotherms. Atrazine sorption, for example, appears hysteretic.

2. The batch method of estimating the distribution coefficient involves vigorous agitation of the sorbent-sorbate mix for several hours. In the field soils are not agitated.
3. According to Pignatello (1989), and Koskinen and Harper (1990), of the processes controlling sorption rate, only one relates to overcoming the energy barrier at the soil-water interface. The others relate to the diffusion of the sorbate through the soil matrix.

Because sorption/desorption is not always instantaneous, other processes may interfere in the meantime. Field soils are not confined in a sealed vessel, as in batch experiments. When the product of desorption is continuously removed from the soil solution, an equilibrium cannot be established between the sorbed and desorbed phase. The batch method accounts for some concurrent processes such as volatilization and degradation, but not for removal of products.

The Freundlich-type equation is an empirical model that fits data obtained at an apparent equilibrium. It does not necessarily have a physical significance, especially when it is not first degree.

Green and Corey (1971) point out that the batch method is unsatisfactory because of poor precision. For ionic solutes, the chemical composition of the solution may change during equilibration. These concerns may be partially offset by modifications to the method, such as the use of soil suspension as a "blank" instead of a solution "blank." Green and Corey propose the "flow equilibration method" in which soil cores are leached with a steady flux of the pesticide solution until attainment of constant concentration in the effluent. The amount adsorbed in the core is determined. The method gives good precision even when sorption is low.

The "flow equilibration method" never became very popular, possibly because it is complicated (Green and Karickhoff, 1990).

The thermodynamics approach is useful for modeling processes that happen nearly instantaneously. Such processes are ion exchange of organocations with monovalent or divalent metal ions on exposed clay mineral surfaces (Pignatello, 1989). Physical surface adsorption that is not diffusion-limited may occur nearly instantly in soil suspensions. Adsorption of atrazine on stirred sediment slurries reached 90% of equilibrium within an average of 8 min (Wauchope and Myers, 1985). Pignatello (1989) notes that phase partitioning may also be nearly instantaneous, at least in the direction of the highest to the lowest free energy state.

Green and Karickhoff (1990) believe that for near-static soil-water systems, such as a soil profile at field capacity without evaporation, the equilibrium constant is a good estimate of pesticide distribution. Their laboratory results with atrazine support this conclusion.

The equilibrium constant may at least be used as an approximation for the rapid stage of sorption. The two-site model (Cameron and Klute, 1977; Selim et al., 1976 [cited in Pignatello, 1989]) distinguishes between "fast" sites where adsorption is almost instantaneous and "slow" sites where adsorption takes longer. Sorption on fast sites is modeled using the equilibrium constant and on slow sites using the rate constant. Yet, Rao et al. (1979 [cited in Pignatello, 1989]) found that this model did not adequately describe breakthrough of two solutes through soil columns.

Precipitation

The chemistry definition of precipitation is the formation of an insoluble or a slightly soluble substance in an aqueous reaction (Mortimer,

1986). For this discussion, precipitation is a three-dimensional, net accumulation of a solid that happens when its concentration in solution exceeds its solubility, regardless of the reason (e.g. chemical or surface reaction, or a drop in temperature). Simulation of precipitation depends on the simulation of the aqueous concentration and factors affecting solubility.

Volatilization

Volatilization may be an important loss pathway for agricultural chemicals. Taylor and Spencer (1990) report that total seasonal pesticide losses from runoff rarely exceed 5 to 10% of the total applied; and that the fraction removed by leaching is even less. In contrast, volatilization may account for losses of 80 to 90%.

According to Taylor and Spencer (1990) volatilization is two distinct processes, evaporation of residues, and dispersion of the resulting vapor by diffusion and turbulent mixing. Evaporation depends on vapor pressure and liquid-solid-vapor partitioning. Jury et al. (1983 [cited in Wagenet and Rao, 1990]) proposes a modified Henry's law for liquid-vapor partitioning. It is analogous to the Freundlich-type relation for liquid-solid partitioning:

$$c_G = K^*_H \, c_L$$

where

c_G = solute concentration in gas phase or vapor density [M/L^3]

K^*_H = modified Henry's law constant

K^*_H is given by:

$$K^*_H = c^*_G / c^*_L$$

where

c^*_G = saturated vapor density [M/L^3]

c^*_L = aqueous solubility [M/L^3]

Most pesticides have very low vapor pressures. Yet, unlike water, the background vapor density in the ambient atmosphere is practically nil. That causes a sharp gradient at the plant-soil-atmosphere interface that helps vapor flux. Diffusive flux is expressed by the following equation, analogous to Fick's law for solutes (Wagenet and Rao, 1990):

$$q_S = -D_o(dc_G/dx)$$

where

q_S = vapor flux density [$ML^{-2}T^{-1}$]

dc_G/dx = gradient of concentration [M/L^3] over distance [L]

D_o = molecular or ionic diffusion coefficient in pure air [L^2/T]

If δ is the distance from the plant or soil surface where concentration becomes zero, at that distance dc_G/dx becomes $c_G(0)/\delta$.

Dispersion of vapors may be further enhanced by turbulent mixing above the soil surface. The appropriate models are reviewed in Taylor and Spencer (1990).

Transformations

Agricultural chemicals change due to chemical and microbial activity. Such transformations are collectively called degradation because usually they result in simpler, lower energy products. Pesticide degradation generally is irreversible. Nutrients, on the other hand, may be continually recycled through the soil system in different forms. The term nutrient cycle often is used to characterize this series of reversible transformations.

Degradation losses may be modeled with the following relations (Wagenet and Rao, 1990):

$$\partial c / \partial t = -\mu c^n \qquad [6]$$

$$\partial c / \partial t = -V_{max}[c/(\alpha + c)]$$

where

c = pesticide concentration (M/L^3)

μ = degradation rate coefficient ($1/T$)

n = reaction order

V_{max} = maximum degradation rate ($ML^{-3}T^{-1}$)

α = constant

When integrated, the general form of Eq. [6] is:

$$c = [(-N + 1)(-\mu t + C)]^{1/(-N + 1)}$$

where $C = c_o^{-N+1} / (-N + 1)$, $n \neq 1$, and $c_o = c(t=0)$. For first-order kinetics (n = 1):

$$c = c_o \exp(-\mu t)$$

$$c\,(t) = c(t\text{-}1) \exp(-\mu) \qquad [7]$$

$$\mu = 0.693 / t_{0.5}$$

where $t_{0.5}$ = half-life, or the time it takes for half the original concentration to disappear.

Plants

Plants may affect chemical fate in several ways. They can act as net sinks while they are alive, but also as net sources as they decompose. By taking up water plants create hydraulic potential gradients that cause convection of water and dissolved chemicals. By selectively absorbing some molecules plants create concentration gradients in the soil solution that affect diffusion and sorption.

Simulation of plant water and nutrient uptake requires simulation of plant growth and development. CERES is a family of soil-crop-atmosphere computer models (Jones and Kiniry, 1986) that are at the core of DSSAT (Decision Support System for Agrotechnology Transfer) originally supported

by the IBSNAT program, the USAID sponsored International Benchmark Sites Network for Agrotechnology Transfer. CERES simulates maize, wheat, sorghum, millet, and barley. Other DSSAT models simulate soybeans (SOYGRO [Jones et al., 1991]), peanuts (PNUTGRO [Boote et al., 1989]), dry beans (BEANGRO [Hoogenboom et al., 1991]), and rice (CERES-Rice [Ritchie et al., 1986]). There are many more crop models worldwide, some of which are SWATR (Feddes et al., 1978), the spring wheat model by van Keulen and Seligman (1987), the root growth model by Jones et al. (1991), and the root water uptake model by Campbell (1991).

SIMULATION OF ATRAZINE

The basic principles of simulation of agricultural chemicals have been reviewed. Because of its significance to this study, a separate section is devoted to atrazine. This section contains additional material that has not been covered in the review of the general principles.

Sorption

The Weed Science Society of America (1983) reports that atrazine normally is not found below the upper 30 cm of soil in detectable quantities, even after years of continuous use. Yet, this study (Chapter 2) suggests that atrazine can be detected down to 140 cm. Distribution coefficients for atrazine sorption (Table 6, and Wagenet and Hutson, 1990) suggest that atrazine adsorbs only to a moderate degree. Possibly the scarcity of extensive published field data is responsible for this apparent contradiction.

More than one mechanism may be involved in atrazine sorption. Triazines are weak bases that protonate at low pH (Mortland, 1970; Koskinen

and Harper, 1990) and thus form ionic type bonds with clay and possibly organic matter. At higher pH, other mechanisms dominate such as H bonding and hydrophobic attraction. Bonding by van der Waals forces has not been proved or disproved. Calvet (1980) and Koskinen and Harper (1990) review several studies that support the claims for each of these mechanisms.

The following are the major factors thought to affect atrazine sorption:

Organic matter. Organic matter is by far the most important factor affecting the sorption of organic molecules in soils (Green and Karickhoff, 1990; Hassal, 1982; Wagenet and Rao, 1990). Atrazine is more readily adsorbed on muck or clay soils than on soils of low clay and organic matter content (Weed Science Society of America, 1983). Though organic matter is a small fraction of the total soil mass, it has a large surface-to-mass ratio and many functional groups with affinity for various organic molecules.

Typically, atrazine sorption is modeled with a Freundlich-type relation, already discussed under "Principles of nutrient and pesticide simulation." Table 6 presents some published K_d and K_{OC} values for first degree models. Models not of first degree cannot be compared unless the shape of the isotherm is known.

Table 6. Published K_d and K_{OC} for Freundlich-type, first-degree models of atrazine sorption.

Author(s)	K_d	K_{OC}	Sorbent
Ballhorn et al. (1984) cited in Scheunert (1992)	1.66	218	Alfisol
Ballhorn et al. (1984) cited in Scheunert (1992)	54.3	1526	Spodosol
Ballhorn et al. (1984) cited in Scheunert (1992)	1.06	95.5	Entisol
Barriuso et al. (1992)	≈1.1		Rambouillet soil (aquic eutrochrept)
Grover and Hance (1970)	0.8-2.1		Begbroke soil
Hance (1969) cited in Calvet (1980)	11.7		Montmorillonite-Ca
Hance (1969) cited in Calvet (1980)	14		85% montm.-Ca plus 15% humate-Ca
Hance (1969) cited in Calvet (1980)	59		Humate-Ca
Hartley and Graham-Bryce (1980)	2.9		Mineral soil
McGlamery and Slife (1966)	4.4-12.9		Drummer clay loam
McGlamery and Slife (1966)	44-840		Humic acid
Swanson and Dutt (1973)	0.21		Mohave sandy loam
Wauchope and Myers (1985)	4.6	418	Bear Creek 5290 sediment
Wauchope and Myers (1985)	21	538	Bear Creek 5356 sediment
Wauchope and Myers (1985)	3.4	262	Lake Chicot 5636 sediment
Wauchope and Myers (1985)	2.3	418	Lake Chicot 5643 sediment

Table 6 (continued)

Wauchope and Myers (1985)	0.6	43	Lake Chicot 5700 sediment
Wauchope and Myers (1985)	25	1923	Wolf Lake 6262 sediment
Wauchope and Myers (1985)	4.4	640	Wolf Lake 6268 sediment
Wauchope and Myers (1985)	7.5	536	Wolf Lake 6272 sediment
Wauchope and Myers (1985)	6.7	827	McWilliams Pond 1 sediment
Wauchope and Myers (1985)	3.2	464	McWilliams Pond 2 sediment
Wauchope and Myers (1985)	9.2	317	Beaver Pond sediment
Wauchope and Myers (1985)	1.2	235	Lake Washington sediment

The distribution coefficient normalized for organic C (K_{OC}) is "essentially independent of soil type" (Wagenet and Rao, 1990). Yet, Table 6 shows that this is an oversimplification. Possible reasons for the deviation from the rule are: Interrelationships between sorption on soil inorganic matter and that on soil organic matter; the heterogeneous distribution of organic matter in soil; bound residues formed on organic and inorganic matter by different mechanisms (Ballhorn et al., 1984 [cited in Scheunert, 1992]). Despite these deviations, K_{OC} for atrazine is less variable than K_d. Rao and Davidson (1980) showed that for a large sample of soils (56) the coefficient of variation was 89.8% for K_d but only 49.1% for K_{OC}.

Less is known of the effect of the composition of organic matter on sorption. Dunigan and McIntosh (1971) investigated the effect of some components of organic matter on the sorption of atrazine. They found that the ether and alcohol-extractable components (i.e. fats, oils, waxes and resins) had a negligible sorptive capacity. On the other hand, hot-water-extractable materials (i.e., polysaccharides) had a stronger effect on adsorptive capacity. In another experiment, nucleic acids, proteins, lignin, and humic acid

showed higher affinity for atrazine than polysaccharides. The results do not fully support the conclusions because the data from the two experiments are not comparable. The first experiment tested the effect of the subtraction of an organic substance from a soil while the second tested the behavior of pure organic materials.

Clay. The K_{OC} approach assumes that hydrophobic pesticides are primarily sorbed by organic matter. However, clays also adsorb atrazine, as shown in Table 6. Mortland (1970) shows that s-triazines adsorb on clays when protonated at low pH. When the fraction of clay mineral (f_{cm}) relative to the fraction of organic C (f_{oc}) is too high, clay contribution to sorption may be significant. Green and Karickhoff (1990) suggest that if f_{cm}/f_{oc} exceeds about 40 then mineral contribution to sorption should be acknowledged. An alternative specific surface method can be used to estimate sorption.

The type of clay mineral may be significant. Swelling clays are more sorptive than nonswelling clays (Calvet, 1980; Green and Karickhoff, 1990).

Metal cations. Atrazine sorption on clays may be reduced or enhanced by metal cations. Metals may compete for sorption sites with positively charged atrazine molecules (Calvet et al., 1964 [cited in Calvet, 1980]). Mortland (1970) suggests that at low pH Al^{3+} released from the montmorillonite lattice could displace protonated *s*-triazines. On the other hand, metal cations may act themselves as adsorption sites indirectly via their hydration envelope. The decreasing order of cations according to their capacity for atrazine adsorption is $Fe^{3+} > Al^{3+} > Ca^{2+}$ (Terce and Calvet, 1977 [cited in Calvet, 1980]).

Metal oxides. Huang et al. (1984) claim that Al and Fe sesquioxides provide a significant amount of adsorption sites for atrazine. They even claim that sesquioxides could be more important than organic matter. Their data do not necessarily support their conclusions. They cite unpublished data

to support a point which should follow only from data or references in their paper.

Temperature. The evidence on the effect of temperature on atrazine sorption is inconclusive. Calvet (1980) cites work that shows that temperature may relate positively to atrazine adsorption on humic acid and lignin (Li and Felbeck, 1972), whereas on peat it makes no difference (Harris and Warren, 1964). Dunigan and McIntosh (1971) hypothesized that temperature is negatively related to adsorption because adsorption processes "are usually exothermic." Yet, their observations show a positive relation. McGlamery and Slife (1966) report a negative relation; an increase in K_d values was effected when the temperature dropped from 40 to 0.5 C°. They do not offer a plausible explanation. Yamane and Green (1972) report that adsorption is negatively related to temperature when C_e (concentration at equilibrium) is used to plot the isotherms. It is positively related when C_e/C_o (concentration at equilibrium/initial concentration) is used. The use of the C_e/C_o ratio reportedly corrects for the temperature effect on solubility. Finally, Huang et al. (1984) did not observe an effect of temperature on atrazine sorption.

Acidity. Yamane and Green (1972) report a 100-fold increase in the K_d of atrazine with a drop of 3 pH units. McGlamery and Slife (1966) found that the K_d of atrazine more than doubled when the pH dropped from 8.0 to 3.9. They attribute the effect to increased van der Waal forces and adsorption via SiOH groups. More recent literature shows that triazines are weakly basic molecules that are easily protonated at low pH. Mortland (1970) and Koskinen and Harper (1990) suggest that *s*-triazines are protonated on clay surfaces, with or without the help of hydrated metal cations. Atrazine

becomes protonated at soil pH 3.7 or less, which is estimated as $pK_b + 2$ assuming $pK_b = 1.7$ (Koskinen and Harper, 1990).[7]

According to Calvet (1980) and Koskinen and Harper (1990) acidity affects not only the sorbate but the sorbent as well. Hydrolysis of clays at low pH may bring Al^{3+} and Fe^{3+} to the surface where they may form highly sorptive hydroxides. Protons at soil surfaces can modify the charge of humus. Finally, low pH may increase the ionic strength of the soil solution which in turn affects triazine adsorption by reducing their solubilities.

Precipitation

The aqueous solubility of atrazine is 33 µg/ml at 27 °C (Weed Science Society of America, 1983). Atrazine precipitates whenever this concentration is exceeded due to changes in temperature or pH.

Volatilization and Wind Erosion

Atrazine has low vapor pressure compared with other pesticides, $9.0\ 10^{-11}$ MPa at 25° (Jury et al., 1983 [cited in Taylor and Spencer, 1990]). Yet,

---

[7] pK_b is the negative logarithm (base 10) of the ionization constant for a weak base at equilibrium:

$$RH_2^+ \rightleftarrows RH + H^+$$

Then $K_b = \{[RH][H^+]\}/[RH_2^+]$ and, at the particle surface, $pK_b = pH_s + p[RH/RH_2^+]$. Assuming $pH_s = pH - 2$ (i.e., surface pH is two units lower than "bulk" pH), then $pK_b = pH - 2 + p[RH/RH_2^+]$. What Koskinen and Harper suggest by $pH \leq pK_b + 2$ is that the ionic species be more or equal to the neutral. Yet, real domination of the ionic species (10-fold concentration or more) would require $pH \leq pK_b + 1$.

because the background concentration in the atmosphere is practically zero, the resulting gradient could cause volatilization. Wienhold and Gish (1993) showed that 35 d after application, up to 9% of the amount applied had volatilized. Glotfelty et al. (1989 [cited in Blumhorst and Weber, 1992]) showed that 2.4% of the applied atrazine volatilized from fallow soil in 21 d. On the other hand, Blumhorst and Weber (1992) observed no volatilization from atrazine-fortified soil samples in the lab, even after 48 d.

A related loss pathway is wind erosion. For less volatile pesticides such as atrazine wind erosion losses may be more significant than volatilization. Glotfelty et al. (1989 [cited in Taylor and Spencer, 1990]) observed wind erosion of atrazine. Though the actual amount lost was small, it might be significant in simulating the long distance transport and deposition of the pesticide.

Runoff

Leonard (1990) cites several studies reporting atrazine losses from runoff. Total seasonal losses ranged from 0 to 5.7 % of application rate. The conclusion from many of those studies is that atrazine losses are greater when the application is temporally closer to the runoff event.

Plant Uptake

Plants may take up atrazine passively with the transpiration stream. Some plants may extract small amounts of covalently bound residues, normally difficult to extract with organic solvents. Capriel and Haisch (1983 [cited in Koskinen and Harper, 1990]) report that 9 yr after the last atrazine

application, 2-hydroxy-4-amino-6-isopropylamino-1,3,5-triazine and 2-hydroxy-4-ethylamino-6-amino-1,3,5-triazine were identified in oat plants.

Plants may interact with chlorotriazines in ways other than uptake. They may release compounds such as N-hydroxy-benzoxazinones to the soil solution. These compounds enhance the displacement of Cl from chlorotriazines and contribute to their degradation (Wolfe et al., 1990).

Transformations

In soils, microbial as well as non-microbial transformations are important. The main transformations of atrazine are shown in Figure 16. Arrows point at the bonds affected. The substitute groups, if any, are noted.

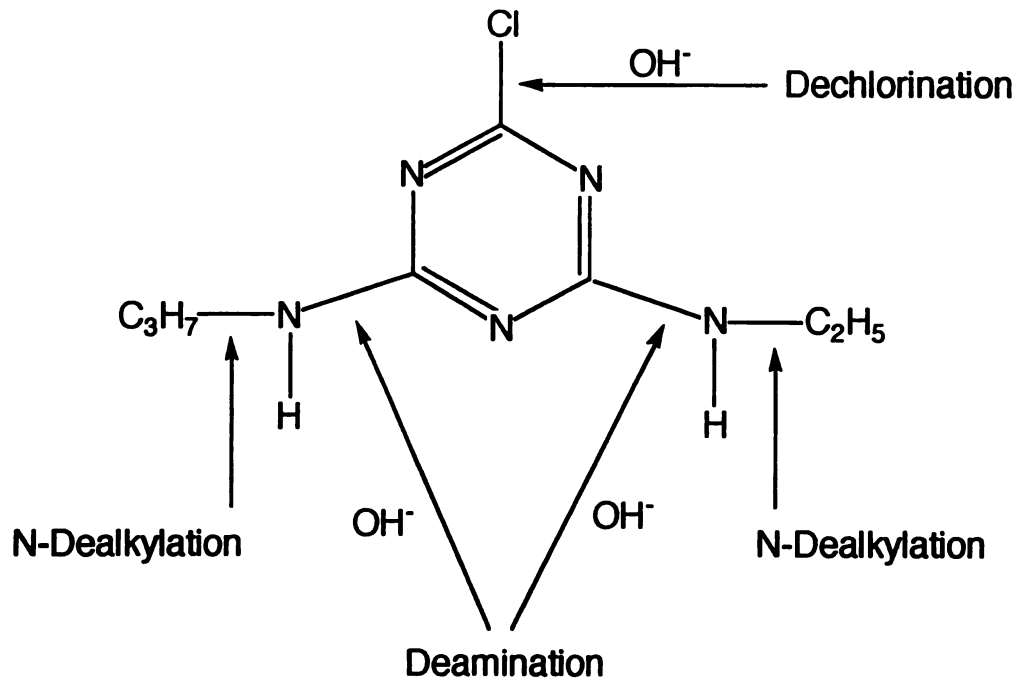

Figure 16. Main transformations of atrazine in soil. Arrows point at the bonds affected. The substitute groups, if any, are noted.

Hydrolysis/Dechlorination. Various nucleophiles cause the displacement of Cl in chlorotriazines. Most commonly OH displaces Cl in atrazine to give hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-1,3,5-triazine; Erickson and Lee, 1989). The addition of OH makes the compound more polar, therefore more water-soluble, and enhances biological reactivity (Bollag and Liu, 1990).

Chemical hydrolysis can happen without microorganisms. Kaufman and Kearney (1970) suggest that hydroxylation is the primary mechanism of anaerobic degradation of *s*-triazines. Clays, especially Al- and H-montmorillonite, catalyze the hydrolysis (Skipper et al., 1978 [cited in Wolfe et al., 1990]). Organic matter, too, catalyzes the reaction. Specifically, fulvic acid enhances atrazine hydrolysis (Khan, 1980 [cited by Wolfe et al., 1990]). On the contrary, Cu(II) in soil solution may retard the catalytic effect of fulvic acid (Haniff et al., 1985 [cited by Wolfe et al., 1990]). Armstrong and Konrad (1974 [cited in Wolfe et al., 1990]) propose that catalysis on organic matter surfaces is caused by a carboxyl functional group that protonates a ring N. Horrobin (1963 [cited in Erickson and Lee, 1989]) proposes a similar theory for acid hydrolysis of chloro-triazines in solution. For alkaline hydrolysis, he proposes direct nucleophilic displacement of Cl by OH.

Soil increases the rate of atrazine hydrolysis 10 times (Jordan et al., 1970 [cited in Erickson and Lee, 1989]). It is unclear whether this is due to clays or organic matter or other factor.

The rate of atrazine hydrolysis is affected by pH (Armstrong et al., 1967 [cited in Erickson and Lee, 1989]). Atrazine half-life decreases as pH decreases within the range 3 to 1, but increases as pH decreases within the range 13 to 11. Armstrong et al. do not provide data for other pH ranges.

The role of microorganisms in the hydrolysis of atrazine to hydroxyatrazine is unclear. *Fusarium roseum* (Couch et al., 1965 [cited in

Erickson and Lee, 1989]) and *Pseudomonas* species (Behki and Khan, 1986) reportedly enhance hydrolysis. The mechanism of microbial catalysis is unclear. Geller (1980 [cited in Erickson and Lee, 1989]) propose an effect of microbial reactions on pH. Cook and Huetter (1984 [cited in Erickson and Lee, 1989]) observed dechlorination of a related compound (deethylsimazine) catalyzed by hydrolases from *Rhodococcus corallinus*. Dechlorination by *Pseudomonas* species has been observed by Behki and Khan (1986) but only on the dealkylated derivatives, not on atrazine. The presence of both alkyl groups on atrazine probably inhibits bacterial dechlorination. The reason is unknown.

N-Dealkylation. Dealkylation seems the first step in microbial degradation of chloro-*s*-triazines. Microbes have both the ability and the incentive to remove the side chains to use them as energy source. Giardina et al. (1980 and 1982 [cited in Bollag and Liu, 1990]) found that N-dealkylation is the primary route of atrazine metabolism by *Nocardia* species. The enzyme involved is a mixed function oxidase. Behki and Khan (1986) observed N-dealkylation of atrazine by *Pseudomonas* species. Deisopropylatrazine was formed preferentially over deethylatrazine. The authors cannot explain this preference for a particular chain. They cite studies (Kaufman and Blake, 1970; Wolf and Martin, 1975) where a preference for the other chain was observed, but in those cases dealkylation was caused by fungi.

Microbial enzymatic catalysis is not necessary for dealkylation, though it is the predominant mechanism. Kearney et al. (1987 [cited in Erickson and Lee, 1989]) chemically oxidized atrazine to 2-chloro-4,6-diamino-*s*-triazine using ozone at pH 10.

Deamination. The amine groups of some atrazine degradation products have been used by microorganisms (pseudomonads, *Klebsiella*

pneuomniae) as a N source (Jutzi et al., 1982 [cited in Erickson and Lee, 1989]). The mechanism appears to be hydrolytic. The reaction may be anaerobic.

Ring cleavage. The triazine ring is stable. But Cook et al. (1985 [cited in Erickson and Lee, 1989]) observed ring cleavage in a degradation product, 2,4,6-trihydroxy-*s*-triazine, by pseudomonads and *Klebsiella pneuomniae*.

Kinetics. Temperature causes an approximate doubling of degradation rate with each 10°C increase, in the range 10 to 30°C. Atrazine degrades faster in the southern USA and during summer months (Erickson and Lee, 1989). Microbial energy sources accelerate atrazine decomposition in soils (McCormick and Hiltbold, 1966 [cited in Erickson and Lee, 1989]). Crops accelerate decomposition (LeBaron, 1970 [cited in Erickson and Lee, 1989]), possibly due to uptake and decomposition in the plant. Degradation is slower in dry soils (Roeth et al., 1969).

Degradation slows down with depth, possibly due to lack of O_2, lower temperature, and lack of energy sources and microbial activity (Erickson and Lee, 1989). Lavy et al. (1973) report that the degradation rate of atrazine decreases with depth under either aerobic or anaerobic conditions. In one soil type, atrazine-treated soil was phytotoxic after a 41 mo incubation at 90 cm depth but almost not phytotoxic when incubated at 40 or 15 cm depth. In another soil type, the effect of depth was confused in part with the effect of the applied rate. Soil at 90 cm was less phytotoxic than at 40 cm, but it was treated with half the rate. Also, the study ignores the possible phytotoxicity of derivative compounds. The study was recently repeated (Lavy et al., 1993) and confirmed that half-lives increase significantly with depth. Klint et al. (1993) found that atrazine does not degrade in groundwater. Atrazine did not degrade 539 d after incubation in groundwater or 174 d after incubation in suspensions of groundwater and aquifer sediment taken from approximately 3 to 7 m depth. Both materials contained active microorganisms. Atrazine

did not degrade even after nutrients and primary substrates were added. Significant atrazine removal occurred only after the aquifer material was inoculated with a small amount of topsoil. Klint et al. cite Agertved et al. (1992) who also found that atrazine is resistant to biodegradation in groundwater.

N-dealkylation is the slowest or one of the slowest steps in the biodegradation of atrazine, therefore, it probably determines the overall biodegradation rate. Jessee et al. (1983 [cited in Erickson and Lee, 1989]) measured anaerobic degradation by a bacterium isolated from industrial wastewater containing cyanuric acid. Approximately 53% of atrazine remained after 7 d, which suggests a half-life of around that much. On the 7th d the rate of disappearance was so low to suggest that degradation practically stops. However, the conditions of the experiment do not necessarily represent conditions in soils. Wagenet and Hutson (1990) using data from Wauchope (1988) report an atrazine half-life of 60 d. Lavy et al. (1993) measured a similar value at around 30 cm depth in the field, but about three times as much below 90 cm. Rao and Davidson (1980 [using data from Ou et al., 1980]) report a field-measured half-life of 20 d (50% CV), and two laboratory-measured ones; one of 48 d (68.8% CV) and one of 6900 d (71.5% CV). Both laboratory values were measured under aerobic incubation. It is unclear why they are so different. The original source is inaccessible. Durand and Barceló (1992) observed a half-life of 30 d in the field. They note that atrazine degradation stops once it reaches 20 to 25 μg/kg in soil, a concentration which they call a "bound" residue or "permanent contamination." Durand and Barceló cite atrazine soil half-lives from the literature ranging from 19 to 125 d. Blumhorst and Weber (1992) measured a half-life of 60 d in fortified soil samples incubated aerobically in the lab. They also accept that atrazine forms "bound" residues.

Species that biodegrade atrazine are not readily found in the environment, which implies that genetic adaptation is important for effective degradation (Erickson and Lee, 1989). Behki and Khan (1986) found that no significant atrazine degradation occurrs within 5 wk in atrazine-fortified soil from fields never before exposed to atrazine. Yet, degradation was observed in soil from fields with a long history of annual atrazine applications.

Degradation rates for simulation modeling are not easy to calculate. There are many possible transformations, each influenced by several environmental factors. Wagenet and Hutson (1990) warn that simple models to correlate microbial degradation rates to chemical structure are in their infancy. Ideally, degradation rates should be measured in situ. Even so, rates are so temporally and spatially variable that simplifying assumptions will be necessary.

Computer Simulation Models

A popular pesticide model is described by Leistra in cooperation with other researchers (Bromilow and Leistra, 1980; Leistra et al., 1980; Leistra and Smelt, 1981). Nicholls et al. (1982) used the Leistra model and a modified version of a model by Addiscott (1977) to simulate movement and degradation of atrazine in a fallow soil. The Addiscott model was modified to simulate soil drying. Both models performed well for soil water content. Predicted soil atrazine concentrations at various dates were outside one standard deviation of measured values, but both models followed the trend in the measured values. The Leistra model proved sensitive to hydraulic conductivity inputs.

Lupi et al. (1988) modified the model by Nicholls et al. (1982). They attempted to increase its utility by replacing measured values of the sorption distribution coefficient with a calculated one, based on organic C. In addition, they distinguished between transport via macropore and matrix flow. Predicted soil concentrations agreed well with the first 120 d of observations. Results from three years worth of simulation are reported but without supporting observations beyond 120 d.

Melancon et al. (1986) used three EPA models (SESOIL, PRZM, and PESTAN) to predict the fate of atrazine, among other chemicals, in soil columns. The first simulation run used literature values for critical parameters such as partition parameters and degradation rates. Predictions of leachate and soil concentrations during 30 d were generally poor. All models except SESOIL underpredicted final soil concentrations. Differences between simulated and measured values were generally higher than differences among the four measured replicates. All models overpredicted total leachate mass about 50 times. The second simulation run used measured values for sorption parameters and degradation rates. SESOIL this time overpredicted final soil concentrations, whereas the predictions of the others improved marginally. It is difficult to evaluate a model merely by reading the report. A possible drawback of the study was that the six pesticides were mixed and applied together. Mixing may eliminate differences in the behavior of chemicals caused by the application method or soil heterogeneity. However, mixing of some pesticides may introduce inter-species competition for sorption sites (Chiou et al., 1985).

GLEAMS was tested by Sichani et al. (1991) with field data from five consecutive years. Mass of alachlor, atrazine, cyanazine and carbofuran leaching through the tiles of a tile-drained field was measured and simulated. Three of the five years were so dry that no pesticide discharge was observed or

simulated. On the remaining years, predictions were variable. The simulated total annual leachate was from one to five times the measured value. The simulation did not predict the observed pesticide loss during the first outflow event after pesticide application. The timing of subsequent peaks for atrazine, cyanazine and carbofuran was accurately predicted, though the absolute mass usually was underpredicted. Authors attribute the discrepancies to preferential flow and the lack of testing of the model in slowly permeable soils.

According to Wagenet and Hutson (1986), PRZM has been not been adequately tested in the field or extensively evaluated against a research model that considers basic processes in a fundamental manner. According to Everts and Kanwar (1990), chemical transport models such as PRZM (Carsel et al., 1984) and GLEAMS (Knisel et al., 1986) do not include solute transport by preferential flow paths.

Wagenet and Hutson (1990) had variable success in simulating aldicarb residues with LEACHM. The authors attribute lack of better agreement to inaccurate relationships between hydraulic conductivity, soil water content, and potential; inadequate prediction of plant water uptake; and inaccurate estimates of transformation rates. Also, the high spatial variability of field-measured residues makes model evaluation harder.

Pesticide simulation has had variable success so far. Sometimes models perform well, but many times not. The variability in performance is understandable, given the lack of knowledge on many processes. There is uncertainty in model inputs. The variability in field-measurements makes model testing even harder.

CERES-P SIMULATION MODEL DEVELOPMENT

The model developed in this study, CERES-P, is based on CERES, a family of soil-crop-atmosphere simulation models. CERES are deterministic, functional models intended primarily for research and management (Ritchie, 1986). The CERES models simulate the N cycle (Godwin and Jones, 1991) but no pesticides or the presence of a water table. The objective of CERES-P is to add the capability of pesticide simulation with the option of a water table. Its aim is to simulate all basic pesticide-related processes but without excessive data requirements that would make the model unusable by others. CERES-P was designed to use all existing DSSAT input files of version 2.1 format, plus some extra inputs. The CERES models simulate corn, wheat, sorghum, millet, and barley. Though many of the changes in CERES-P apply to all crops, these changes have been tested only for corn.

Water Balance

The water balance is an important component of the CERES models. It affects crop growth and development, and N transport and transformations. The daily change in the storage capacity (ΔS) of the soil profile is estimated as follows:

$$\Delta S = (\text{Precipitation}) + (\text{Surface Irrigation}) + (\text{Subirrigation}) - (\text{Runoff}) - (\text{Deep Drainage}) - (\text{Tile Drainage}) - (\text{Soil Evaporation}) - (\text{Plant Evaporation})$$

If there is a soil water deficit relative to plant evaporative demand, the program calculates drought stress coefficients that are used by the subprograms of plant growth and development. The plant subprograms in

turn affect water uptake by adjusting leaf area and root growth, and so on. The water balance subprogram is called by the main program on a daily basis.

Figure 17 is a flowchart of the water balance program in CERES-P. The names of sub-programs are in uppercase. CERES-P was built around CERES version 2.1 (Ritchie et al., 1989). Regarding the water balance, the main contribution of this study is the addition of a water table option. A description of the changes follows. Other changes have been incorporated since version 2.1. Those will be briefly described as well.

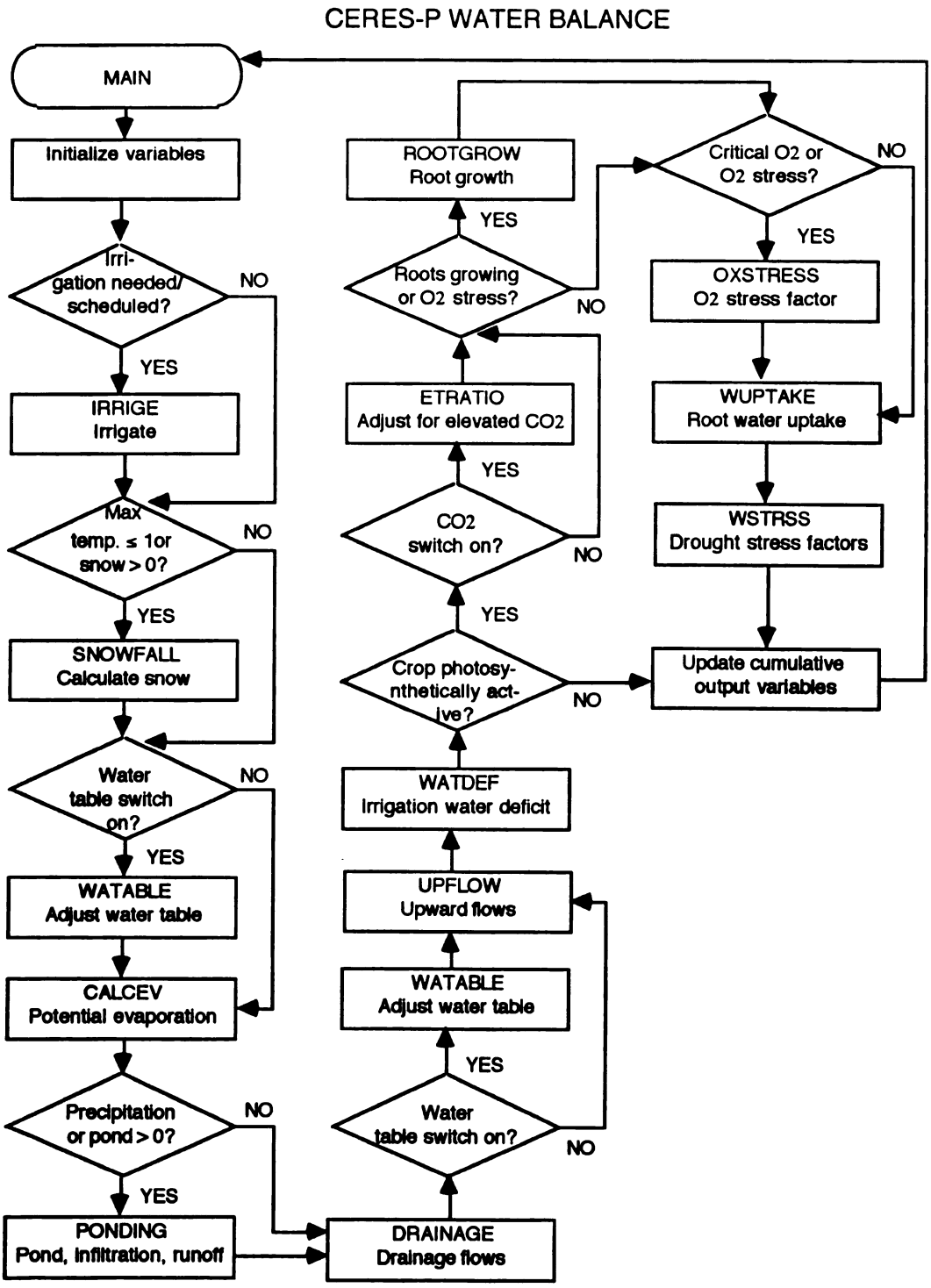

Figure 17. Flowchart of the water balance in CERES-P.

Initialization. The water table variables are initialized once at the beginning of each season. The program prompts the user for one of three choices:

1. No water table.
2. Water table without management.
3. Water table with management.

Choice 1 (the default) runs the model assuming a well-drained soil profile. Choice 2 allows the water table to rise but without human intervention. Choice 3 requires the user to prepare a file with the target water table depths for each day, and a switch to specify whether the drains are open or closed. By default, the target depth is the bottom of the profile. Water will be added or drained to reach the target depth, subject to limitations imposed by soil properties and antecedent water content. The user is also prompted for the tile layer depth. Unless otherwise specified, the tile layer is the deepest layer.

Water table adjustment. If the option "water table without management" is on, the model compares the current water content of each soil layer with its saturated water content. The water table is defined as the surface of the largest contiguous block of saturated layers, counting from the bottom of the profile upward. The water table cannot be deeper than the soil profile or else the model wouldn't be able to keep track of its depth. After drainage, the water table depth may be re-adjusted based on the drained soil water content.

If the option "water table with management" is on, at the beginning of the simulation day the model decides whether subirrigation is needed to raise the current water table depth to the target depth. After drainage, the water table depth may be re-adjusted based on the drained soil water content.

Output. On screen, a new module optionally plots the water-filled porosity with depth at the end of each daily run. The user may select an arbitrary starting date for display, and may cancel the display at any time. The vertical axis (depth) is plotted approximately to scale. This allows for a quick visual check of the proper operation of subirrigation and drainage. A new output file records the important components of the water balance: precipitation, irrigation, infiltration, deep drainage, tile drainage, ponding, runoff, soil evaporation, plant evaporation, potential evaporation, subirrigation, and water table layer. A mass balance check for the entire season is appended at the end of each treatment run. Output files are further discussed in this Chapter under "Changes in Input/Output Since CERES 2.1."

Other changes. Several changes not directly related to this study have been incorporated into the water balance since CERES 2.1. Because these changes are not documented elsewhere, a brief description is given here. Contributors include J. Ritchie, D. Godwin, B. Baer, J. Lizaso, T. Chou, I. White, S. Prathapar, P. Wilkens, and the author.

Version 2.1 runoff was being calculated based on a modification of the Soil Conservation Service curve number approach (Williams, 1991). Infiltration was the difference between daily precipitation and runoff. Chou (1990) proposed a time-to-ponding approach that relates rainfall rate to "time" into the storm, expressed as cumulative rainfall. Duration and peak intensity of a storm are generated as a function of total daily precipitation. The storm is further disaggregated into intervals of equal rainfall amount. For each interval, the water that cannot infiltrate is added to a new variable, "POND." When "POND" exceeds the maximum ponding depth, the excess water is added to runoff. The maximum ponding depth is specified by the user in the soil properties file.

Drainage fluxes are a function of the water-retaining capacity of the soil. First, the water content at equilibrium (after drainage) is estimated from empirical functions (J. T. Ritchie, 1993, personal communication). Then, downward fluxes are estimated as the difference between current and drained water content. If there is a flow-restricting layer in the profile, downward fluxes are reduced to the maximum flow rate that can permeate the restricting layer. If the drainage tiles are open, the effective permeability of the tile layer increases to the drainage capacity of the tiles.

Evaporation from the top three soil layers is now calculated based on empirical functions of current water content and air-dry water content. Upward flows for layers four and below are estimated with a Richards-type equation, based on soil water content gradients and diffusivity (J. T. Ritchie, 1993, personal communication).

Potential root water uptake is a function of plant-available water, a maximum root water uptake constant defined for each layer, and root length density (J. T. Ritchie, 1993, personal communication). Actual uptake is limited by the energy available for transpiration.

Lizaso (1993) added the effect of anoxic conditions caused by excess soil water. The calculated soil aeration factors affect dry matter accumulation and partitioning, leaf and root growth, and crop phenology.

Nitrogen Balance

Because of the importance of N for the health of the crop and the environment, N simulation in CERES is well developed (Godwin and Jones, 1991). Nitrogen affects the crop and vice versa. If there is a soil deficit relative to plant demand, CERES calculates N stress coefficients that impact

on plant growth and development. In turn, plant growth and development affect the demand for N, and so on.

Unlike the water balance, the N model is not a single sub-program. Nitrogen subroutines are called at several places in CERES. A set of options allows crop simulation with unlimited N supply, in which case the N balance is canceled. The N balance is also deactivated when the water balance is canceled, because simulation of the N cycle requires knowledge of water fluxes and soil water content. Figure 18 is a flowchart of the N-related modules in CERES-P, in approximate calling sequence. Module names are in uppercase.

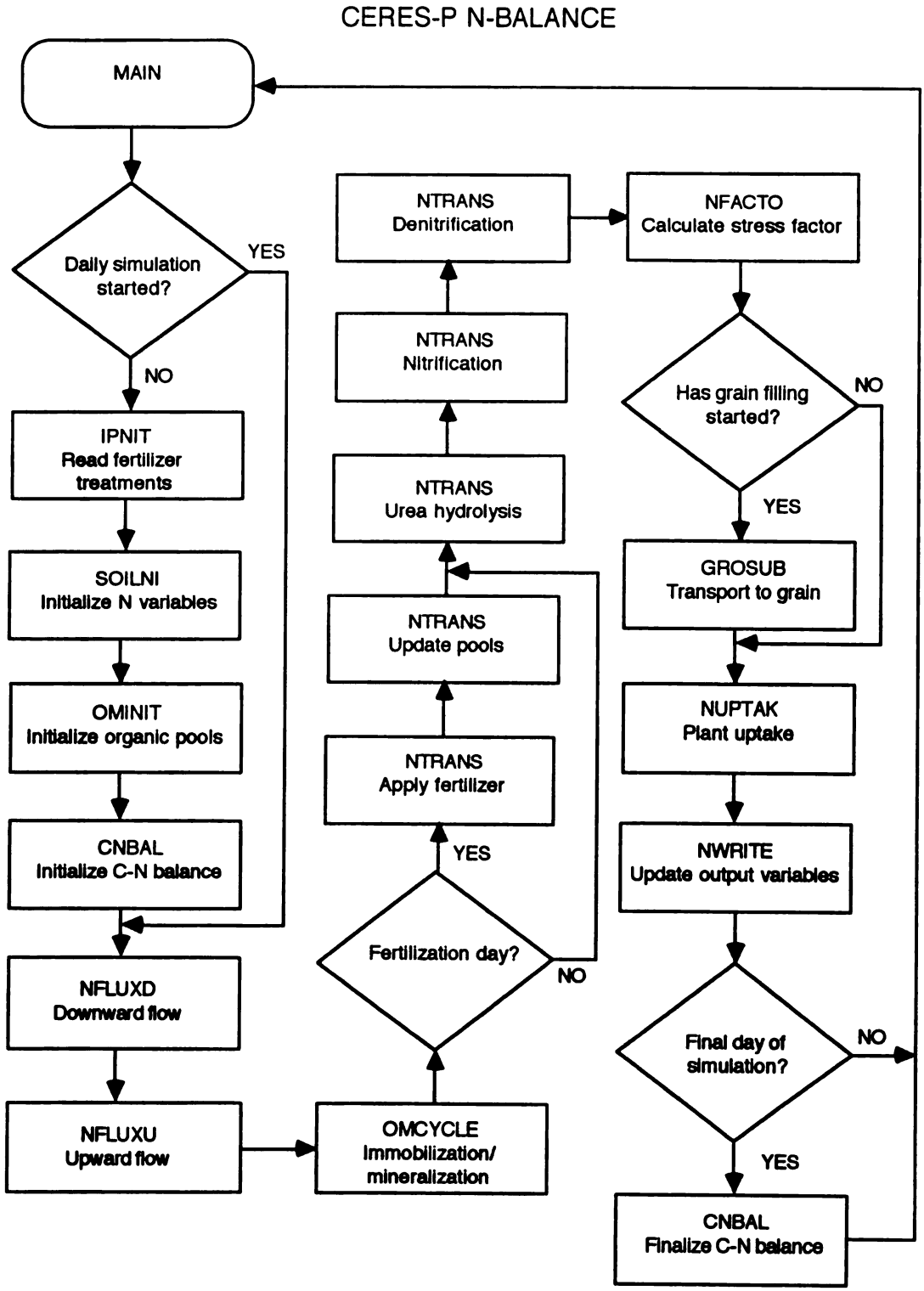

Figure 18. Flowchart of the N balance in CERES-P.

Nitrogen leaching is affected by the changes in the water balance, especially the new drainage and the inclusion of a water table. Denitrification is enhanced due to the high water-filled porosity below the water table. However, the denitrification rate recommended by Godwin and Jones (1991) had to be increased even more to improve agreement of observed with simulated NO_3-N leaching. This is further discussed under "Simulation of Chemical Leaching." Other changes in the N balance were made by D. Godwin (1992, personal communication). Specifically, the organic matter cycle is now separate from the N cycle, and it is simulated in more detail. Other programming revisions are: A rearrangement in the calling sequence of some modules, and the rearrangement of the FORTRAN common blocks into smaller common block files.

Nitrogen leaching has changed from the Godwin and Jones (1991) version. Nitrogen leaching now has a convective and a dispersive component. The relative importance of the each components depends on soil water content, water fluxes, properties of the soil, and the concentration gradient between layers. The simulation of N movement is analogous to that of the pesticide, and it is discussed in more detail under "Pesticide Model."

A new input file stores measured NO_3-N concentrations for model calibration. New output files record simulated NO_3-N concentrations, total leachate escaping through the drains, and total C/N balance for the season. These files are described under "Changes in Input/Output Since CERES 2.1."

Pesticide Model

The pesticide model was designed with maximum modularity in mind. The pesticide subprogram may be canceled easily by removing a calling statement in the main program. Table 7 identifies the links between

the main program and the pesticide subprogram. Figure 19 is a flowchart of the pesticide model. Subroutine names are in uppercase.

Table 7. Links between the main program and the pesticide component of CERES-P.

Variable description	Name	Variable description	Name
Bulk density (g/cm^3)	BD	Root water uptake factor	RUF
Concentration in solution (μg/L)	CL	Root water uptake maximum (cm)	RWUMX
Cum. leaching through tiles (kg/ha)	TPLCHT	Run number	NREP
Day cumulative output begins	DOYOUT	Saturated water content (cm/cm)	SAT
Day of simulation	JUL	Soil properties input file	FILE2
Day of the year	DOY	Soil temperature (°C)	ST
Downward water flow (cm)	FLOWD	Tile layer number	TILEL
Drainage constant (fraction)	SWCON	Total number of layers	NLAYR
Drainage flag	DRFLAG	Treatment number	NTRT
Drained upper limit (cm/cm)	DUL	Upward water flow (cm)	FLOWU
Layer thickness (cm)	DLAYR	Water before drainage (cm/cm)	SWBEFD
Net pesticide leaving layer (kg/ha)	NPOUT	Water content (cm/cm)	SW
Operating system code	OPSYS	Water table switch	ISWWT
Pesticide input file	INPFILE		

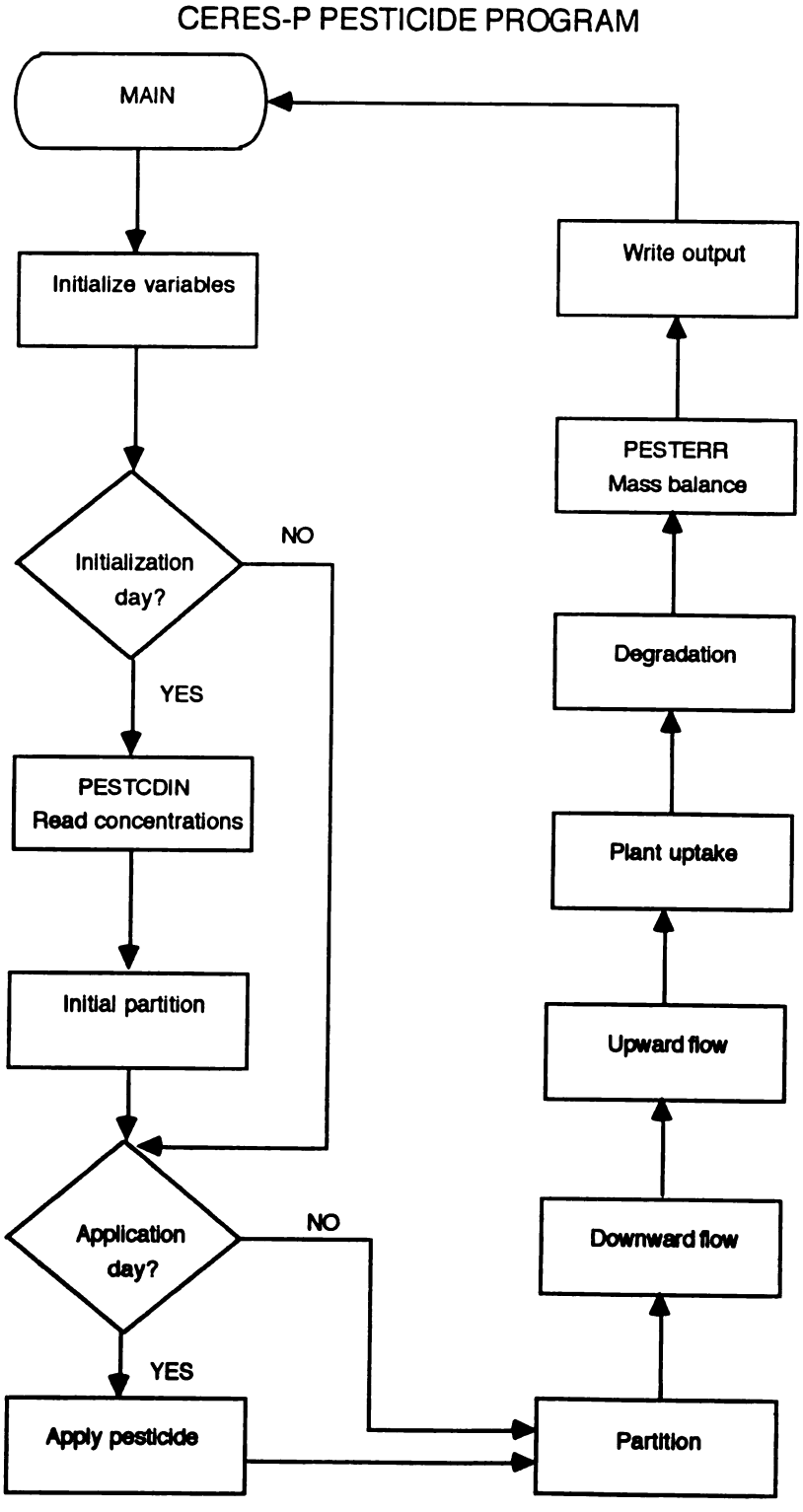

Figure 19. Flowchart of the pesticide program in CERES-P.

A description of the steps in the pesticide program follows:

Initialization. On the first day of simulation, pesticide properties and initial soil concentrations are read from the pesticide input file with extension ".mzp." Other local variables are initialized every day. The pesticide information file stores the following information: Species name, aging factor for residues, dispersivity denominator, Freundlich distribution coefficient, molar volume, aqueous solubility, half-life, IBSNAT experiment and treatment code, date of application, amount applied, and initial concentration for each soil layer.

Application. On the day of application, the prescribed amount is added to the top layer.

Partition. The pesticide is partitioned between the solid and liquid phases. The concentration in the gas phase is ignored because the saturated vapor density of atrazine is about 10^7 times less than its aqueous solubility (Jury et al., 1983 [cited in Taylor and Spencer, 1990]). However, this assumption is subject to revision. Recently, Wienhold and Gish (1993) showed that up to 9% of atrazine applied can volatilize within 35 d from application.

Partition is modeled with a first degree Freundlich-type model. Though it applies to systems at equilibrium, which are rarely attained in nature, the following reasons tend to favor this model:

1. The Freundlich-type model is fast and simple. A first approximation of the sorption coefficient is possible by looking up a previously published value for a similar soil. The experimental determination is straightforward (McCall et al., 1980).

2. The Freundlich-type model ignores the kinetics of sorption, yet within the time step of the model (1 d) adsorption should be substantially complete, at least on the "fast" adsorbing sites. Adsorption of atrazine on

stirred sediment slurries is 90% complete within an average of 8 min (Wauchope and Myers, 1985). Though field soils are not stirred, the Wauchope and Myers study suggests that at least on a local scale the reaction is fast.

3. Molecular diffusion often is cited as the rate-limiting step in the kinetics of sorption. The solute has to move from the relatively mobile interaggregate pore water into or out of the relatively immobile intraaggregate pore water. Diffusion has received thorough treatment in the study of weathering (Stumm, 1987), industrial catalysis (Satterfield, 1970), and water-saturated, somewhat static systems such as river bottom sediments (Wu and Gschwend, 1986). In soils, convective forces inside aggregates are probably more important in transporting pesticide to and from sorption sites. Diffusion could indeed be a rate-limiting step when matrix suction is very low. No satisfactory model of intraaggregate diffusion was found with parameters that can be reasonably approximated.

Two distribution coefficients for this model were experimentally determined, one for the top soil (3 cm depth) and one for the subsoil (75 cm depth). The soil was taken from a fallow turf strip at the edge of the field to obtain the lowest possible background concentration. Cores were taken with a cylindrical probe (6.8 cm height, 3.3 cm diameter) attached to the end of an iron pole about 2 m long. The deep cores were taken from the bottom of holes drilled with an auger, about 10 cm in diameter. The soil was immediately transported to the lab where it was air-dried, ground, mixed, and passed through a 2 mm sieve. Air-dry soil water content was determined gravimetrically.

The batch equilibration method was used (McCall et al., 1980). A solution of 25.7 mg/L (approximately 80% of solubility) of technical grade atrazine in deionized water was selected as the highest initial concentration.

This amount of atrazine could not be easily dissolved, so the highest concentration was reduced to 12.8 mg/L. Three-quarters (9.6 mg/L) and one-half (6.4 mg/L) of this concentration were also prepared by serial dilution.

The sorbent mass was calculated as follows: A K_d of 2 mL/g was predicted from the literature (Hartley and Graham-Bryce, 1980) and from the equation $K_d = f_{OC} K_{OC}$, using a K_{OC} of 100 mL/g (Wauchope, 1988; [cited in Wagenet and Hutson, 1990]) and measured organic C (Chapter 2). The following equation was solved for C_e, the concentration at equilibrium (mg/mL) for various values of m_w, air-dry soil mass (g):

$$q = (C_i - C_e) V_i / m_w$$

where

q = amount of atrazine sorbed per unit dry soil (mg/g)

C_i = initial concentration (mg/mL)

V_i = initial volume (25 mL)

The objective was to find a soil mass to maximize $C_i - C_e$. The constraints were to keep C_e above detection limit and to avoid exceeding the capacity of the centrifuge tubes. In the end, 5 g of dry soil were used. The soil was mixed with 25 mL of atrazine solution in a Corex® (Corning) 30 mL glass centrifuge tube with teflon-lined cap. This step was repeated for each concentration. Water "blanks" (tubes with no soil) were used to measure losses to volatilization, sorption onto glass and caps, degradation, etc. during equilibration. Soil "blanks" (tubes with no atrazine) were used to measure the background concentration from any atrazine residues. The tubes were shaken at 200 cycles/min at 23 °C for 24 h. Then they were centrifuged at 9,000 rpm (or an average of 7410 in Relative Centrifugal Force units) for 20 min. An aliquot of the supernatant was diluted 10^3 times to bring the concentration within the detection range of the analytical method. The solutions were analyzed by immunoassay, as described in Chapter 2.

The amount sorbed was calculated as follows:

$$q = (r\, C_i V_i - C_e V_e 10^3) / [m_w/(w + 1)]$$

where

r = recovery rate, estimated by C_e/C_i of water "blanks"

w = gravimetric water content of air-dry soil (g/g)

V_e = volume at equilibration (mL) estimated by $25 + w m_w/(w + 1)$

The adsorption isotherms were derived by curve fitting as shown in Figure 20. The slope of the curve is an estimate of K_d.

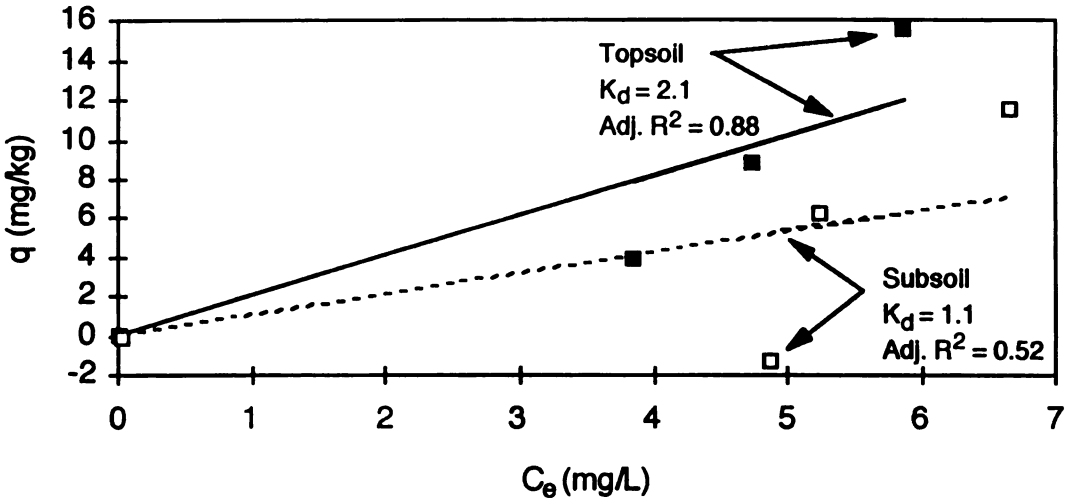

Figure 20. Atrazine adsorption isotherms for topsoil (3 cm depth) and subsoil (75 cm depth).

The K_d values are in the range reported in the literature for mineral soil (Table 6). As expected, the K_d in the subsoil is lower due to lower organic C content. Differences in pH probably were too small to affect K_d (Table 2). One data point for the subsoil shows "negative" adsorption. This shows the poor precision of indirect methods such as the batch equilibration method on subsoils and generally whenever sorption is low (Green and Karickhoff,

1990). In such cases, the direct flow equilibration method of Green and Corey (1971) may be more suitable.

The experimentally-derived K_d values disagree with field-measured concentrations. Soil concentrations were 34 to 138 µg/Kg but effluent concentrations in the same period were only 1 to 6 µg/L (Chapter 2). The above effluent concentrations were in slowly moving water that should approximate the average composition of the soil solution. It is possible that initial soil concentrations in part "aged" residues. Atrazine was used in the previous year and probably for many years, because corn was one of the rotational crops in that field. Sorption non-singularity or hysteresis has been shown for atrazine by Swanson and Dutt (1973). Boesten and van der Pas (1983 [cited in Koskinen and Harper, 1990]) report a two to three and a six to eight times increase in desorption coefficients of cyanazine and metribuzin measured 56 and 121 d after application, as opposed to 1 d after application. Hysteresis has been attributed to experimental artifacts, changes in the sorption mechanism with time, or simply non attainment of true equilibrium (Koskinen and Harper, 1990; Schrap and Opperhuizen, 1992). Durand and Barceló (1992) observed "bound residues" or "permanent contamination" in a field with long-term atrazine use, and discuss theories about their formation. They estimate the "bound" residues as 20–25 µg/kg. In CERES-P, the initial soil concentrations can be modified to reflect "effective" concentrations based on the measured effluent concentration and K_d. This is done so that at least early-season predictions agree with measured values.

The K_d at 3 cm is used for the top 26 cm. The K_d at 75 cm is used for depths below 26 cm, because at approximately 26 cm the soil type changes (Appendix A). After partitioning, if the concentration in solution exceeds the aqueous solubility, the model reduces concentration to the aqueous solubility.

Leaching. The amount of pesticide available for leaching is the amount in solution, calculated during partitioning. Downward water flows have been calculated in the water balance. The model distinguishes between "slow" and "fast" flow. Slow is any amount less than the maximum amount of water that can drain from a layer in one day, based on the difference between saturated water content and the drained upper limit. Fast flow is any amount that exceeds slow flow. The pesticide leached by slow flow is the product of the slow flow volume times the concentration in solution. The pesticide leached by fast flow is subject to dispersion. It is proportional to a coefficient and the concentration gradient between two adjacent layers. The dispersion coefficient, that incorporates the effect of diffusion, is (Marshall and Holmes, 1988):

$$D = D_m b\theta D_o + \alpha v / \theta$$

D_m = effective molecular diffusion coefficient [L^2/T]

b = tortuosity factor, approx. 0.6

D_o = molecular diffusion coefficient in bulk solution [L^2/T]

α = dispersivity [L]

v = Darcian velocity [L/T]

Dispersivity probably depends on the scale of observation (Enfield and Yates, 1990; Wagenet and Rao, 1990). In the model, it is estimated as a fraction of the thickness of two adjacent layers for which a dispersivity value is sought. The increasing thickness of the layers with depth accounts for the scale effect. The exact value of the fraction is estimated during model calibration, discussed later in this chapter. The molecular diffusion coefficient in bulk solution is estimated as the minimum of either the Wilke-Chang or the Stokes-Einstein coefficient, according to Satterfield (1970):

$$D_{\text{Wilke-Chang}} = 7.4\ 10^{-10} T(XM)^{0.5} / \mu V_b^{0.6}$$

$$D_{\text{Stokes-Einstein}} = 1.05\ 10^{-9} T / \mu V_b^{1/3}$$

where

T = temperature in K

X = empirical "association parameter" of water, approx. 2.6

M = molecular weight of solvent, 18 for water

μ = viscosity in poise

V_b = molar volume of solute in cm^3/g-mol, from Kopp's law, approx. 248 for atrazine

During evaporation, the water balance program calculates upward water flows. The amount of pesticide that moves upwards is the product of the upward flow volume times the concentration in solution.

Uptake. The model assumes that the pesticide is carried passively with the transpiration stream. Though Capriel and Haisch (1983 [cited in Koskinen and Harper, 1990]) suggest that plants may actively extract pesticide residues, there is not enough information to simulate this process. Water uptake is calculated in the water balance. Pesticide losses are the product of the water uptake volume times the concentration in solution.

Degradation. Little is known of atrazine degradation kinetics in the field. First order kinetics often are assumed (Wagenet and Rao, 1990; Stearman, 1992). Lavy et al. (1973; 1993) report that the degradation rate of atrazine decreases with depth under either aerobic or anaerobic conditions. In CERES-P, a half-life of 60 d is assumed for the top 57 cm, based on Wauchope (1988 [cited in Wagenet and Hutson, 1990]) and Lavy et al. (1993). A half-life of 120 d is assumed for deeper layers, based on Lavy et al. (1993). The amount of pesticide species that remains each day is calculated.

Mass Balance Check. A mass balance check ensures that no pesticide is unaccounted for. The following equation must be true:

total mass in soil yesterday + today's additions = total mass in soil at the end of the day + net leaching + plant uptake + degradation losses

If pesticide mass is not preserved on any given day, an error message is generated and the model pauses.

Changes in Input/Output Since CERES 2.1

The following are technical notes for users of version 2.1 who wish to test CERES-P with existing DSSAT-compatible input files. This documentation is in addition to IBSNAT technical report 5 (IBSNAT, 1986).

Inputs. The model uses all existing DSSAT input files with the following exceptions: Soil layer thicknesses are no longer user-defined. For the top eight layers the thicknesses must be, from top to bottom, 2, 5, 8, 11, 14, 17, 20, and 23 cm (each layer has the thickness of the previous layer plus 3). For the ninth layer and deeper, thickness must be 25 cm. Thinner layers near the surface allow for a more precise estimate of mass and energy transfer near the surface (Ritchie, 1993, personal communication).

The following inputs must be added to the soil properties file (File 2): Macropore saturated hydraulic conductivity in each layer (KSMACRO), macropore saturated hydraulic conductivity below the profile (KSDEEP), matrix saturated hydraulic conductivity (KSMTRX), a root water uptake constant (RWUCON), the maximum ponding depth (PONDMAX), and the maximum flow rate through the tile drains (FLOWMX). The saturated macropore hydraulic conductivity below the profile defaults to the same value as for the bottom layer. Maximum ponding depth defaults to 5 cm.

Two new input files are required to run CERES-P. A file with extension ".mzw" stores the water table management depths and a switch to show whether the drains are open on a given day. A file with extension ".mzp" stores pesticide properties, the initial pesticide concentrations in the soil, and management information. Another input file (inconc.mz) may be

used to store measured concentrations of NO_3-N and pesticide escaping from the tile drains. This file is optional, and may be used for model calibration.

Output. Several new output files were created. A water balance output file (outwb.mz) records basic water balance outputs in a comma-delimited format, readable by most spreadsheets. The leaching output file (outlch.mz) records cumulative drainage, cumulative NO_3-N leaching, and cumulative pesticide leaching starting either on the first day of simulation or on an arbitrary date. The concentrations output file (outconc.mz) stores simulated NO_3-N and pesticide concentrations. A detailed pesticide output file (outp.mz) stores pesticide mass, total concentration, and solution concentration for each day and for each layer. Finally, the C/N balance file (outcnb.mz) stores initial and final C and N balance outputs.

To use these new files, two extra lines of information must be added to the experiment file directory (mzexp.dir) for each experiment. The experiment file directory previously contained three lines for each experiment. The fourth line should list the new files for water table input, measured concentration input, pesticide input, water balance output, leaching output, and concentration output. The fifth line should list the new files of pesticide and C/N balance output. Filenames use the twelve-character DOS naming convention and must be separated by a blank space. Filenames of less than twelve characters must be padded with blank spaces at the end. Samples of the input and output files used for testing the model are in Appendix C.

RESULTS AND DISCUSSION OF SIMULATION MODEL TESTING

The flooding experiment described in Chapter 2 was simulated. Samples of the input files are in Appendix C. Total N and pesticide balance

were not calculated. As explained in Chapter 2, there were not sufficient measurements to calculate a total mass balance. Final soil concentrations could be measured, but the soil was to remain undisturbed for the preferential flow observation, described in the next chapter.

Simulation of Water Content

Figure 21 shows observed versus simulated volumetric water content during the season. By default, the model prints the simulated water contents of the top five layers (0 to 40 cm depth) in output File 3 (out3.mz). For Figure 21, the model was modified to print the water content for the five layer groups that correspond to the five measurements depths. The measurement depths, 13, 26, 42, 67, and 89 cm, correspond, in that order, to model layer groups one to four, four to five, five to six, seven, and eight. The thickness of model layers is the first data column of the soil properties input File 2, in Appendix C.

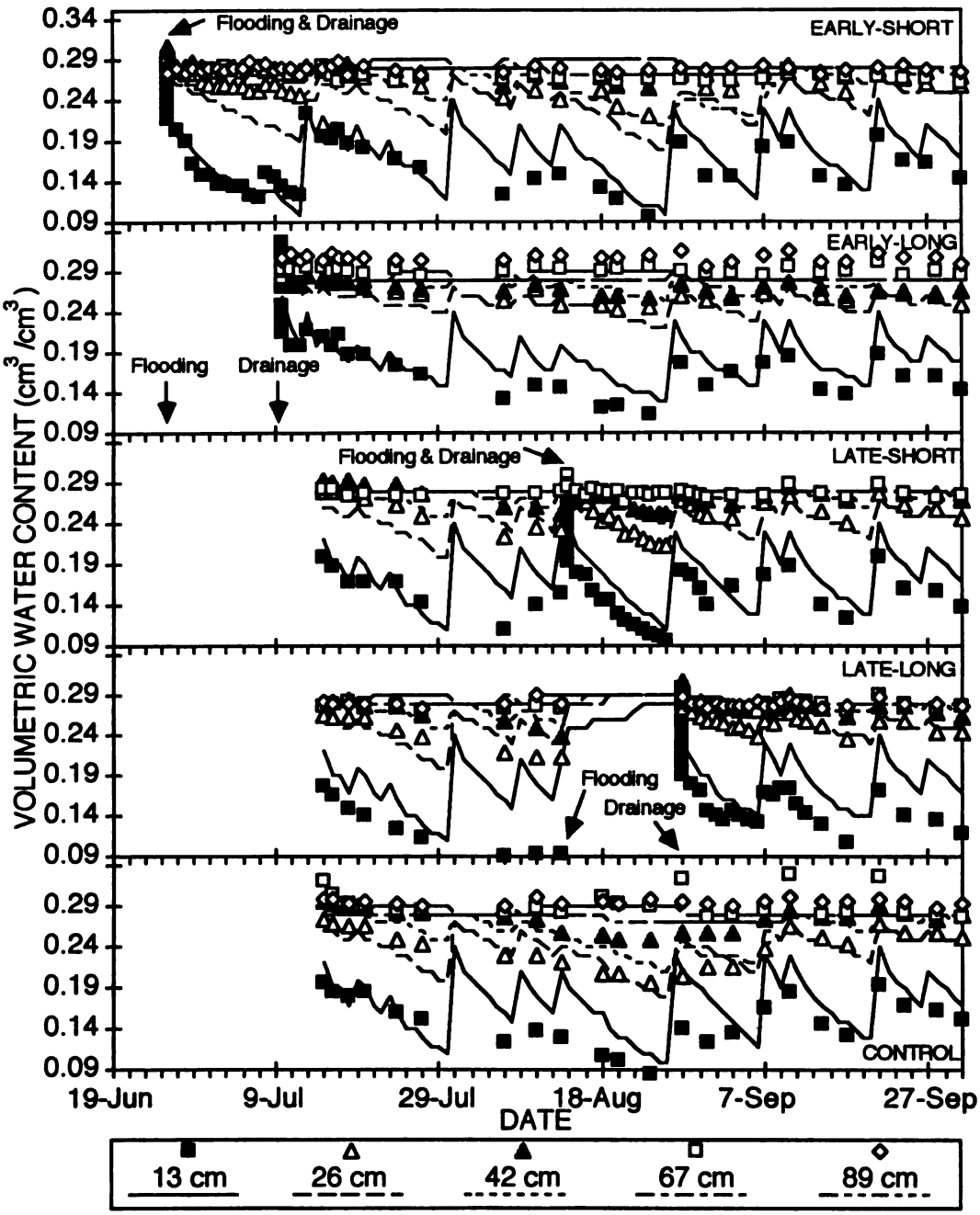

Figure 21. Volumetric water content at five depths during the season. Markers are measured values, lines are simulated values.

The trend in water content is simulated well at 13 cm, particularly after drainage. Water content at 26 cm occasionally is underpredicted, although

prediction improves late in the season. The water content of the deepest layers in Early-Long and Control sometimes is underpredicted. In Early-Long the bias is systematic, and it could be because of bias in neutron meter calibration.

Soil water content is the combined result of several processes. Climate, soil, and plants comprise a complex system that affects soil water content. Therefore, there are several potential sources of error. One class of errors comes from simplifying assumptions, such that the water table moves in whole layer increments. Natural processes are distributed continuously over space and time, yet for computational reasons models divide space and time into discrete increments. This may result in discontinuities in the model output. In all models, the size of space and time increments is a compromise between accuracy and computational efficiency. In CERES-P, there is the additional requirement of compatibility with the input and output file format of the DSSAT models.

The other class of errors relates to measurements. There is some error in the calibration of the neutron meter. There is random error in the neutron counts, which is partly offset by averaging several counts over time. The neutron meter samples a theoretical volume of about $3x10^{-2}$ m^3 (Marshall and Holmes, 1988) but that volume changes with water content. Soil properties, such as the water content limits, are considered uniform across lysimeters. The assumption is reasonable because of the small area of the facility, compared with the entire field. Yet, there could be small scale variation.

Figure 22 shows the water balance components. Deep drainage corresponds to the "unaccounted" water that was discussed in the experimental results section (Chapter 2). Subirrigation is approximately equal to deep drainage, as expected, except for the two long flooding treatments

wh

and

Ob

me

where substantial surface additions also contribute to deep drainage. Rain and surface irrigation are measured. The other components are simulated. Observed versus simulated tile drain flow is in Figure 23. Uninterrupted measurements were available only for the limited period following drainage.

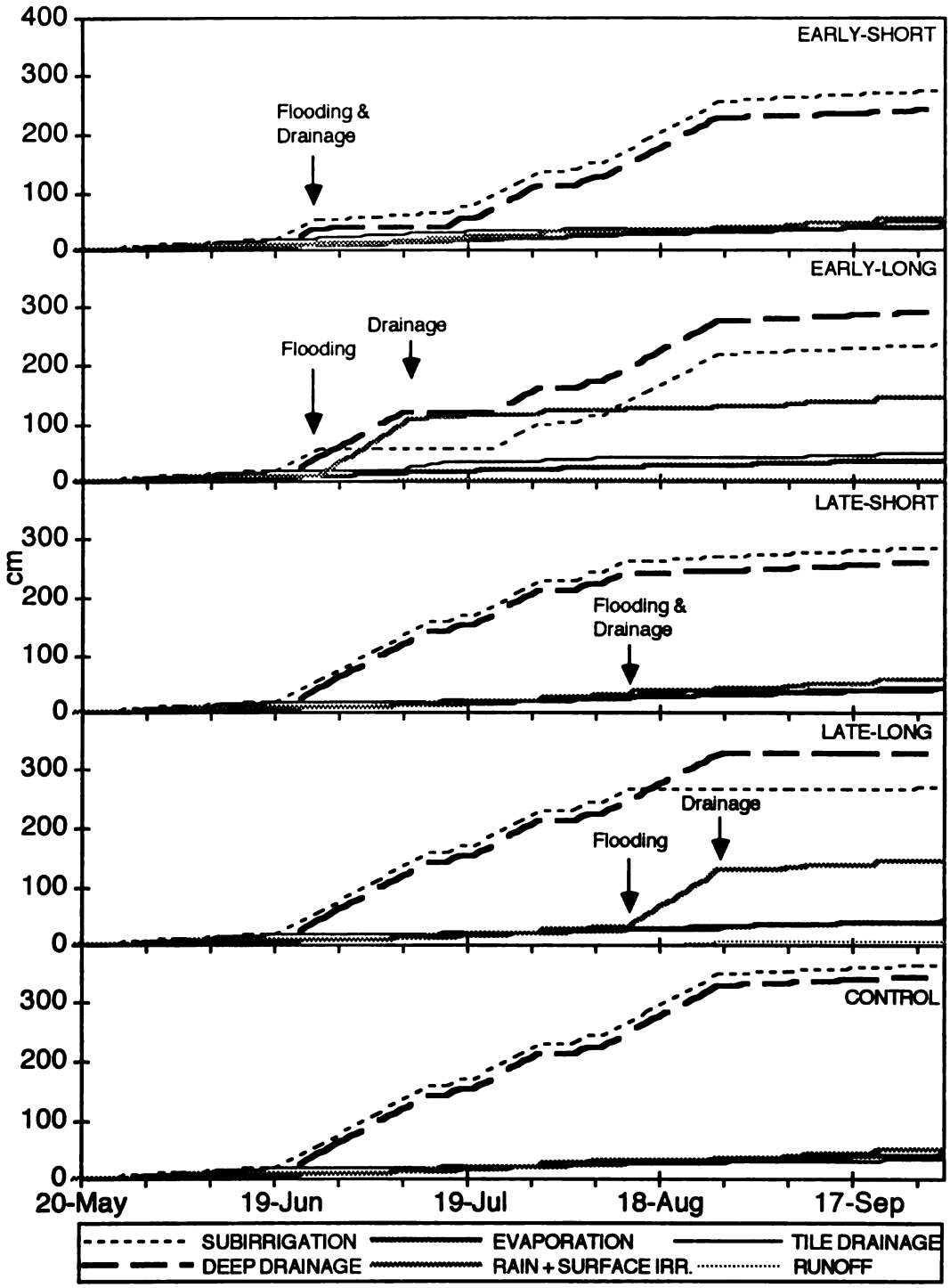

Figure 22. Simulation of cumulative water balance components. Rain and surface irrigation are measured.

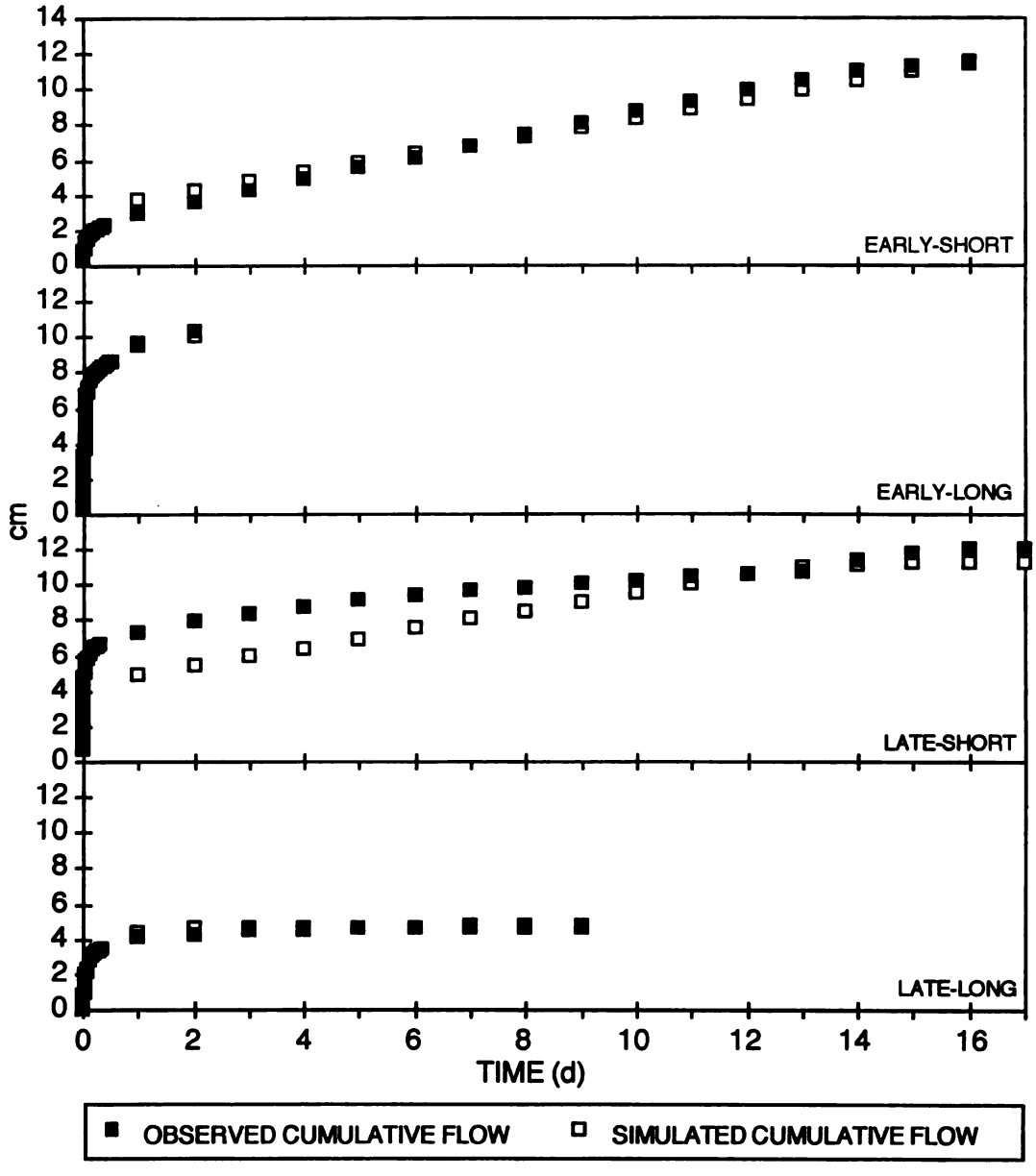

Figure 23. Observed versus simulated cumulative tile drain flow for the period following drainage of the flooded treatments.

Simulated tile drain flow agrees well with observed tile drain flow, except for an early lag in the simulated flow of Late-Short. After several days, observed and simulated cumulative flows coincide.

Simulation of Chemical Leaching

To improve model performance, calibration of some model parameters is required. Calibration is needed because of uncertainty in the parameters such as dispersivity, the "aging factor" for residues, and degradation rate. For simple mathematical models, parameter estimation often is done by curve-fitting. Enfield and Yates (1990) calculated dispersivity using a least squares fit to data from breakthrough experiments. White (1985) suggests that dispersivity be derived by curve-fitting, though he encourages independent estimation, possibly based on an index of soil structure. Dispersivity estimates vary from 0.1 to 20 cm (White, 1985) to 200 cm (Enfield and Yates, 1990). For numerical models and for a limited number of parameters, trial-and-error may be used. Laboratory experiments and trial-and-error were used by Wagenet and Rao (1990) to estimate optimum transformation rates of aldicarb and its derivatives in the field. Optimizers such as Box's complex (Kuester and Mize, 1973) also are available for nonlinear, multiple parameter estimation with optional inequality constraints.

Box's complex was used in CERES-P to estimate best values for dispersivity and the aging factor for atrazine residues. The criterion minimized was the sum of squared deviations between observed and simulated concentrations. The inequality constraints were as follows: Dispersivity had to be between 0.1 to 200 cm, a range commonly encountered

in the literature. The aging factor had to be a fraction between 0.01 and 1.0. These constraints were necessary to avoid illogical results and save computer time. The results of the search were as follows: For each pair of adjacent layers, optimum dispersivity (in cm) was the thickness of the layers divided by 7.6. The thickness of the layers was introduced in the calculation because dispersivity probably is scale-dependent (Enfield and Yates, 1990; Wagenet and Rao, 1990). The optimum aging factor was 0.12.

Early simulation results (not shown here) significantly overpredicted the amount of NO_3-N leaching from the Late-Short treatment. Either the efficiency of the sinks was too low or the efficiency of the sources was too high. A simple solution was to increase denitrification so that when Late-Short is drained, less N is available in the soil for leaching. The denitrification rate recommended by Godwin and Jones (1991) was increased 7.2 times.

Figures 24 and 25 show observed versus simulated NO_3-N and atrazine concentrations. Further fine-tuning of model parameters is possible, but it will not necessarily improve the fit to the data. One limitation in testing deterministic models is the variability inherent in the field. For example, between 18 and 20 June three of the five treatments had NO_3-N peak concentrations above 15 ppm. The other two treatments did not. Yet, until that date all treatments were treated the same. The cause of these differences is not a known soil property or management variable, therefore this variability cannot be simulated. An alternative would be to build a stochastic model that would associate a measure of uncertainty with each prediction. Alternatively, CERES-P could be modified to run in Monte-Carlo mode.

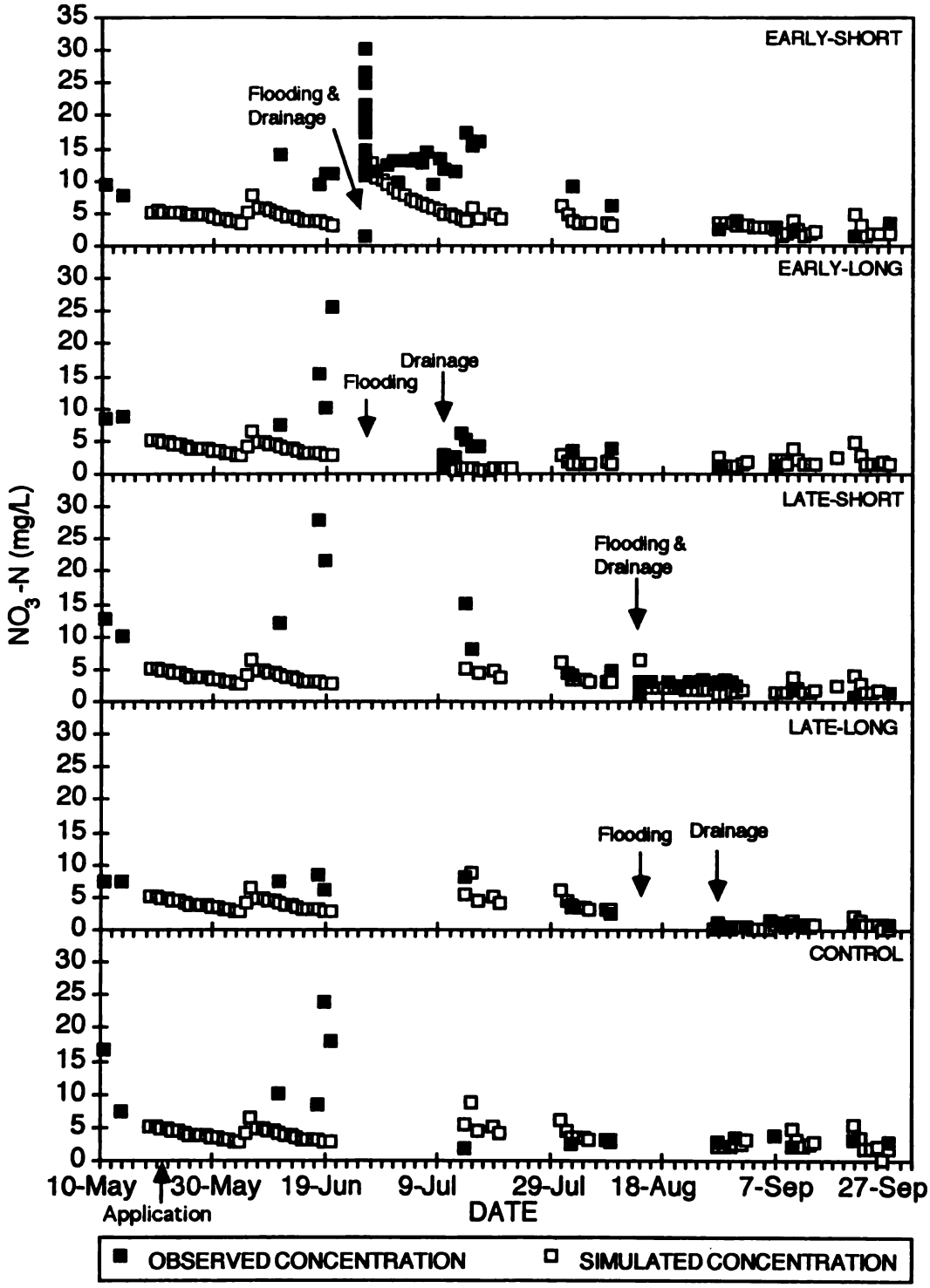

Figure 24. Observed versus simulated NO_3-N concentrations.

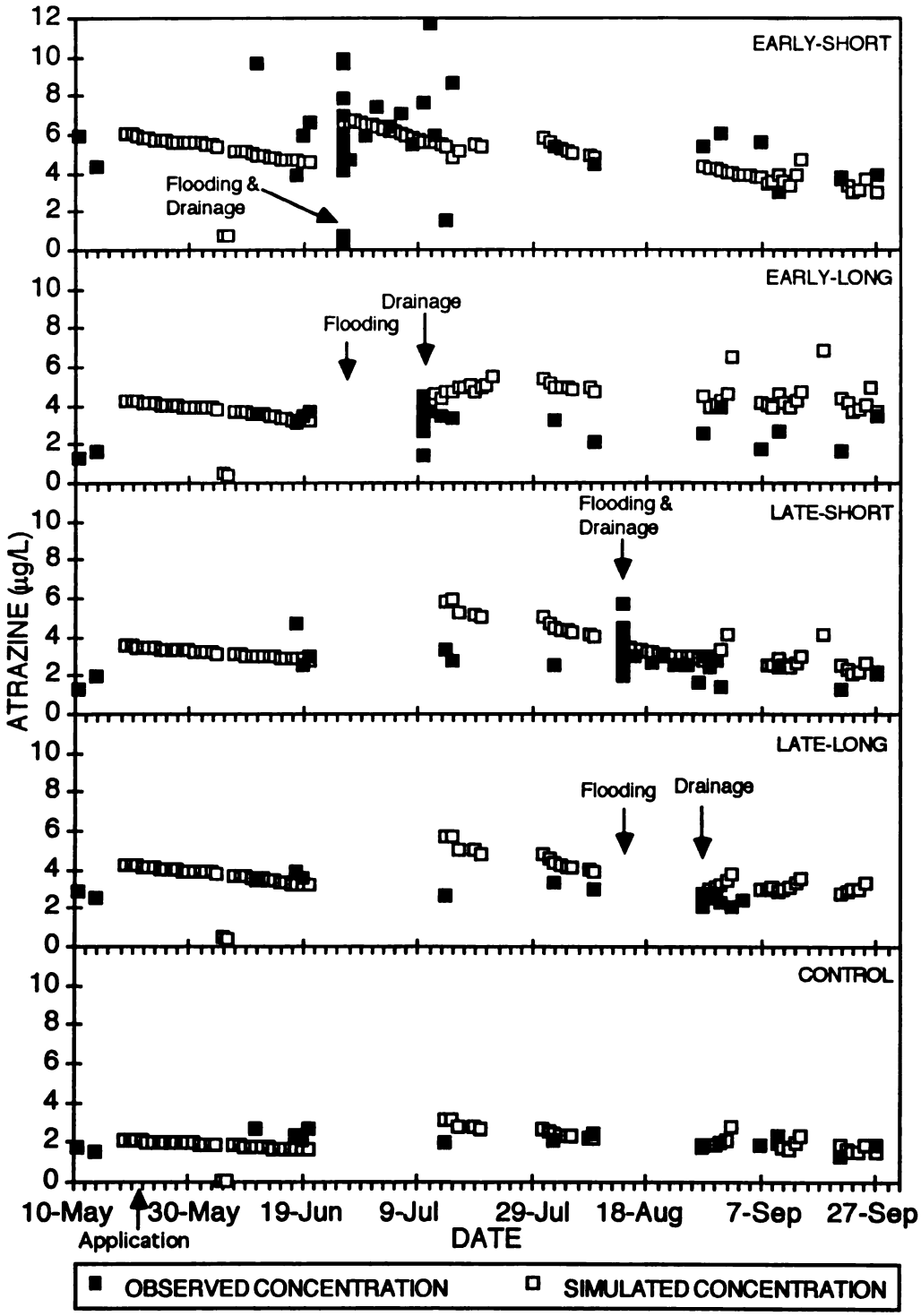

Figure 25. Observed versus simulated atrazine concentrations.

Figure 26 shows observed versus simulated cumulative NO_3-N and cumulative atrazine that escaped the drains following drainage of the four flooded treatments. Nitrate-N and atrazine are shown as % and ‰ of quantity applied. To show small differences, the scale of each graph differs.

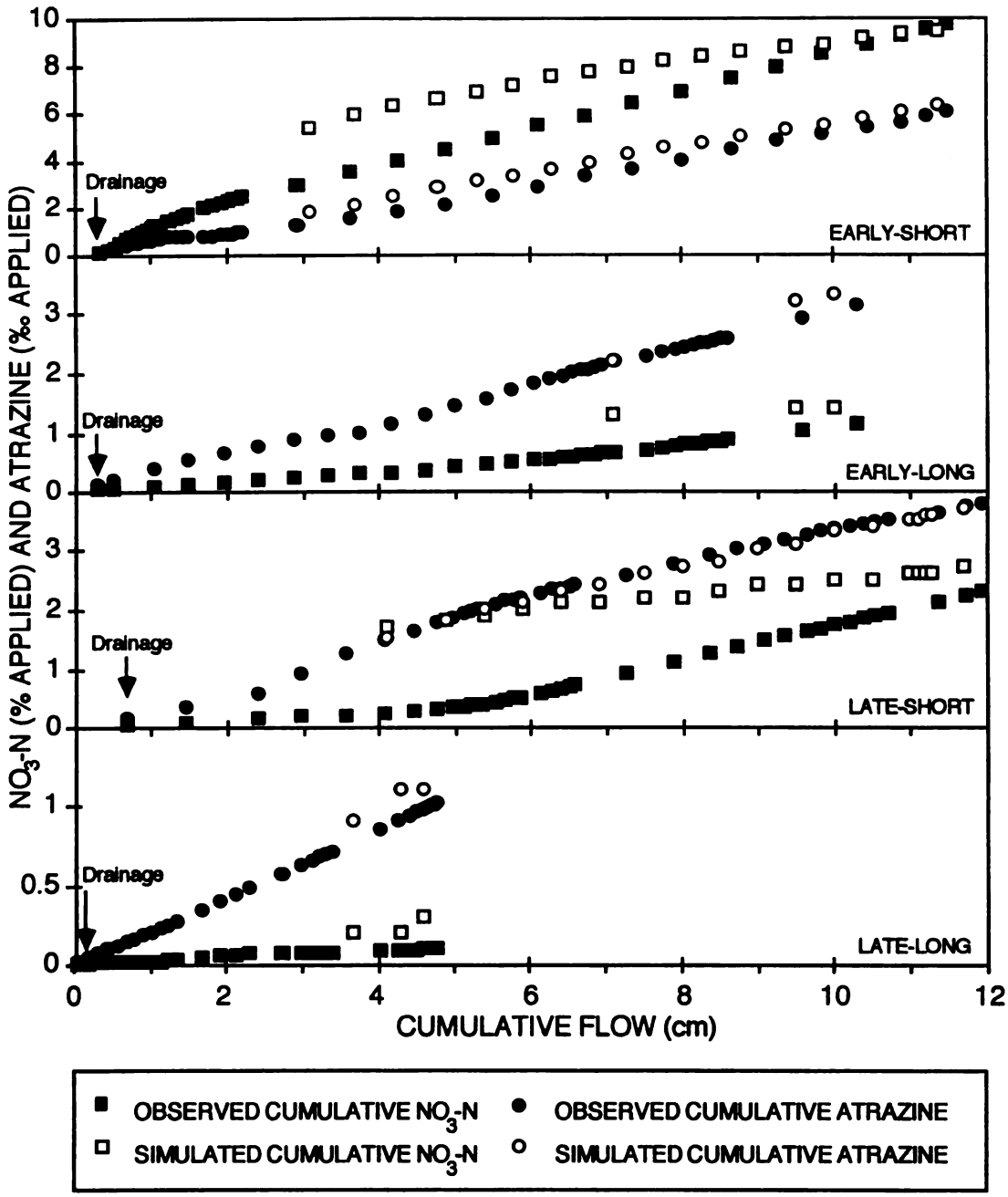

Figure 26. Observed versus simulated cumulative NO_3-N and cumulative atrazine that escaped the drains following drainage of the four flooded treatments.

In Figure 26, the model leaches NO_3-N "faster" (using drainage as a measure of time) than the rate observed in the field, though eventually simulated values approach the observed values. There are two likely explanations for N leaching "fast." In the long-term flooding treatments, it may be an underestimation of the N dissipation rate, so that too much N remains in the soil by the end of the flooding period. As explained, increasing the denitrification rate was necessary to improve estimates for Late-Short. For the short-flooded treatments, the most likely explanation is an effect of by-pass flow. In both of these treatments, surface irrigation was applied at a high rate to raise the water table to the surface. Soil matrix forces held N in the intraaggregate solution, protected from leaching. By the time the soil was near-saturated, matrix suction dropped significantly, yet N could not diffuse fast enough into the mobile water of the interaggregate pore space.

Other possible reasons for disagreement between measured and simulated values are:

1. Lateral intrusion of groundwater into the lysimeter that could influence concentration measurements.

2. The rounding error from moving the water table in whole layer increments. Deeper layers become progressively thicker, therefore rounding error increases with depth.

3. Preferential flow. By-pass of the intraaggregate solution has been somewhat discussed. Though macropore flow may cause less of the solute to leach at any one rainfall event, it may cause the solute to appear sooner in the tile effluent. This is especially true soon after fertilizer application, when N had not had the chance to move inside the aggregates. For example, heavy precipitation on 17 and 18 June (2.5 cm) apparently increased NO_3-N concentrations in the tile effluent of some plots. Yet,

according to the model, most of this water was absorbed by the dry soil surface, instead of reaching the drains. Sichani et al. (1991) report a similar problem when they tested GLEAMS; the model did not predict the observed pesticide loss during the first outflow event after pesticide application. A preferential flow mechanism not considered in the CERES-P is fingering. "Fingers" of solution may advance faster than the main wetting front and affect outflow concentrations.

4. Most drainage samples were taken around mid-day. Simulated concentrations, however, represent daily means. The concentration at mid-day does not necessarily coincide with the mean, especially when the water regime changes fast.

5. Nitrate leaching is affected not only by the spatial heterogeneity in water flows, but by the spatial heterogeneity of N over short distances. The uneven distribution of N fertilizer and mineralized N contribute to this heterogeneity (White, 1985). In this study, N fertilizer was not spread uniformly but placed in bands close to the seed. The distribution of atrazine is more predictable because it was applied uniformly.

Plant Measurements

Table 8 shows observed and simulated plant measurements. At harvest (3 October) the crop was not at physiological maturity, due to cooler-than-normal temperatures. Observed and simulated yield and biomass are on the date of harvest.

An adjustment was made in the phenology of the model. CERES assumes 1 ear/plant. In the field, a mean of 1.9 ears/plant were observed. As a result, the number of kernels per plant was underpredicted. Because yield calculation depends on the number of kernels per plant, the number of

kernels in the model was increased 1.3 times to match the observed count. The increase factor was 1.3 and not 1.9 because the second and third ear have fewer kernels than the first.

Table 8. Plant measurements at harvest, observed vs. simulated.

	Treatment									
	Early-Short		Early-Long		Late-Short		Late-Long		Control	
	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.
Kernels/m^2	2567	3069	1014	1506	2000	3023	2484	2211	3025	3030
Kernel weight (g)	0 .24	0.18	0.22	0.06	0.25	0.18	0.24	0.18	0.25	0.18
Grain yield(kg/ha)†	7317	6364	2619	1065	5905	6271	6929	4585	9080	6285
Biomass (kg/ha)	15167	16159	5507	4975	12814	15493	14021	13872	15999	15429

†Includes 15.5% moisture.

Most yields were underpredicted, in part because the increase in simulated denitrification rate resulted in increased N deficiency. Nitrogen deficiency showed as an increase in the N stress coefficients. Another reason for the underprediction is the uncertainty about the effect of waterlogging on roots and yield. The work of Lizaso (1993) on the effect of waterlogging on root growth was incorporated in the model, but more experimental information is needed. Comparisons of observed versus simulated biomass are more favorable than those for yield. This implies that the partitioning of biomass among plant organs may need adjustment for the particular conditions.

CONCLUSIONS

Pesticide simulation is complex. It involves many processes, each influenced by several biotic and abiotic factors. All basic processes have been included in the model. Yet, knowledge is lacking in many areas. Some processes are not well known. Detailed simulation of some processes would require a prohibitive quantity of data. Simplifying assumptions regarding sorption, degradation, mass transport, and plant uptake were made. The objective of CERES-P was to produce realistic simulations without excessive data requirements that would make it impractical to use. For optimum performance, some parameters have to be calibrated for each site.

Model performance should be evaluated within the context of uncertainty of field observations. Given the above limitations, the model adequately simulated water balance, atrazine and NO_3-N concentrations for the season, and total leaching for the limited period following drainage. Total biomass was predicted reasonably well though grain yield was underpredicted for most treatments. Future work should focus on simulation of preferential flow and its effect on solute movement.

CHAPTER IV

DEMONSTRATION OF PREFERENTIAL SOLUTE MOVEMENT

PROBLEM STATEMENT

Water does not always wet the soil as a uniform, planar and abrupt wetting front or "piston flow." Preferential flow pathways have been demonstrated in several works, such as those reviewed by Beven and Germann (1982). Preferential flow frequently occurs at or near saturated conditions, such as those found in subirrigation/drainage systems. Water may by-pass the bulk of the soil matrix and rapidly transport contaminants below the root zone causing economic loss and environmental damage. In other cases, preferential flow may be beneficial; it may by-pass solute located within soil peds and reduce the total amount of solute leached.

Despite its potential importance, preferential flow does not show prominently in the simulation of solute transport. In their model of water and pesticide movement, Wagenet and Hutson (1986) cite the lack of preferential flow as a possible cause for inaccurate results.

Because of its potential significance in subirrigation/drainage systems, an observation of preferential flow was included as part of this study. This chapter describes the results from the field observation and discusses potential applications to simulation modeling.

REVIEW OF THE LITERATURE

History of Preferential Flow

Preferential flow has been recognized for more than a century. Beven and Germann (1982) review the major milestones, summarized in the following paragraph.

In 1864, Schumacher wrote: "the permeability of a soil during infiltration is mainly controlled by big pores, in which the water is not held under the influence of capillary forces." In 1882, Lawes et al. reported of early plot drainage experiments: "The drainage water of a soil may thus be of two kinds: it may consist (1) of rainwater that has passed with but little change in composition down the open channels of the soil; or (2) of the water discharged from the pores of a saturated soil." Horton (1942) coined the term "concealed surface runoff" for rapid turbulent flows through cracks in the soil surface. Hursh (1944) reported "hydraulic pathways" created by soil aggregates and soil organisms who upset the laws of traditional soil mechanics.

Childs et al. (1957) were surprised to find that some clayey soils approach the permeability of gravel. They attributed that to fissures in clay: "It is perhaps surprising that large cracks should exist below the water table." Ritchie et al. (1972) and Kissel et al. (1973) are some of the first to trace preferential flow with chemical tracers. Hill and Parlange (1972) were the first to publish in English a entire report on fingering, according to Baker and Hillel (1991). More recently, Germann and Beven (1981a and 1981b), Beven and Germann (1981 and 1982) and Bouma (1981) are credited with reviving interest in preferential flow. The bulk of the preferential flow literature dates after 1981.

Definition of Preferential Flow

Several synonyms are used: By-pass flow, channeling, macropore flow (Beven, 1991); short circuiting flow, fingering, funneling (Kung, 1990b); wetting front instability, partial volume flow (Baker and Hillel, 1991). Channeling, macropore flow, short circuiting flow, fingering and funneling usually imply specific mechanisms. Channeling, macropore flow and short circuiting flow often mean flow in large pores. According to Beven and Germann (1982), channeling also implies continuity and connectivity that is not true of all large pores. Kluitenberg and Horton (1990) believe that the term should depend on the scale of observation. Thus preferential and by-pass flow happen at any scale, whereas macropore flow is flow through interaggregate space, shrink-swell cracks, and faunal tunnels.

Non-capillary structural voids seem to be one cause of preferential flow. Another cause would be the instability of the wetting front under certain conditions, even without obvious structural channels. Beven (1991) proposes the following simple definition: Preferential flow is the phenomenon in which, during wetting, local wetting fronts propagate into the soil to significant depths thus bypassing the intervening matrix. This definition will be used throughout this study because it is independent of mechanism.

Macropore Flow

Poiseuille showed that the flow rate through a single cylindrical tube is proportional to the pressure drop per unit distance and proportional to the fourth power of the radius (Hillel, 1982):

$$Q = \pi R^4 \Delta p \; / \; 8\eta L$$

where

Q = volume flow rate [L/T]

R = radius [L]

Δp / L = pressure drop per unit distance [$ML^{-2}T^{-2}$]

η = viscosity [$ML^{-2}T^{-1}$]

L = length of tube [L]

Poiseuille's law suggests that even a small increase in the radius of a soil pore will effect a dramatic increase in the flow rate along the pore. It is conceivable that the relative contribution of macropore flow can be estimated from the number and size of water-filled pores.

Unfortunately, Poiseuille's law assumes a cylindrical (or at least known shape) pore and laminar flow. Yet, soil pores have irregular geometry, they are not necessarily connected, and flow is not necessarily laminar. This has led to alternative definitions of macropores, such as that of equivalent radius. It is later discussed in "Simulation of Preferential Flow."

High water application rates promote macropore flow compared with low rates (Omoti and Wild, 1979b). The same is true of the pulse method of solute application compared with the drip method (Kluitenberg and Horton, 1990). Because macropores have larger radius, they fill at lower suction than the soil matrix, thus they are activated when the soil is at or near saturation. Exceptions are cited by Beven and Germann (1982). For example, stem flow and drip from plant canopy can create locally saturated conditions that may initiate macropore flow.

Fingering

Fingering is the break up of a uniform wetting front into protrusions or "fingers" that advance faster than the bulk of the flow. This wetting front

instability happens at a horizontal boundary where water passes from a fine to a coarse layer, when a dense solution displaces a less dense one, or when soil air is compressed (Hill and Parlange, 1972; Kung, 1990b). Fingering is unpredictable. Baker and Hillel (1991) report that in sand that has been repeatedly wetted and dried, only some fingers traverse the same paths repeatedly. It is unknown, however, whether this is caused by a rearrangement of the particles between wettings. Hill and Parlange (1972) report that the number of fingers per unit area is directly proportional to the flow rate. The width of the fingers is not.

Funneling

Funneling or funneled flow happens when coarse sand layers or densely-packed fine layers in an interbedded soil behave as the walls of a funnel. Water flows laterally along the funnel walls before it descends as a concentrated column (Kung, 1990b).

When a coarse layer underlies a finer one, funneling happens because the matrix suction of the lower layer is less than the matrix suction of the upper layer. For water to jump across the interface (a "Haines jump") the height of the water inside the capillary pores of the upper layer must exceed a critical value which depends on the radii of the pores of the two layers. When a densely-packed, low permeability layer underlies a less dense one, funneling happens because of the restricting hydraulic conductivity of the denser layer (Kung, 1990b).

Anisotropy

Anisotropy is the numerical ratio of the horizontal hydraulic conductivity to the vertical hydraulic conductivity (Childs et al., 1957). Anisotropy results in preferential flow, in the sense that the water can move easier in one direction than another. Childs et al. found a very wide range of anisotropies in field soils, from 1 (isotropic) to 7 10^4.

Simulation of Preferential Flow

Though the importance of preferential flow has been known for long, only recently it was introduced in simulation models of water and solute movement. For a single cylindrical pore, macropore flow could be adequately described by Poiseuille's law. Because Poiseuille's assumptions of known pore shape and laminar flow do not necessarily hold in soils, alternative models have been devised.

The capillarity equation is (Marshall and Holmes, 1988):

$$p = -\rho g s = -(2\gamma\cos\alpha)/r$$

where

p = pressure of the water [$ML^{-1}T^{-2}$]

ρ = density of water [M/L^3]

g = acceleration of gravity [L/T^2]

s = suction [L]

γ = surface tension of water [M/T^2]

α = contact angle, usually assumed zero

r = tube or pore radius [L]

When solved for r, the above equation gives the equivalent or effective radius of the narrowest pore that would empty at an arbitrary

suction. This led Germann and Beven (1981a) to define macroporosity as the effective radius at 1 cm suction, which is about 0.15 cm. The exact value depends on temperature, the actual contact angle, the direction of change (wetting versus drying), and changes in matrix volume due to swelling/shrinking.

A change in suction effects a change in soil water content, which can be predicted by the characteristic curve and the direction of change. Thus, macroporosity can also be defined as the water filled porosity that empties at a given suction. Water filled porosity, in turn, affects hydraulic conductivity. Germann and Beven (1981a) found that a decrease in the volumetric water content of two samples by 0.01 and 0.045 decreased hydraulic conductivity by factors of 18 and 4.3 respectively.

Using Brülhart's data (1969) and their own observations, Germann and Beven (1981a) suggest a dual mode flow model (also called a two-domain model [Beven and Germann, 1982]). As suction increases from zero, conductivity drops sharply (flow mode 1), then is about constant until the air phase in the micropores becomes continuous, and decreases again (flow mode 2). Macropore flow occurs during the small change in water content when suction is just above zero and capillary forces are not yet in effect.

In another work, Germann and Beven (1981b), using data from Burger (1927, 1929, 1932, 1937, and 1940), modeled macropore saturated flux density as a polynomial function of macropore volume. Macropore volume was defined as the volume fraction of water draining in 24 h:

$$Q_{ma} = 3.266\, e_{ma}^{2.412}$$

where

Q_{ma} = macropore saturated volume flux density [$cm^3\,cm^{-2}\,s^{-1}$]

e_{ma} = macropore volume [cm^3/cm^3]

In the same work, Germann and Beven, using Ehlers' data (1975), showed that the volume flux in a worm hole is proportional to approximately the fourth power of the hole's radius:

$$q_p = 66.7\, r^{4.136}$$

where

q_p = volume flux through a single pore [cm^3/s]

r = pore radius [cm]

This model resembles Poiseuille's law. Yet, this is because worm holes are more likely to be regular in shape and more cylindrical than other macropores.

RESEARCH OBJECTIVES AND GENERAL APPROACH

The above simple models ignore the effect of scale and pore connectivity. These can be decisive factors in water and solute movement as demonstrated by Ritchie et al. (1972) and Kissel et al. (1973). They also ignore mechanisms such as fingering and funneling. Finally, solute flow is not just a function of water flow rate. It may be simultaneously affected by adsorption, diffusion and dispersion. Thus, a field observation was designed to reach some practical conclusions about the combined effect of all these factors. These conclusions are intended to improve on the model developed in Chapter 3, rather than generate an all-purpose by-pass flow model.

The experimental approach was to leach a surface-applied pulse (slug) of chemical tracers with clean water. The irrigation rate was high enough to induce saturated conditions at the surface and promote preferential flow.

MATERIALS AND METHODS

Tracer Selection

Several materials have been used to trace water and chemical movement in soils and groundwater; fluorescent and non-fluorescent organic dyes, ionized substances, solid granules, microorganisms, fluorocarbons, gases, stable and radioactive isotopes. These are reviewed in Davis et al. (1980). Some types are preferred for ground water tracing, others for soils. The ideal tracer for use in soils has the following properties: Low toxicity, low cost to purchase and analyze, high aqueous solubility, high sensitivity, low detectability,[8] low background concentration, low diffusion, moderate adsorption, high visibility, and resistance to chemical, photochemical and microbial degradation. Probably no single tracer has all these attributes, so the choice should be guided by the application.

Two tracers were sought for this study. One had to be non-adsorptive and non-degradable, to simulate movement of water and NO_3. The other would have to be adsorbed to some degree, to simulate movement of organic pesticides. Bromide was selected as a non-adsorptive tracer because of its availability, low cost of purchase and analysis, low background concentration, low toxicity, and earlier successful use (Davis et al., 1980; Everts et al., 1989; Czapar and Kanwar, 1991; van Es et al., 1991). The adsorptive tracer was to be a dye, to provide some visual identification of flow pathways.

---

[8]Sensitivity depends both on the efficiency of the dye in converting excitation energy into fluorescence and the transmission of the filter combination, if a filter fluorometer is used. Detectability also depends on the background or "blank" fluorescence (Smart and Laidlaw, 1977).

Fluorescent organic dyes are particularly popular. Their chief advantages are: High aqueous solubility, high sensitivity, low detectability, visibility in soil (Smart and Laidlaw, 1977; Smettem and Trudgill, 1983). Potential limitations are: High adsorption, sensitivity of fluorescence to pH, photo-decomposition, background fluorescence, and breakdown of soil structure (Smart and Laidlaw, 1977; Trudgill, 1987). Table 9 shows properties of the fluorescent and non-fluorescent dyes that were candidates for this study. A dye was a candidate if it was orange and fluorescent or if it was cited in another work. Orange fluorescent dyes are especially suitable because background fluorescence of soils is minimal (Smart and Laidlaw, 1977). Some values are missing from Table 9 either because they were not available or they were application-specific. An ordinal ranking (high, medium, or low) was given where possible, lacking quantitative data.

Table 9. Candidate dye tracers. Data with no footnote reference are from Smart and Laidlaw (1977).

Common Name	Color	Aqueous Solubility	Photo-chemical Stability	Chemical Stability	Visibility in Soil	Back-ground Fluore-scence	Adsorpt-ive Loss on Humus	λ (nm) of Maximum Excitation	λ (nm) of Maximum Fluoresc-ence
Fluorescein	green		low			high	medium	490, 470†	520, 510†
Lissamine yellow FF	green	high‡	high, high‡		low§	high	low	420	515
Pyranine	green		low	low†	only in the lab†	high	low	455 (405), 396†	515, 510†
Rhodamine B	orange		high			low	high	555	580
Rhodamine WT	orange		high		high§	low	medium	555	580
Sulpho-rhodamine B	orange	high‡	high, high‡			low	low	565	590
Acid Red 1	red	high¶			high¶	N/A	low¶,#	N/A	N/A
Dispersed Orange 3	orange	low¶				N/A		N/A	N/A
Methylene Blue	blue				low††	N/A	high††	N/A	N/A

†Omoti and Wild (1979a)

‡Smettem and Trudgill (1983)

§Kung (1990a)

¶Ghodrati and Jury (1990)

#Corey (1968)

††Warner & Young (1991)

Of all candidates, rhodamine WT was selected based on its availability, photochemical stability, visibility, low background fluorescence, high water solubility, and reports of successful use (Everts et al., 1989; Kung, 1990a; Trojan and Linden, 1992).

An analytical problem with all rhodamines is the small distance (25 nm) between the wavelengths of maximum excitation and maximum emission. This may cause the two peaks to overlap. It can be solved by exciting the dye at a wavelength other than that of maximum excitation, and by narrowing the wavelength range of the exciting beam. Another problem is the possible reduction in infiltration rate caused by breakdown of soil structure. The probable cause is a combination of Na^+ dissociation from the dye functional groups and swelling and exfoliation of clay particles caused by the strong adsorption of large dye molecules (Trudgill, 1987). The effect is especially marked when the soil is acid or has high clay content. The soil used in this study was not acid (pH 7.6 to 7.8) and the topsoil was a loam, that contains at most about 27% clay. Trudgill used a soil of 70% clay to demonstrate the problem. A reduction in infiltration rate cannot be completely ruled out and it is accepted as a trade-off against the dye's other advantages.

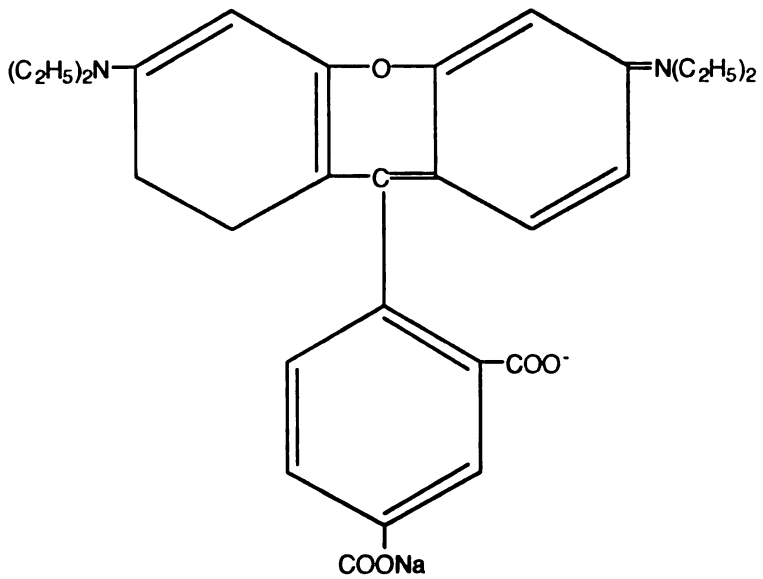

Figure 27. Chemical structure of rhodamine WT.

Rhodamine WT was developed specifically for water tracing to replace the more adsorptive rhodamine B and the more expensive sulpho rhodamine B (Smart and Laidlaw, 1977). The chemical structure of rhodamine WT is in Figure 27. Its molecular weight is 566. Rhodamine WT is called an orange dye (Smart and Laidlaw, 1977). Yet, under ordinary light it is pink.

Site Selection and Preparation

The tracer mix was applied at the Michigan State University Box Farm, in one of the lysimeters of the controlled subirrigation/drainage facility described in Chapter 2 (Figure 2). On 2 October, 2 d before the application, the soil was soaked by raising the water table 10.5 cm above the soil surface through subirrigation. After 1 h the plot was drained. The plot was allowed to drain for 2 d to approach a somewhat stable soil water content. The water content at saturation and after 2 d is shown in Figure 28. The drained water

content of the soil surface was not measured, so it was simulated with CERES-P (Chapter 3). The simulated drained water content is also plotted in Figure 28.

The saturated and drained water content coincide at 42 cm, possibly because the soil texture changes from loam to clay loam below 38 cm and to loam below 71 cm (Appendix A). More clay could mean slower drainage from that depth.

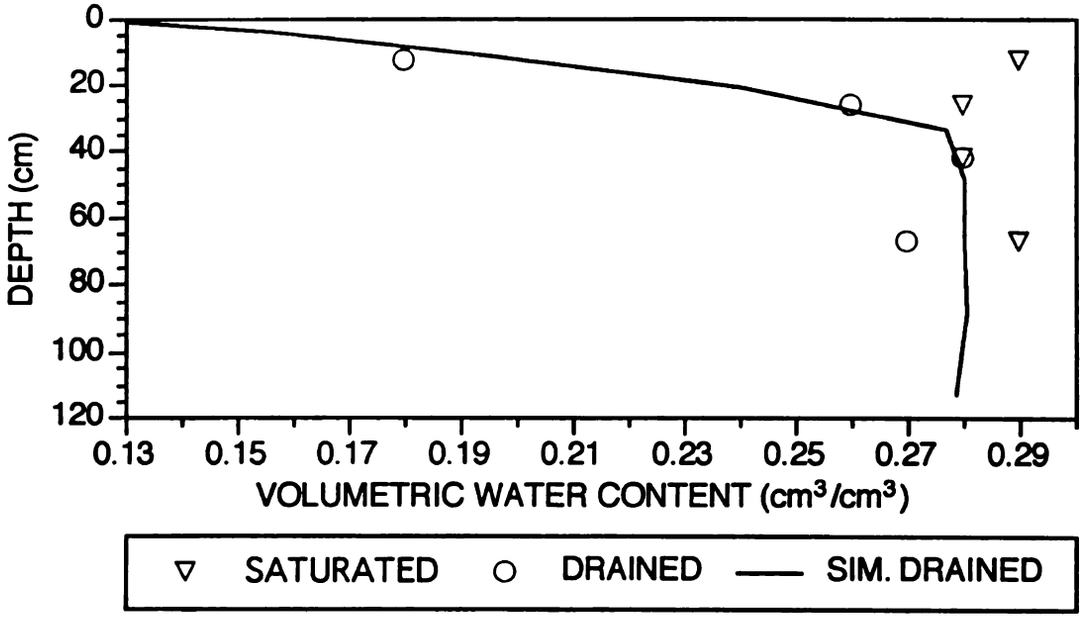

Figure 28. Measured saturated and drained water content, and simulated drained water content.

On 3 October the corn grown on the plot was hand harvested. The thicker roots were removed to facilitate cultivation. The plot was lightly cultivated with a shovel. The bigger aggregates were broken and the soil surface leveled with a rake.

Application

A wide range of Br application rates has been used in soil water tracing; from 2.1 g/m^2 (Hornberger et al., 1990) to 260 g/m^2 (Jardine et al., 1990). An even wider range of rhodamine WT application rates has been used; from 16 10^{-3} g/m^2 (Trudgill, 1987) to 30 cm^3/m^2 (approximately 34 g/m^2 [Trojan and Linden, 1992]). In this experiment, Br was applied at 75.3 g/m^2 and rhodamine WT at 31.5 g/m^2.[9]

The solution was applied with a backpack sprayer. The sprayer tank was filled with 11.3 L of an aqueous solution containing 301.2 g of Br as KBr and 126 g of rhodamine WT in a commercial formulation (Keystone Aniline Corp., 2501 W. Fulton St., Chicago, IL). A boom with four nozzles (Teejet® 730308) spaced 0.60 m apart delivered a 0.283 cm pulse at a mean rate of 1.1 cm/h. After the application the tank was rinsed thrice and the rinsate

---

[9] The rates were determined as follows: Bromide would have to be detectable down to 1.25 m depth. It was assumed that after application and subsequent irrigation the Br will be dissolved in at least one water-filled pore volume. Based on the maximum sampling depth (1.25 m), the surface area of the lysimeter (4 m^2) and the bulk density, one water-filled pore volume would be 1.46 m^3. The middle of the straight portion of the calibration curve of the Br-specific electrode is about 10 mg/L (Orion Research Inc., 1991). To achieve this concentration in the lysimeter, 14.6 g of Br would be needed. This mass was multiplied times 10, the approximate dilution factor during extraction of the tracer. The result was doubled to allow for safety margin.

Rhodamine WT is detectable even at 13 ng/L (Smart and Laidlaw, 1977) so it could be applied at a much lower rate than Br. However, preliminary observations showed that very dilute dye solutions, though measurable, did not visibly stain the soil. The applied rate was thought sufficient to visibly stain at least the top 30 cm of soil.

sprayed on soil in the same way. Then the plot was irrigated with clean water pumped from a nearby pond. Irrigation was applied with a hose and sprinkler at a rate high enough to saturate the surface and create slight ponding. In all, 6.4 cm of irrigation at a mean rate of 4 cm/h was applied after the initial tracer pulse. During irrigation the water table rose from 107 cm to 30 cm. The drains were opened so that the soil would be sufficiently dry for the first sampling, scheduled after 15 h. Because sampling would last several days, the plot was covered with plastic to protect it from precipitation and upward water flow that could alter sample concentrations.

Sampling

Samples were taken from eight horizontal sections or "slices" at 0, 2.5, 8, 15, 26, 40, 57, and 77 cm depth. The original objective was to excavate to 125 cm depth but the water table was too high to permit sampling below 100 cm. The depths were selected to match the standard depths used in CERES-P (Chapter 3), because the data were to be used in simulation. At the surface (0 cm section), cores were taken every 10 cm along two horizontal transects traversing through the center of the plot and at right angles to each other. The cores were taken with a cylindrical probe with tapered ends, 3.5 cm high and 3 cm in diameter, pushed 2 cm into the soil. Each core was placed in a 100 cm^3 plastic container and temporarily stored in an ice cooler. The probe was rinsed with clean water between samples.

Each subsequent section was excavated with a shovel. All the soil was removed at each depth to allow visual observation and to photograph the dye stains. Visual observations and photographs were used only for qualitative assessment of the dye distribution. Beginning with the 2.5 cm section, the exposed soil was sampled along one central transect running W-E. Beginning

with the 8 cm section, the sampling interval was increased to 20 cm. These modifications were to minimize the total sampling time. Smart and Laidlaw (1977) show that rhodamine WT may biodegrade in the presence of microorganisms, though it is not known whether favorable conditions exist in soil. The soil was covered with plastic at the end of the workday to protect it from precipitation and evaporation.

One tile drainage sample was taken daily for the next 3 d and then sporadically for 23 d. The drainage samples were temporarily stored and transported in an ice cooler. Three cores for bulk density were taken from each sampling depth with a cylindrical metal probe (6.8 cm height, 3.3 cm diameter). At the end of the workday, all soil and water samples were frozen at –20 °C until analysis.

Analysis

The first step was to extract the tracers from the soil. No well-known method of Br extraction exists. The book on methods of soil analysis published by the American Society of Agronomy and the Soil Science Society of America reports: "No attempt has been made to discuss methods of extracting Br from soil for analysis" (Adriano and Doner, 1982). The same is true of rhodamine WT.

Dye extraction requires more steps than Br extraction. Because the dye is measured photometrically, the extract must be free of suspended material, thus it requires centrifugation. Unlike the ion-specific electrode that was used for Br, the response of the fluorometer is directly proportional to concentration. The range of concentrations measured with one calibration is limited, making sample dilution necessary. Because the dye degrades with time, the samples must be frozen if significant time elapses between steps.

Finally, converting extract concentrations to soil concentrations requires calculation of desorption isotherms. Because dye extraction is more demanding, a procedure best suited for the dye was followed based on Smettem and Trudgill (1983), and Trudgill (1987).

The soils were thawed and mixed with a spatula. Each sample was split in three subsamples. Two subsamples of 7.06 g (±0.1 g) each were placed in 30 ml Corex® (Corning) centrifuge tubes with teflon lined caps. The remainder was used for gravimetric water content determination. Fifteen mL of a 0.07M K_2SO_4 solution were added to each tube. Because the approximate gravimetric water content was 24.3%, this addition resulted in a 3:1 solution-to-soil ratio. The tubes were shaken for 2h on a shaker at 200 cycles/min and then centrifuged at 4,000 rpm (equivalent to an average of 1464 Relative Centrifugal Force units) for 20 min. A 4 mL aliquot of the supernatant was collected and stored at –20 °C for rhodamine WT analysis. The rest of the supernatant was analyzed for Br within 1 or 2 d.

Br was analyzed with a Br-specific electrode model 94-35 (Orion, 529 Main St., Boston, MA 02129) connected to a pH/volt meter (Corning). The method is described by Orion (1991).

Rhodamine WT was analyzed with an LS-5 luminescence spectrometer (Perkin-Elmer, Beaconsfield, England), commonly called a fluorometer. The principle of fluorometry is when a fluorescent substance is excited at a certain wavelength, it emits light at a longer wavelength. The fluorescence emitted from a solution is directly proportional to concentration.

The maximum excitation and maximum emission peaks of rhodamine WT overlap, as shown in Figure 29. The fluorometer sensor cannot distinguish excitation from emission energy passing through the sample if their wavelength is similar. Therefore it was necessary to excite the

dye at a wavelength other than that of maximum excitation. A suitable wavelength was found at 500 nm. Maximum emission was detected at 580 nm.

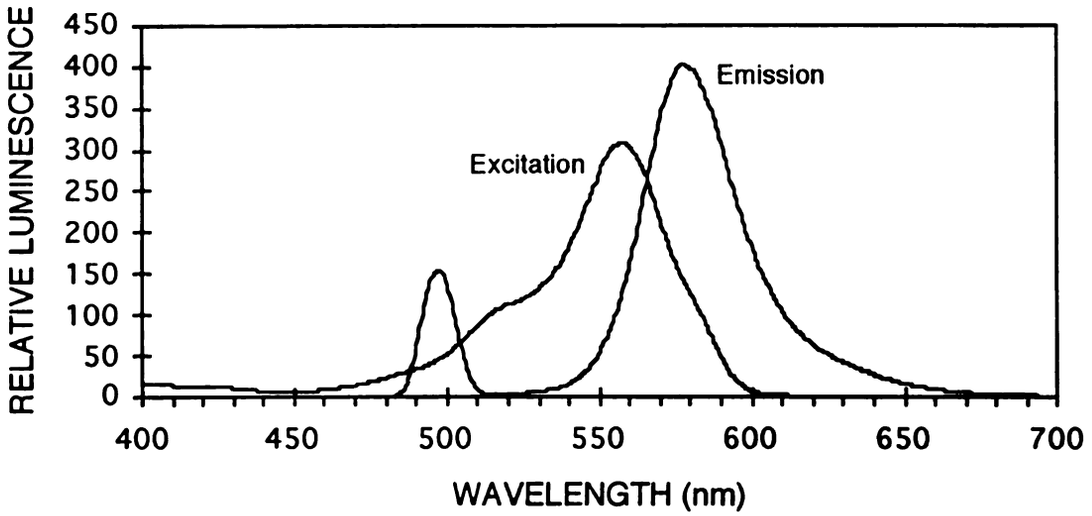

Figure 29. Excitation and emission spectra for rhodamine WT.

The method for rhodamine WT analysis is described by Perkin-Elmer (1982).

The drainage samples were thawed and the suspended particles allowed to settle for 6 h. No centrifugation was necessary. They were analyzed for Br and rhodamine WT as soil extracts without further preparation.

Once the dye concentrations in the extracts were determined, they had to be converted to soil concentrations. The dye is anionic, so little sorption would be expected. But as a complex organic molecule, it may sorb on clay or organic matter with a variety of mechanisms such as Van der Waals forces, H-bonding, and electron donor/acceptor complexes (Trudgill, 1987). Desorption isotherms were constructed as follows: Soil samples with no dye were taken from the surface (6 cm depth) and subsoil (62 cm depth). They

were air-dried, ground and passed through a 3 mm sieve. The soils were mixed with the following known dye concentrations: $5\ 10^{-3}$, $2.5\ 10^{-3}$, 10^{-3}, $5\ 10^{-4}$, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7}, 10^{-8} and 0 mg/L. Preliminary observations had shown that this range would result in extract concentrations in the range obtained from field samples. The amount of added dye solution brought the gravimetric water content to the approximate 25% water content of the field samples. The soils were left covered with paraffin sheet for 24 h at 22 °C to equilibrate. Then the dye was extracted and measured with the procedure described for the field samples.

The desorption isotherms could not be approximated with a single first degree model because the slope decreased with increased concentration at equilibrium (C_e). One model was fitted for each concentration interval shown below. The amount sorbed per unit soil is denoted by q:

At 6 cm:

$$q = 12.6\ C_e,\ C_e \in [0,\ 1.9\ 10^{-6})$$

$$q = 3.0\ C_e + 1.8\ 10^{-5},\ C_e \in [1.9\ 10^{-6},\ 8.9\ 10^{-5})$$

$$q = 0.5\ C_e + 2.4\ 10^{-4},\ C_e \in [8.9\ 10^{-5},\ 2.5\ 10^{-4}]$$

At 62 cm:

$$q = 4.2\ C_e,\ C_e \in [0,\ 7.5\ 10^{-6})$$

$$q = 2.2\ C_e + 1.5\ 10^{-5},\ C_e \in [7.5\ 10^{-6},\ 2.1\ 10^{-4})$$

The top 30 cm of soil are homogenous in texture and color and they approximately correspond to the Ap horizon (Appendix A). For depths above 30 cm the first set of models was used, for the other depths the second set of models was used.

Trudgill (1987) measured adsorptive losses of 90 to 99% for rhodamine WT on most soils and 60% on sand. If adsorptive loss in 1 g of soil is defined as:

$$\text{mass adsorbed} / (\text{mass adsorbed} + \text{mass in solution})$$

then for the first segment of the Freundlich-type model it is given by the formula:

$$q/(q + 3C_e) = K_d / (K_d + 3)$$

where 3 represents the solution-to-soil ratio. Replacing K_d with the values fitted above, adsorptive losses are 81% for the topsoil and 58% for the subsoil. These values are somewhat lower than Trudgill's, possibly because the organic C and clay content of his soil were higher.

The K_d values fitted above can be converted to K_{OC} if they are normalized by organic C content. Organic C is 2.0% in the topsoil and 1.1% in the subsoil (Chapter 2). For the first segment of the Freundlich-type model, K_{OC} would be 630 in the topsoil and 382 in the subsoil. Sabatini (1989 [cited in Everts et al., 1989]) measured much higher K_{OC} values, 1400 to 3700 in a sand and gravel aquifer material. The original source is unpublished so it cannot be evaluated. Generally, the K_{OC} approach for highly water-soluble chemicals such as rhodamine WT is unreliable (Green and Karickhoff, 1990). In addition, the organic C content of aquifer materials typically is so low that a small measurement error could significantly affect K_{OC}.

RESULTS AND DISCUSSION

Results from Measurements

Using bulk density to estimate soil mass and soil concentrations from the Freundlich type model, the amount of tracer could be estimated. Figure 30 shows bulk density, Figures 31 and 32 and show concentration per unit of dry soil and recovered tracer at each depth, as a fraction of applied. Initial estimates of recovery from soil were 62% for Br and 101% for rhodamine WT, in the 0 to 78 cm depth. However, desorption isotherms were made with soil

passed through a 3 mm sieve. The undisturbed soil contained about 6% "pebbles and cobbles" (Soil Conservation Service, 1980) that didn't pass through the sieve and whose contribution to sorption should be negligible. Thus cumulative recovery from soil was adjusted to 58% for Br and 95% for rhodamine WT.

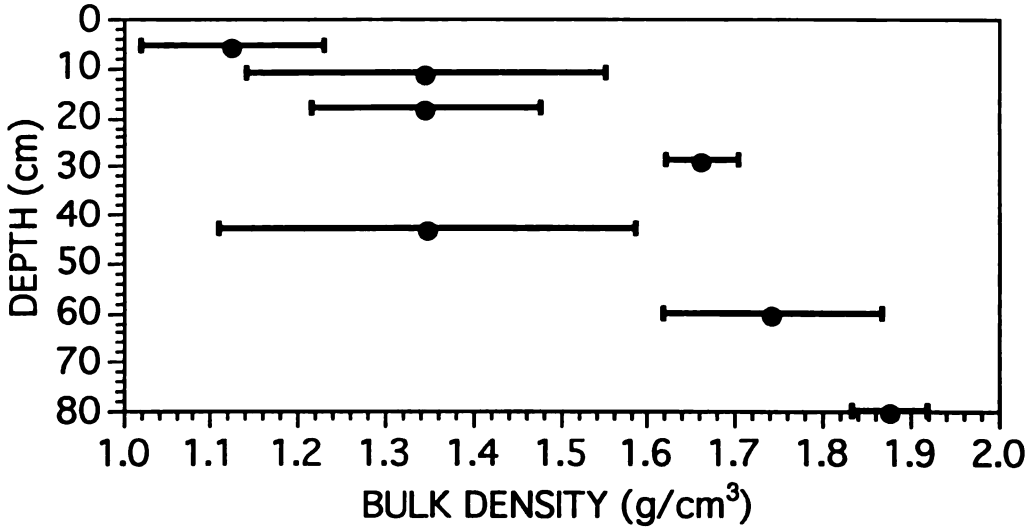

Figure 30. Bulk density of experimental plot. Horizontal bars represent ±1 SD.

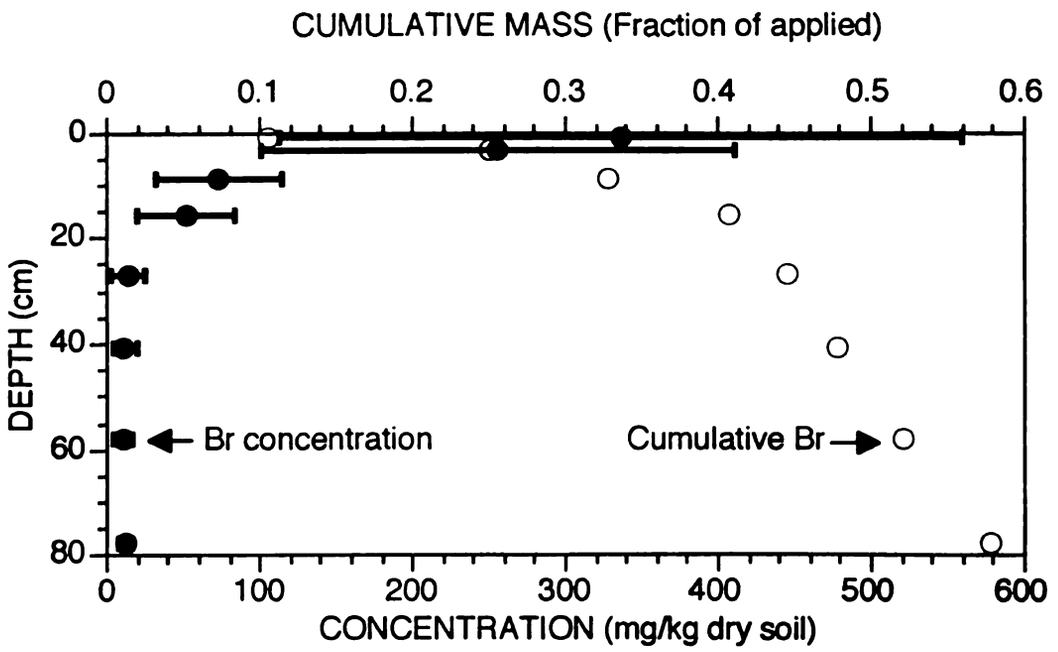

Figure 31. Br concentration and cumulative recovery with depth. Horizontal bars represent ±1 SD.

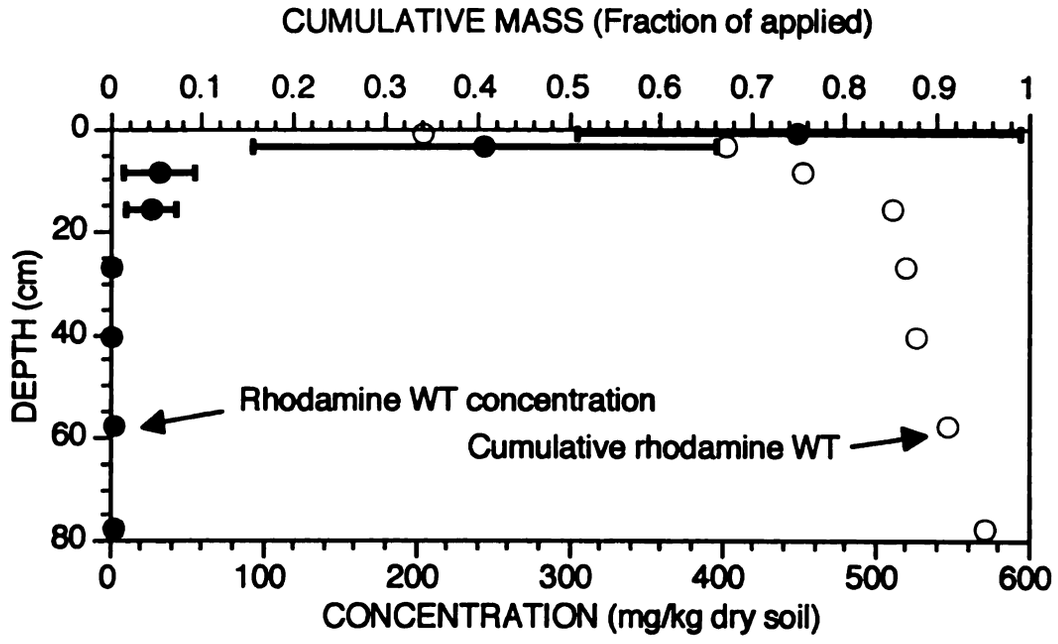

Figure 32. Rhodamine WT concentration and cumulative recovery with depth. Horizontal bars represent ±1 SD.

Tracer in tile drainage during the first 3 d was estimated from measured concentration and from the drainage volume during an earlier observation (Chapter 2). Ten percent of applied Br and 2% of applied rhodamine WT were recovered in tile drainage. Tracer losses in drainage beyond the 3rd d were thought to be small because most of tracer-rich topsoil had been removed. In total, 68% of Br and 97% of rhodamine WT were accounted for. Some of the unaccounted quantity likely leached below tile depth before it could drain through the tiles. Some unaccounted quantity may be due to measurement error.

If irrigation had displaced the tracer pulse as a "piston" (a planar and abrupt wetting front) then it would have displaced the tracer completely from the top 22 cm. This is the theoretical depth of percolation based on the irrigation amount (6.4 cm) divided by the saturated water content (0.29 cm^3/cm^3). Yet, about 41% of the Br and 85% of the dye remained above 22 cm. This shows that a significant amount of irrigation by-passed the bulk of the soil matrix.

When the pulse was applied, the soil was unsaturated. Under positive matric suction, the tracer would have moved into the soil aggregates. Though irrigation decreased matric suction, there was not adequate time for equilibration between the tracer in the intraaggregate solution and the tracer in the interaggregate solution. This may explain why a significant fraction resisted leaching. Omoti and Wild (1979b) report similar results. They leached a pulse of Cl with 5 cm of irrigation under conditions similar to this experiment, though at a lower application rate (1 cm/h). A little less than one-half of Cl (which should be as mobile as Br) remained above 22 cm. Observations by Ghodrati and Jury (1990) also agree with these results. They applied a pulse of Acid Red 1 dye and irrigated at two rates. One treatment received a flood irrigation of 10 cm; the other received five sprinkler

irrigations of 2 cm each. Vertical sections revealed that sprinkler irrigation acted like a "piston," completely displacing the dye from the surface. At the flood irrigated soil, most of the dye remained at the top 10 cm and was even visible at the surface.

Comparison of cumulative Br versus cumulative dye with depth shows that Br is more mobile than rhodamine WT. This was expected because rhodamine WT adsorbs significantly, whereas Br does not. The higher mobility of Br was also evident by the higher proportion of Br recovered in tile drainage during the first 3 d (10% versus 2%). Omoti and Wild (1979a) observed that pyranine and fluorescein, two other organic dyes, lag behind Cl. Fluorescein had a distribution coefficient of 10.3 cm^3/g, similar to that of rhodamine WT.

Visual observations of the excavated soil agree with the measurements. The dye was clearly visible at the surface. Each subsequent section revealed less dye. Beginning with the 15 cm section, almost no dye was visible. The dye pattern was not uniform, especially beneath the surface. There were spots and cracks with more intense color than the rest of the matrix, which confirms that the dye moved preferentially. Roots were visibly stained even at the 57 cm depth, even though the soil matrix wasn't. This suggests either that roots provide preferential flow channels or that they absorb more dye.

Application to Simulation

This field observation recreated only one set of conditions of solute movement, i.e., application of a pulse under positive matric suction and subsequent leaching under high irrigation rate. The data are insufficient to develop a generic model of solute movement under different andecent soil

conditions and different irrigation rates. Yet, these data may define an upper limit for the fraction of a solute that leaches from the soil. Table 10 shows how. The second column in Table 10 is the measured cumulative Br mass in a layer. This mass was also in Figure 31. The third column is the mass leaving the layer, or the difference between 100% and cumulative mass. The fourth column is the ratio of each cell of the third column divided by the cell above it, i.e., the leaching fraction. This value appears somewhat constant across layers, and it is independent of layer thickness. Using the median value of the leaching fraction (89.5%) as a constant, the leaching mass is predicted in the fifth column. The leaching mass leaving the last layer is accurately predicted within 3 g.

Table 10. Calculating a leaching fraction for Br.

Layer	Cumulative Mass (%)	Mass Leaving (%)	Mass Leaving / Mass Entering (%)	Predicted Mass Leaving (g)
1	10.7	89.3	89.3	269
2	25.2	74.8	83.8	241
3	32.9	67.1	89.6	216
4	40.8	59.2	88.2	193
5	44.7	55.3	93.5	173
6	47.8	52.2	94.3	154
7	52.1	47.9	91.7	138
8	58.0	42.0	87.8	124
		Median =	89.5	

Assuming that small anions such as Br and NO_3 behave the same, a new condition was added to the N flow component of CERES-P. In addition to other calculations, an upper limit is now defined for NO_3 leaching. If the soil water content was at or below the drained upper limit before drainage, and water flows equal or exceed the amount of irrigation applied in this experiment, the leachate mass is limited by the leaching fraction defined in Table 10.

Table 11. Calculating a leaching fraction for rhodamine WT.

Layer	Cumulative Mass (%)	Mass Leaving (%)	Mass Leaving / Mass Entering (%)	Predicted Mass Leaving (g)
1	34.2	65.8	65.8	87
2	67.4	32.6	49.6	60
3	75.4	24.6	75.2	42
4	85.3	14.7	59.9	29
5	86.9	13.1	89.1	20
6	88.0	12.0	91.8	14
7	91.3	8.7	72.5	9
8	95.3	4.7	54.4	7
		Median =	69.1	

Table 11 shows the leaching fraction for rhodamine WT. The leaching fraction is not as constant as for Br, possibly because adsorption interferes with the movement of rhodamine WT. Yet, using the median leaching fraction (69.1%) as a constant, it is possible to predict the quantity leaving the last layer, partly because the median is close to the leaching fraction of the top layer. The more dye is in a layer, the more important is to accurately estimate the leaching fraction.

Rhodamine WT adsorbs stronger than atrazine. Their distribution coefficients are 12.6 versus 2.1 cm^3/g, for equilibrium concentrations less than 1.9 mg/L.[10] Therefore, rhodamine WT is not a suitable surrogate for atrazine.

---

[10]This statement ignores adsorption-desorption hysteresis. Some organic chemicals have a higher distribution coefficient for the desorption isotherm than for the adsorption isotherm (Schrap and Opperhuizen, 1992).

CONCLUSIONS

Beven and Germann (1982) wrote on macropore flow, "what is needed first is experimental information." This study aimed at producing such information. Under high flow rate, a pulse of two tracers was leached, a mobile one (Br) and an adsorptive one (rhodamine WT).

A significant fraction of the tracers remained in the topsoil, despite the high irrigation rate. The flow by-passed the tracer that was absorbed within the aggregates. The management implication is that chemical applications on relatively dry soil may help reduce leaching losses from subsequent heavy precipitation or irrigation. However, a significant fraction of a mobile chemical will still leach below the root zone. In this experiment, over one third of the mobile tracer was lost in one irrigation. To completely eliminate leaching losses below the root zone, applications on dry soil should perhaps be combined with lower irrigation rates, so that the residence time of the chemical in the rhizosphere is maximized. Even so, there is not guarantee of zero leaching; even if irrigation is optimally managed, precipitation remains unpredictable. Also, in irrigation management there is more than one criterion to optimize for; soil surface should not be so dry as to impede plant growth or reduce the effectiveness of pesticides and nutrients in reaching their targets.

In this study, the dye could be visually identified only in the upper layers. If the tracer is intended mainly for visual identification, a less adsorptive dye should be used. It is possible that excitation of the dye with ultra-violet light would enhance its visibility, as it does for other fluorescent dyes (Omoti and Wild, 1979b; Ritchie et al., 1972). Higher concentrations would enhance visibility but they should be avoided for the following

reasons: First, high concentrations of rhodamine WT can have an adverse effect on soil structure (Trudgill, 1987). Second, any tracer that is denser than water increases the overall density of the solution and could cause unwanted fingering (Hill and Parlange, 1972).

Based on the experimental results, a leaching fraction may be calculated that could be useful in solute simulation. More data are needed on the effect of different irrigation rates and antecedent moisture.

CHAPTER V

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

SUMMARY AND CONCLUSIONS

Subirrigation systems have been introduced in areas of Michigan. Yet, there is little information on the impact of subirrigation/drainage on chemical losses through tile drains. The general objective of this study was to measure and simulate tile drainage losses of NO_3-N and atrazine, two chemicals commonly used in corn.

Tile drainage sampling is an effective way to study the effect of water table management on leaching because it integrates flow and concentration over the study area. The effect of timing and duration of flooding on chemical losses and plant growth was observed in five subirrigated/drained lysimeters with independently controlled water table.

Shorter flooding was associated with higher peaks of NO_3-N and atrazine concentration. Also, shorter flooding possibly increases total NO_3-N losses in tile drainage. The duration of flooding did not affect total atrazine losses. Early inundation was associated with higher NO_3-N and atrazine concentration peaks. Early inundation was associated with more total NO_3-N and atrazine in tile drainage.

Plant damage is greatest for prolonged inundation at an early vegetative stage. The same inundation has much less effect if applied at a later stage, probably because the plant uses N and carbohydrate reserves.

Using the above information and appropriate theory, CERES, a soil-

crop-atmosphere model, was modified to simulate water table and pesticide fate. Given the uncertainty of field observations, the model adequately simulated water balance, atrazine and NO_3-N concentrations for the season, and total leaching for the limited period following drainage. Total biomass was predicted reasonably well though grain yield was underpredicted for most treatments.

A tracer application on a field lysimeter followed by intense irrigation revealed pronounced by-pass flow. A substantial fraction of the tracers, especially the most adsorptive one, remained in the topsoil. Based on the results, the N flow component of the simulation model was modified. An upper limit was set to the fraction of N that leaches under conditions comparable to the field observation. The dye tracer was not an appropriate surrogate for atrazine due to different sorption rates.

RECOMMENDATIONS FOR FURTHER RESEARCH

More data are needed to define the relationship between flow rates, antecedent moisture, and leaching of agricultural chemicals. Frequent flow volume monitoring systems with automatic effluent sampling devices would increase quantity and quality of information.

Research on the spatial distribution of flow is needed to improve simulation estimates. Classical statistics (Biggar and Nielsen, 1976) and geostatistics (Webster and Oliver, 1990) provide measures of spatial distribution. These can be used to define optimum sampling schemes to detect preferential flow. Simplicity is desirable. As Beven (1991) warns, simulation of preferential flow can easily result in overparameterized, hard to calibrate models.

An optimum balance must be found between the level of detail and usefulness of chemical fate models. Extensive data requirements reduce the

model's attractiveness to users other than the model developer. The ideal model should yield reasonably accurate predictions with relatively few inputs, such as the sorption distribution coefficient, soil texture, precipitation, and the spatial and temporal distribution of these variables. The ideal model should provide a measure of uncertainty of its predictions. It should be easy to use and it must be able to make intelligent management recommendations.

Experimentation and simulation needs to extend to the field and landscape scale. In the words of D.R. Nielsen (1992), past president of the American Society of Agronomy:

> "Deterministic concepts and mass balance equations for steady-state conditions are still being used for minutes, days, weeks, and often times no longer than the growing season. They do little for our improved understanding of how agricultural practices impact on the quality of water leaving a cultivated or rangeland region . . . Experimentation on whole fields and ensembles of fields is the future—I envision fewer, much fewer small *representative* plots to help us manage the landscape (p.132)"

To this end, methods must be developed to efficiently acquire and process large volume of data. Promising methods are remote sensing techniques (Myers et al., 1983), coupled with Geographic Information Systems (GIS [Burrough, 1986 and 1989). Geographic Information Systems can model runoff, groundwater flows, and airborne losses and gains not possible with one-dimensional models. Expert systems and expert databases (Robinson et al., 1987) can add the intelligence that would extend the utility of the models to less trained end users. Simulation modeling, remote sensing, and GIS are mutually approaching. The "Manual of Remote Sensing" predicts that the future of remote sensing is in "data-base integration and modeling activities" (Marble and Peuquet, 1983).

Site-specific management is a new research area that promises to manage soil spatial variability to the benefit of the farmer and the environment (Larson and Robert, 1991; Mulla, 1991). Global Positioning

Systems (GPS [Leick, 1990]) can efficiently and accurately geo-reference information. Technologies should emerge that can vary chemical application rates to match soil productivity and minimize waste.

Accurate and easy techniques are needed for dynamic, within-season calibration of chemical fate models. Methods of within-season calibration of yield models are known (Kenig et al., 1993; Maas, 1993). Plants could be used as indexes of soil nutrients, such as N. Tissue analysis (Binford et al., 1990) and chlorophyll measurements (Piekielek and Fox, 1992) can rapidly assess the N status of the plant and provide feedback to models. Remote sensing of the plant canopy can predict the within-season water and nutrient status of the crop (Myers et al., 1983; Ritchie and Amato, 1990). Research is needed to show whether plants can be used as indexes of pesticide residues to supplement or replace current expensive analytical methods.

APPENDIX A

APPENDIX A

SOIL CONSERVATION SERVICE DESCRIPTION OF CAPAC SERIES

This section contains a detailed description of the Capac series (Aeric Ochraqualfs; fine-loamy, mixed, mesic) quoted from the soil survey (Soil Conservation Service, 1979). The series consists of somewhat poorly drained, moderately and moderately slowly permeable soils on till plains and moraines. These soils formed in medium and moderately fine textured deposits. Slopes are 0 to 4%.

This Capac soil has a seasonal high water table within 30 to 61 cm (1 to 2 ft) of the surface in winter and spring. The available water capacity is high. Surface runoff is slow.

The major limitation in cropland is the excess water, which delays planting and harvesting in many years. Tile and surface drains are needed.

Typical pedon of Capac loam, 0 to 3% slopes, 268 m (880 ft) N and 58 m (190 ft) W of SE corner sec. 26, T. 1 N., R. 1 E.

Ap–0 to 23 cm (0 to 9 in); very dark grayish brown (10YR 3/2) loam, light brownish gray (10YR 6/2) dry; weak medium granular structure; friable; few very fine roots; neutral; abrupt smooth boundary.

B&A–23 to 28 cm (9 to 11 in); light olive brown (2.5YR 5/4) loam (B2); brown (10YR 5/3) coatings on vertical faces of peds (A2); few fine distinct yellowish brown (10YR 5/6) and few fine faint grayish brown (10YR 5/2) mottles; weak medium granular structure; friable; few thin

discontinuous dark grayish brown (10YR 4/2) clay films on vertical faces of peds; medium acid; clear wavy boundary.

B21t–23 to 38 cm (11 to 25 in); brown (10YR 5/3) loam; common fine distinct yellowish brown (10YR 5/6) and common fine faint grayish brown (10YR 5/2) mottles; moderate medium angular blocky structure; firm; light brownish gray (10YR 6/2) fine sandy loam coatings on vertical faces of peds; thin discontinuous dark grayish brown (10YR 4/2) clay films on faces of peds; slightly acid; gradual wavy boundary.

B22tg–38 to 71 cm (15 to 28 in); grayish brown (10YR 5/2) clay loam; common fine distinct yellowish brown (10YR 5/6) mottles; moderate medium angular blocky structure; firm; thick continuous dark grayish brown (10YR 4/2) clay films on faces of peds; neutral; gradual wavy boundary.

B23t–71 to 81 cm (28 to 32 in); brown (10YR 5/3) loam; common medium distinct yellowish brown (10YR 5/6) and common fine faint light brownish gray (10YR 6/2) mottles; weak medium subangular blocky structure; firm; thick dark grayish brown (10YR 4/2) clay films on faces of peds; mildly alkaline; abrupt wavy boundary.

Cg–81 to 152 cm (32 to 60 in); grayish brown (10YR 5/2) loam; common fine faint olive gray (5Y 5/2) and common medium distinct light olive brown (2.5Y 5/4) mottles; weak medium subangular blocky structure in upper part and massive in lower part; friable; slight effervescence; moderately alkaline.

Thickness of the solum and depth to effervescent material range from 66 to 102 cm (26 to 40 in). Reaction ranges from medium acid to mildly alkaline in the solum. Coarse fragment range from less than 1 to 10% throughout the pedon.

The Ap horizon has hue of 10YR, value of 3 or 4, and chroma of 2 or 3 moist. It has value of 6 or more dry. The texture is dominantly loam, but the range includes sandy loam or fine sandy loam. In some pedons an A2 horizon is present. In uncultivated areas an A1 horizon is present.

The Bt horizon has hue of 10YR or 2.5Y, value of 5 or 6, and chroma of 1 to 3. It averages 18 to 35% clay.

The C horizon has hue of 10YR or 2.5Y, value of 5 or 6, and chroma of 2 or 3. It is loam or clay loam.

APPENDIX B

APPENDIX B

SOURCE CODE

This appendix contains the source code that has been added or modified by the author since CERES 2.1.

MASTER PESTICIDE PROGRAM

```
C +-------------------------------------------------------------------------+
C | Determine pesticide fate.                                               |
C +-------------------------------------------------------------------------+
C |                          GLOSSARY                                       |
C | AGEFAC      : Age factor to reduce effective conc. of aged residues     |
C | APPDAY      : Application day                                           |
C | CL(L)       : Concentration in liquid phase (ug/L)                      |
C | CT(L)       : Concentration total in soil   (ug/L)                      |
C | D           : Dispersion coefficient (cm2/d)                            |
C | DEGRAD      : Amount degraded daily (kg/ha)                             |
C | DISPRS      : Dispersivity (cm)                                         |
C | Dm          : Molecular diffusion coefficient (cm2/d)                   |
C | DMAX        : Max. drainage for a layer (cm)                            |
C | DmSE        : Molecular diffusion coefficient Stokes-Einstein (cm2/s)   |
C | DmWC        : Molecular diffusion coefficient Wilke-Chang (cm2/s)       |
C | DOYOUT      : Day of the year to start printing cumulative output       |
C | DRFLAG(366): Flag to denote whether tiles are open today               |
C | EQCOEF      : Equilibration coefficient for mixing of flow w/ chemical  |
C | FAST        : Fast flow (cm)                                            |
C | FILE2       : Soils input file 2                                        |
C | INPFILE     : Pesticide initial conditions and management file          |
C | ISWWT       : Switch for water table management option (0-2)            |
C | JUL         : Date of simulation                                        |
C | Kd(L)       : Distribution coefficient of sorption model                |
C | Kr          : Degradation constant                                      |
C | MOLVOL      : Molecular volume of solute (cm3/g-mol)                    |
C | NPOUT(L)    : Net pesticide out (kg/ha)                                 |
C | NREP        : Number of replications                                    |
C | NTRT        : Number of treatment                                       |
C | OPSYS       : Operating system code                                     |
C | OUTP        : Pesticide out of a layer                                  |
C | OUTPP       : Pesticide coming from previous layer                      |
C | OUT1        : Pesticide out of a layer w/ slow flow                     |
C | OUT2        : Pesticide out of a layer w/ fast flow                     |
C | PESTIN      : Pesticide applied in a layer (kg/ha)                      |
C | PESTSP(L)   : Pesticide species (kg/ha)                                 |
C | PPB2KG(L)   : Conversion factor (see below)                             |
C | RUF         : Roor uptake factor                                        |
```

```
C | SLOW       : Slow flow (cm)                                                  |
C | SOLUB      : Aqueous solubility (ug/L)                                       |
C | SPECNM     : Species name                                                    |
C | SWBEFD     : Soil water before drainage (cm3/cm3)                            |
C | THALF(L)   : Half life (d)                                                   |
C | TILEL      : Tile layer                                                      |
C | TORT       : Tortuosity                                                      |
C | TPEST      : Total pesticide in profile (kg/ha)                              |
C | TPESTY     : Total pesticide in profile yesterday (kg/ha)                    |
C | TPlchd     : Total pesticide leaching deep (kg/ha)                           |
C | TPlcht     : Total pesticide leaching through tiles (kg/ha)                  |
C | UPTAKE     : Plant pesticide uptake (kg/ha)                                  |
C | VISCOS     : Viscosity (poise)                                               |
C +------------------------------------------------------------------------------+
C | Conversion between ug/L & Kg/ha/layer:                                       |
C |                              /ppb2kg                                         |
C |                            ---------->                                       |
C |           Kg/ha/layer                        ug/L                            |
C |                            <----------                                       |
C |                              *ppb2kg                                         |
C | where ppb2kg = 1e-4*dlayr(l)                                                 |
C +------------------------------------------------------------------------------+
C | Created by:  aris gerakis, 8 january 1993                                    |
C | Merged with the crop model: 2 february 1993                                  |
C | Last revision: Mar. 1994 [optimized parameters with complex]                 |
C +------------------------------------------------------------------------------+

      SUBROUTINE PESTCD (CL, Doy, Doyout, Drflag, File2, Inpfile, Iswwt,
     +                   Jul, NPout, nrep, ntrt, opsys, Ruf,
     +                   Swbefd, Tilel, TPlcht)

      IMPLICIT NONE
      include 'evaptrn.blk'
      include 'extwater.blk'
      include 'nleach.blk'
      include 'omatter.blk'
      include 'soildep.blk'
      include 'soiltemp.blk'

      real ruf, Swbefd(*), TPlchd, TPlcht
      double precision D, Dm, DmSE, DmWC, Disden, Disprs, Molvol, Tort,
     &       Viscos, Agefac, CT(20), CL(20), degrad, Dmax, Eqcoef, Fast,
     &       Kd(20), Kr, NPout(0:*), OUTP, Outpp, Outpl, Outp2,
     &       PESTIN, pestsp(20), ppb2kg(20), Slow, SOLUB, THALF(20),
     &       tpest, tpesty, Uptake
      INTEGER APPDAY, DOY, Doyout, Iswwt, j, JUL, K, L, M,
     &        ntrt, nrep, Tilel
      CHARACTER Inpfile*12, File2*12, opsys*3, SPECNM*12
      logical Drflag(*)

c     Initialize variables

      D = 0.0
      Disprs = 0.0
      Dm = 0.0
      Dmax = 0.0
      DmSE = 0.0
      DmWC = 0.0
      Degrad = 0.0
      Eqcoef = 1.00
      Fast = 0.0
      K =1
c     net mass leached, conv. factor between ug/L & Kg/ha/layer
      do j = 1, nlayr
         NPout(j) = 0.0
         ppb2kg(j) = 1e-4 * dlayr(j)
```

```
      enddo
      Kr = 0.0
      L = 1
      M = 1
      Slow = 0.0
      OUTP = 0.0
      OUTP1 = 0.0
      OUTP2 = 0.0
      tort = 0.6
      tpest = 0.0
      uptake = 0.0
      Viscos = 1e-2

c     Initialize pesticide concentrations & total leachate.
c     CT, CL are in ug/L, PESTSP in Kg/ha/layer

      IF (JUL.EQ.1) THEN
         call pestcdin (agefac, appday, bd, ct, disden, dlayr, File2,
     +                  inpfile, Kd, Molvol, nlayr, ntrt, pestin, Solub,
     +                  Specnm, Thalf)
         tpesty = 0.0
         do L = 1, nlayr
c           Reduce apparent concentration with age factor of "aged" residues
            ct(L) = ct(L) * Agefac
            pestsp(L) = ct(L) * ppb2kg(L)
            tpesty = tpesty + pestsp(L)
            CL(L) = CT(L) / (SW(L) + Kd(L)*BD(L))
            IF (CL(L).GT.SOLUB) THEN
               CT(L) = CT(L) + (CL(L) - SOLUB) * SW(L)
               PRINT*, 'SOLUBILITY EXCEEDED ON DAY ',DOY,' AND LAYER ',L
               PRINT*, 'CL = ', CL(L)
               CL(L) = SOLUB
            ENDIF
         enddo
         write (10, 3000) nrep
3000     format ('RUN ', i2)
         TPlchd = 0.0
         TPlcht = 0.0
      ENDIF

c     Apply pesticide (surface application)

      IF (DOY.EQ.APPDAY) THEN
         PESTSP(1) = PESTSP(1) + PESTIN
      ENDIF

c     Leaching
c     OUTP is the amount leaving layer

      outp = 0.0
      Do L=1, nlayr

c        Flow from previous layer depends on whether tiles were open or not

         If (iswwt.ne.2.or.L.ne.tilel.or..not.drflag(doy)) then
            PESTSP(L)=PESTSP(L)+max(0.0, OUTP)
            Outpp = max(0.0, Outp)
         Else
            Outpp = 0.0
         Endif

         Dmax=(Sat(l)-Dul(l))*dlayr(L)*swcon(L)*2.0 !max drainage

c        Partition Flow into slow and fast

         If(flowd(L).gt.Dmax)Then
```

```
            Fast=flowd(L)-Dmax
            Slow= Dmax
         Else
            Fast=0.0
            Slow=flowd(L)
         Endif

c        Molecular diffusion coefficient as a f(T[K], viscosity[poise],
c        molar volume of solute[cm3/g-mol]) (Wilke & Chang, quoted in
c        Satterfield, 1970)

         Viscos = st(L) * (-2.15e-4) + 1.48e-2  ! in poise (Marshall & Holmes)
         DmWC = 5.06e-9 * (st(L) + 273.0) / (Viscos*MOLVOL**0.6)

c        Molecular diffusion coefficient as a f(T[K], viscosity[poise],
c        molar volume of solute[cm3/g-mol]) (Stokes-Einstein, quoted in
c        Satterfield, 1970).  Take the minimum.

         DmSE = 1.05e-9 * (st(L) + 273.0) / (Viscos*MOLVOL**0.33)
         Dm = amin1(DmWC, DmSE) * 3600.0 * 24.0 ! convert to cm2/d

c        Disp. prob. scale dependent.  More like a fitting parameter.

         If (L.lt.nlayr) then
            DISPRS = (dlayr(L)+dlayr(L+1)) / Disden
         Else
            DISPRS = dlayr(L)*2.0 / Disden
         Endif

c        Dispersion coefficient as a f(Dm, dispersivity, flow velocity,
c        SW, tortuosity) (Marshall & Holmes, 1988).  Should be in the order of
c        0.3 cm2/d.

         D = Dm*TORT*SW(L) + DISPRS*Fast/SW(L)

c        Leach out.  How was the 1e-4 reached at: ug/(Lcm) * cm2/d = e-4 kg/ha

         OUTP = ppb2kg(L)*CL(L)*Slow/Dlayr(L)
     &         -1e-4 * D * (CL(L+1)-CL(L)) / ((Dlayr(L+1)+Dlayr(L))/2.0)

         if (L.eq.8) then
c           write(*, 1001) doy, outp, disprs, flowd(8), slow, d, cl(1),
c    &                     cl(1+1)
1001        format(i3, 1x, 7(e8.1, 1x))
         endif

c        With high flows can't leach more than the leaching fraction
c        Can't leach more than 90% anyway.

         If (L.gt.1.and.Pestsp(L-1).Ge.Pestsp(L)-Outpp.and.Flowd(L).le.
     &   6.4.and.Swbefd(L).le.Dul(L).and.Outp.gt.0.895*Outpp) then
             Outp = 0.895*Outpp
         Elseif (Outp.gt.0.90*CT(L)*ppb2kg(L)) then
             Outp = 0.90*CT(L)*ppb2kg(L)
         Endif

         PESTSP(L)=PESTSP(L)- max(0.0, OUTP)
        NPout(L) = max(0.0, OUTP) !in Kg/ha per layer
      Enddo

c     Upward fluxes
c     OUTP is the amount leaving layer

      outp=0.0
      Do L=2,nlayr
         K=L-1
```

```
            If(Flowu(L).gt.1e-6) Then
              outp=cl(L)*ppb2kg(L)*Flowu(K)/Dlayr(L)
              pestsp(L)=pestsp(L)-outp
              pestsp(K)=pestsp(k)+outp
              NPout(L)=NPout(L)-outp
            Endif
         Enddo

c        Total amount leached

         If (doy.ge.doyout) then
            TPlchd = TPlchd + max(NPout(nlayr), 0.0)
            If (iswwt.eq.2.and.drflag(doy)) then
               TPlcht = TPlcht + max(NPout(tilel-1), 0.0)
            Endif
         Endif

c        Calculate how much lost by plant uptake
c        Little information available.  For now assume pesticide is taken
c        passively with transpiration stream.

         uptake = 0.0
         DO 400, L = 1, NLAYR
            PESTSP(L) = PESTSP(L) - CL(L)*ppb2kg(L)*dble(RUF*RWUMX(L)/
     &                  dlayr(L))
            uptake = uptake + CL(L)*ppb2kg(L)*dble(RUF*RWUMX(L)/dlayr(L))
400      CONTINUE

c        Calculate degradation
c        The kinetics of the transformations are not well known.  Assume order 1
c        and use published value for t1/2 (Wagenet & Hutson, Annu.Rev. Phyto-
c        pathol. 28:316). Order 1 also supported by Stearman, Agr. Abstracts 1992.

         IF (DOY.GT.APPDAY) THEN
            degrad = 0.0
            DO 300, L = 1, NLAYR
               Kr = 0.6932 / THALF(L)
               degrad= degrad + pestsp(L) * (1.0-dexp(-Kr))
               PESTSP(L) = PESTSP(L) * dexp(- Kr)
300         CONTINUE
         ENDIF

c        Calculate sorption/desorption.  Use equilibrium constants.  Not
c        unreasonable assumption given that we operate on 1 d time step.

         L = 1
         DO WHILE (JUL.GT.1.AND.L.LE.NLAYR)
            CT(L) = PESTSP(L) / ppb2kg(L)
            CL(L) = CT(L) / (SW(L) + Kd(L)*BD(L))
            IF (CL(L).GT.SOLUB) THEN
               CT(L) = CT(L) + (CL(L) - SOLUB) * SW(L)
               PRINT*, 'SOLUBILITY EXCEEDED ON DAY ', DOY, ' AND LAYER ', L
               PRINT*, 'CL = ', CL(L)
               CL(L) = SOLUB
            ENDIF
            L = L + 1
         ENDDO

c        Mass balance check

         If (iswwt.eq.2.and.drflag(doy)) then
            call pesterr (appday, degrad, doy,NPout(nlayr)+NPout(tilel-1),
     +                    nlayr, opsys, pestin, pestsp, tpest, tpesty,
     +                    uptake)
         Else
            call pesterr (appday, degrad, doy, NPout(nlayr), nlayr,
```

```
     +                opsys, pestin, pestsp, tpest, tpesty, uptake)
      Endif

c     Save total amount of pesticide for next day's error check

      tpesty = tpest

c     Write Output:

      WRITE (10, 1500) DOY, TPlcht, (PESTSP(L), CT(L), CL(L),
     &       L=1,NLAYR)
1500  FORMAT ('DOY = ', I3 , ' TPlcht = ', F10.6, /,
     &        '      MASS, CT, CL IN EACH LAYER',
     &        10(/, 3(2X, F10.4)))
      RETURN
      END
```

PESTICIDE INITIALIZATION

```
C +-------------------------------------------------------------------+
C | Initialize pesticide concentrations in soil.  Patterned after ipswin. |
C | Input file format similar to File5 of CERES 2.1                   |
C +-------------------------------------------------------------------+
C | Created by: a. gerakis, june 1993                                 |
C +-------------------------------------------------------------------+

      SUBROUTINE pestcdin (agefac, appday, bd, ct, disden, dlayr, File2,
     +                     Inpfile, Kd, Molvol, nlayr, ntrt, pestin,
     +                     Solub, Specnm, Thalf)

      Implicit None
      INTEGER appday, I, Filen, L, nlayr, Nnlayr, ntrt, TRTNO
      real bd(*), dlayr(*)
      double precision Agefac, analys, ct(*), Disden, dnlayr(20), Kd(*),
     +                 Molvol, pestin, Solub, Thalf(*)
      Character Inpfile*12, File2*12, Specnm*12
      logical fexist

      INQUIRE(FILE=Inpfile,EXIST=FEXIST)
      IF(FEXIST) then
           Filen = 7
           OPEN(Filen,FILE=Inpfile,STATUS='OLD')
           Rewind(Filen)
      ELSE
           write(*,*) ' Pesticide information file missing.'
           read(*,*)
      ENDIF

c     Read initial values common to all treatments

      READ (Filen,201,END = 700,ERR = 500) Specnm, Agefac, Disden
201   Format (a12, /, d4.2, /, d5.1)
      READ (Filen,202,END = 700,ERR = 500) (Kd(i),i=1,nlayr)
202   Format (20(:, d5.1, 1x))
      READ (Filen,203,END = 700,ERR = 500) Molvol, Solub
203   Format (d6.1, /, d9.1)
      READ (Filen,202,END = 700,ERR = 500) (Thalf(i),i=1,nlayr)

c     Read treatment number, application day, amount applied (Kg/ha)

100   READ (Filen,200,END = 700,ERR = 500) TRTNO, appday, pestin
200   Format(i2, 10x, i3, 1x, f6.3)
```

```
      I = 0
300   If(I.eq.20.and.trtno.eq.ntrt) then
       IF(DNlayr(I).ne.-1.0) then
        I=20
        Write(*,330) Inpfile
330     Format('  Maximum number of 20 soil layers needed by model have
     1 been reached.',/,'   Modification of File ', a12,    ' may be req
     2uired.')
        Endif
       Goto 450
      Endif
      I = I + 1
c     read pesticide concentration from soil analysis (ug/Kg soil = ppb mass)
      READ (Filen,400,END = 700,ERR = 500) DNLAYR(I), analys
c     convert from ug/Kg soil to ug/L
      ct(I) = analys * BD(I)
400   format(3x, f3.0,1x, f5.0)
      IF (DNLAYR(I) .GE. 0.0) GO TO 300
      IF (TRTNO .NE. NTRT) GO TO 100
450   NNLAYR=I-1
      GO TO 900
  500 WRITE (*,600) Inpfile
  600 FORMAT(/10X,'Error! FORMAT DATA MISMATCH IN FILE: ',A12,/10X,
     1     'Program will stop to enable modification of file.')
      Stop
  700 WRITE (*,800) Inpfile
  800 FORMAT(/10X,'Error! END OF DATA IN FILE: ',A12,/10X,
     1     'Program will stop to enable modification of file.')
      Stop
900   IF(NLAYR.EQ.NNLAYR)THEN
        DO  1000 I=1,NLAYR
          IF(DLAYR(I).NE.DNLAYR(I))THEN
            GOTO 1120
          ELSE
            If (analys.lt.0.0) goto 1500
          ENDIF
1000      CONTINUE
      ELSE
         WRITE(*,1110) Inpfile, File2
         Stop
      ENDIF
      GOTO 1130
1120  WRITE(*,1140) Inpfile, File2
      Stop
1130  continue
      close(Filen)
      RETURN
1110  FORMAT(1x,'Number of layers in ', A12,' does not match with'
     1,/,1x,'the number of layers in ', A12, '.',
     1/,10x,'Program will stop to enable modification of file.')
1140  FORMAT(1x,'Layer thickness in ',A12,' does not match with'
     1,/,1x,'the layer thickness in ', a12, '.',
     1/,10x,'Program will stop to enable modification of file.')
1500  write(*,1600) Inpfile
1600  FORMAT(/,' Error! MISSING VALUES OR VALUES OUT OF RANGE IN: ',A12)
      END
```

PESTICIDE MASS BALANCE CHECKING

```
C +-------------------------------------------------------------------+
C | Mass balance check for pesticide                                  |
C +-------------------------------------------------------------------+
```

```
C | Created by: a. gerakis, june 1993                                        |
C +--------------------------------------------------------------------------+

      SUBROUTINE pesterr (appday, degrad, doy, netlch, nlayr, pestin,
     +                    pestsp, tpest, tpesty, uptake)

      IMPLICIT NONE
      double precision amappl, degrad, error, netlch, pestin,
     +     pestsp(*), tpest, tpesty, uptake
      INTEGER appday, DOY, L, NLAYR
      Integer  ieeer, ieee_flags
      Character out*16

c     tpest and possibly ERROR create inexact numbers that have to clear

      ieeer =  ieee_flags ( 'clear', 'exception', 'inexact', out)
      ieeer =  ieee_flags ( 'clear', 'exception', 'underflow', out)
      if (ieeer .ne. 0) then
          print *,' *** ieee_flag can not clear (pesterr) ***'
          read(*,*)
      endif

c     Calculate total pesticide in soil at end of the day

      tpest = 0.0
      do 204, L = 1, nlayr
          tpest = tpest + pestsp(L)
204   continue

c     Add pesticide applied on the day of application

      if (doy.eq.appday) then
         amappl = pestin
      else
         amappl = 0.0
      endif

      ERROR = tpesty + amappl - tpest - netlch - uptake - degrad

      IF (abs(ERROR).GT.1e-5) then
         WRITE(*,1246) ERROR, DOY, tpesty, tpest, amappl, netlch,
     &                 uptake, degrad
1246     FORMAT (/, 22X, 1H+, 38(1H-), 1H+ , /, 22X,
     1   '| ERROR IN PESTCD =',(F12.9),' DOY=',I3,'|' ,
     2   /,22X,  1H+, 38(1H-), 1H+ ,/,
     3   /, 2X, 'tpesty  = ', (F13.9),
     3   /, 2X, 'tpest   = ', (F13.9),
     3   /, 2X, 'amappl  = ', (F13.9),
     3   /, 2X, 'netlch  = ', (F13.9),
     3   /, 2X, 'uptake  = ', (F13.9),
     3   /, 2X, 'degrad  = ', (F13.9))
         write(*,*) ' Press <return> to continue ...'
         read (*,*)
      ENDIF
      RETURN
      END
```

DRAINAGE

```
C +--------------------------------------------------------------------------+
C | This subroutine drains water downward.  The routine also                 |
C | accomodates the effects of a water table and a layer restricting         |
```

```
C | drainage.                                                          |
C +--------------------------------------------------------------------+
C | Created by: j.t. ritchie & d. godwin, aug 1992                     |
C | Modified by: a. gerakis,feb. 1994 [separated saturated from uns. flow]|
C +--------------------------------------------------------------------+

      Subroutine Drainage (Add, Dlayr,doy, Drflag, Dul,Flowd,
     +                     Idrsw,
     +                     Iswwt, Ksmacro, Ksopen, Nlayr, Overflow,
     +                     pinf, Sat,
     +                     Sw, Tilel, Wtlayr)

      Implicit None
      real Add, Dlayr(*),Dul(*),Flcon,Flowmx, Flowpr, Sweq1,Sweq2,
     +     Flowd(0:*),
     +     Sat(*), Sw(*),Swy,pinf,Tmpadd, Excess,Overflow,Ksmacro(*),
     +     Ks_min, Ksopen,
     +     Hold
      Integer doy, Iswwt, K, L, Layr, Nlayr, Tilel, Wtlayr
      LOGICAL Drflag(*), IDRSW

c     Initialize variables

      Flcon = -0.2
      Flowd(0) = pinf ! downward flow (cm)
      Flowmx = 0.0  ! maximum flow (cm)
      Flowpr = 0.0  ! flow from previous layer (cm)
      IDRSW = .FALSE.
      Overflow = 0.0

c     Separate drainage into unsaturated and saturated zone

c     Find the deepest layer for unsaturated drainage

      If (iswwt.eq.2.and..not.drflag(doy)) then
         Layr = wtlayr-1
      Else
         Layr = nlayr
      Endif

c     First, do unsaturated drainage

      Do 100 L = 1, Layr
          Swy = Sw(L)    ! sw yesterday
          Excess = 0.0  ! above water holding capacity (cm)
          Tmpadd = 0.0  ! temporary addition (cm)

c         Flow from previous layer depends on whether tiles were open
c         and whether we add any lateral flow

          If (iswwt.eq.2.and.L.eq.wtlayr) then

c            Find the most restricting Ksmacro beneath the water table.  Take
c            1/20.0 of that as an estimate of lateral flow  contribution
c            from the water table surrounding the lysimeter = ks_min.

             ks_min = ksmacro(wtlayr)
             do K = wtlayr+1, nlayr
                ks_min = min(ksmacro(K), ks_min)
             enddo
             ks_min = ks_min / 20.0

             If (L.eq.tilel) then
                Flowpr = ks_min
                Tmpadd = ks_min  ! external source later added to subirr.
             else
```

```
                Flowpr = max(Flowd(L-1), ks_min)
                Tmpadd = max(0.0, ks_min - Flowd(L-1))
             Endif
          Elseif (iswwt.eq.2.and.drflag(doy).and.L.eq.tilel) then
             Flowpr = 0.0
          Else
             Flowpr = flowd(L-1) ! as is usu. the case
          Endif

c
c         Only drain water if above DUL
c
          If(Sw(L)+Flowpr/Dlayr(L).Gt.Dul(L)+0.0004) Then
c
c         Calculate equilibrium water content for both held water(SWEQ1)
c         and drained water(SWEQ2) and potential flow from that layer
c
              Sweq1 = Dul(L) + (Sat(L)-Dul(L))*
     &         (1-Exp(Flowpr*Flcon))
              Sweq2 = Swy - ((Swy - Dul(L))*0.5)
              Sw(L) = max(Sweq1,Sweq2)
              Flowd(L) =  Flowpr - (Sw(L) - Swy)*Dlayr(L)
c             If the estimated flow is negative, adjust sw , flowd
              If (flowd(L).lt.0.0) then
                 sw(L) = sw(L) + flowd(L)/dlayr(L)
                 flowd(L) = 0.0
              endif
              IDRSW = .TRUE.
c
c  Check that KsMacro or drain capacity do not constrict potential flow -
c  if so compute an excess which will be used to back water up:
c
              If ((iswwt.eq.0.and.L.eq.Nlayr).or.(iswwt.eq.2.and.
     +        L.eq.tilel-1.and.drflag(doy))) then
c                Estimate the maximum that the drains can carry.  Use Ks
c                measured with open drains as flowmx
                 flowmx = Ksopen
              elseif (iswwt.eq.2.and.L.eq.wtlayr-1.and.wtlayr.le.nlayr.
     +        and..not.drflag(doy)) then
c                water table normally restricts flow, unless it's at the
c                bottom so water can escape laterally
                 flowmx = 0.0
              else
                 flowmx = ksmacro(L+1)
              endif

              excess = flowd(L) - flowmx
c
c  If necessary back water up from Excess - loop starts where we are at
c  and runs back to surface - if there is still excess this is put into
c  the pond.
c
              K = L
              DO WHILE (EXCESS.GT.0.0.AND.K.GE.1)
                 Hold=(Sat(K)-Sw(K))*Dlayr(K)
                 If(Excess.lt.Hold)Then
                    Flowd(K) = Flowd(K) - Excess
c                   If the estimated flow is negative, adjust flowd
                    If (flowd(K).lt.0.0) then
                       flowd(K) = 0.0
                    endif
                    Sw(K)=Sw(K)+Excess/Dlayr(K)
                    Excess=0.0
                 Else
                    Flowd(K) = Flowd(K) - Excess
c                   If the estimated flow is negative, adjust flowd
```

```
                    If (flowd(K).lt.0.0) then
                       flowd(K) = 0.0
                    endif
                    Sw(K)=Sat(K)
                    If (iswwt.eq.2.and.drflag(doy).and.k.eq.tilel) then
                       Excess = 0.0
                       Tmpadd = 0.0
                    Else
                       Excess = Excess - Hold
                    Endif
                 Endif
                 K = K -1
              ENDDO
           Else  ! If not enough water to drain, no flows:
              Sw(L) = swy + Flowpr/Dlayr(L)
              Flowd(L)=0.0
           Endif
c
c          Excess water  from surface layer is redirected to the pond
c
           If (excess.gt.0.0) then
              Overflow=overflow + Excess
           Endif

c          Any subirrigation needed is added

           Add = Add + Tmpadd

100    Continue !End drainage loop for this layer--move one deeper

c      Do the saturated drainage, with drains closed

       If (iswwt.eq.2.and..not.drflag(doy)) then
          Do L = max(wtlayr, tilel), nlayr
             Flowd(L) = Ksmacro(nlayr+1)
             If (L.eq.nlayr) then
                add = add + ksmacro(nlayr+1)
             Endif
          Enddo
       Endif

       Return
       End
```

SCREEN OUTPUT

```
C +-------------------------------------------------------------------------+
C | Graphically display the soil water for each layer as water-filled       |
C | porosity.   Each layer automatically scaled down proportional to its    |
C | real thickness                                                          |
C +-------------------------------------------------------------------------+
C | Created by: a. gerakis, june 1993                                       |
C +-------------------------------------------------------------------------+

       subroutine drawprof (nlayr, dlayr, doy, opsys, wfps)
       real avwfps, cumdep, depinc, dlayr(*), weight, wfps(*), xdlayr
       integer doy, icount, j, k, m, n, nlayr, numcol, numlin
       character blank*1, opsys*3, symbol*1

       avwfps = 0.0
       blank = ' '
       cumdep = 0.0
```

```
      depinc = 7.0
      icount = 0
      symbol = '#'
      weight = 0.0
      xdlayr = 0.0
      call clear(opsys)
      write (*, 1003) doy
1003  format (22x, 'WATER-FILLED POROSITY ON DOY = ', i3)
      write (*, 1002)
1002  format (4x, '0.000    0.125    0.250    0.375    0.500    0.625
     & 0.750    0.875    1.0')
      write (*, 1000)
1000  format (5x, '+--------+--------+--------+--------+--------+-------
     &-+--------+--------+-')
      do k = 1, nlayr
         cumdep = cumdep + dlayr(k)
c        If the top layers are too thin, save the extra depth
         if (cumdep.lt.depinc) then
            icount = k
            xdlayr = xdlayr + dlayr(k)
         else
c           If the top layers are grouped together, average their wfps
            if (icount.gt.0) then
               do n = 1, k
                  weight = dlayr(n) / cumdep
                  avwfps = avwfps + weight * wfps(n)
               enddo
               icount = 0
            else
               xdlayr = 0.0
               avwfps = wfps(k)
            endif
c           Number of lines displayed per layer
            numlin = nint((dlayr(k)+xdlayr) / depinc)
c           Scale wfps to 72 columns width
            numcol = nint(72*avwfps)
            do m = 1, numlin
                  write (*, 1001) cumdep, (symbol, j = 1, numcol)
     &                           ,(blank, n = 1, 72-numcol)
1001              format (1x, f4.0, '|', 72a, '|')
            enddo
         endif
      enddo
      return
      end
```

NITROGEN FLUX

```
C +--------------------------------------------------------------------+
C | N flow                                                             |
C +--------------------------------------------------------------------+
C | Created  by: aris gerakis, mar 94                                  |
C +--------------------------------------------------------------------+

      SUBROUTINE NFLUX (Dlayr, Doy, Drflag, Dul, fac, Flowd, Flowu,
     +                  iflag,isflag,Iswwt, Nlayr, NNout, sat, spec,
     +                  sppm,sw, Swbefd, swcon, Tilel)

      Include 'soiltemp.blk'

      Implicit none
      Integer Doy, iflag, isflag, Iswwt, k, L, M, nlayr, Tilel
```

```
      Real D, Disprs, Disden, Dlayr(*), Dm, Dmax, DmSE, DmWC, Dul(*),
     +     Fac(*), Fast, Flowd(0:*), Flowu(0:*),
     +     Molvol, NNout(0:*), Outn,  Outn1, Outn2,
     +     Outnp, Sat(*), Slow, spec(*), sppm(*), sw(*), Swbefd(*),
     +     Swcon(*), Tort, Viscos
      Logical drflag(*)

c     Initialize variables

      D = 0.0
      Disden = 1.2  ! calibrated with complex
      Disprs = 0.0
      Dm = 0.0
      Dmax = 0.0
      DmSE = 0.0
      DmWC = 0.0
      Fast = 0.0
      K =1
      L = 1
      M = 1
      MOLVOL = 50.0 ! cm3/g-mol
      Slow = 0.0
      outn = 0.0
      outn1 = 0.0
      outn2 = 0.0
      tort = 0.6
      Viscos = 1e-2

c     Leaching

      If (iflag.eq.0) then

c     outn is the amount leaving layer

      outn = 0.0
      Do L=1, nlayr

c        Flow from previous layer depends on whether tiles were open or not

         If (iswwt.ne.2.or.L.ne.tile1.or..not.drflag(doy)) then
            spec(L)=spec(L)+max(0.0, outn)
            outnp = max(0.0, outn)
         Else
            outnp = 0.0
         Endif

         Dmax=(Sat(l)-Dul(l))*dlayr(L)*swcon(L)*2.0 !max drainage

c        Partition Flow into slow and fast

         If(flowd(L).gt.Dmax)Then
            Fast=flowd(L)-Dmax
            Slow= Dmax
         Else
            Fast=0.0
            Slow=flowd(L)
         Endif

c        Molecular diffusion coefficient as a f(T[K], viscosity[poise],
c        molar volume of solute[cm3/g-mol]) (Wilke & Chang, quoted in
c        Satterfield, 1970)

         Viscos = st(L) * (-2.15e-4) + 1.48e-2  ! in poise (Marshall & Holmes)
         DmWC = 5.06e-9 * (st(L) + 273.0) / (Viscos*MOLVOL**0.6)

c        Molecular diffusion coefficient as a f(T[K], viscosity[poise],
```

```
c        molar volume of solute[cm3/g-mol]) (Stokes-Einstein, quoted in
c        Satterfield, 1970).  Take the minimum.

         DmSE = 1.05e-9 * (st(L) + 273.0) / (Viscos*MOLVOL**0.33)
         Dm = amin1(DmWC, DmSE) * 3600.0 * 24.0 ! convert to cm2/d

c        Acc. to Wagenet & Rao, disp. is scale dependent.  Enfield & Yates
c        fit disp. values from 2e-1 to 2e+2 cm. More like a fitting parameter.

         If (L.lt.nlayr) then
            DISPRS = (dlayr(L)+dlayr(L+1)) / Disden
         Else
            DISPRS = dlayr(L)*2.0 / Disden
         Endif
c         Disprs = 0.1 ! derived from complex

c        Dispersion coefficient as a f(Dm, dispersivity, flow velocity,
c        SW, tortuosity) (Marshall & Holmes, 1988).  Should be in the order of
c        0.3 cm2/d.

c         D = Dm*TORT*SW(L) + DISPRS*Flowd(L)/SW(L)
         D = Dm*TORT*SW(L) + DISPRS*Fast/SW(L)

         sppm(L)=spec(L)*fac(L)
         sppm(L+1)=spec(L+1)*fac(L+1)

c        Leach out. How was the 1e-1 reached at: mg/(Lcm) * cm2/d = e-1 kg/ha

         outn = spec(L)*Slow/Dlayr(L)
     &        -1e-1*D*(sppm(L+1)-sppm(L)) / ((Dlayr(L+1)+Dlayr(L))/2.0)

         if (L.eq.8) then
c            write(*, 1001) doy, outn, disprs, flowd(8), slow, d, cl(1),
c     &                     cl(1+1)
1001        format(i3, 1x, 7(e8.1, 1x))
         endif

c        Can't leach more than the leaching fraction:

         If (L.gt.1.and.spec(L-1).Ge.spec(L)-outnp.and.Flowd(L).le.
     &   6.4.and.Swbefd(L).le.Dul(L).and.outn.gt.0.895*outnp) then
             outn = 0.895*outnp
         Elseif (outn.gt.0.90*spec(L)) then
             outn = 0.90*spec(L)
         Endif

         spec(L)=spec(L)- max(0.0, outn)
        NNout(L) = max(0.0, outn) !in Kg/ha per layer
       Enddo

       Else

c      Upward fluxes
c      outn is the amount leaving layer

       outn=0.0
       Do L=2,nlayr
          K=L-1
          If(Flowu(L).gt.1e-6) Then
            outn=spec(L)*Flowu(K)/Dlayr(L)
            spec(L)=spec(L)-outn
            spec(K)=spec(k)+outn
            NNout(L)=NNout(L)-outn
          Endif
       Enddo
```

```
      Endif ! end if upward or downward flow

c     Total amount leached

c      If (doy.ge.doyout) then
c         TPlchd = TPlchd + max(NPout(nlayr), 0.0)
c         If (iswwt.eq.2.and.drflag(doy)) then
c            TPlcht = TPlcht + max(NPout(tilel-1), 0.0)
c         Endif
c      Endif

c     Mass balance check

c      If (iswwt.eq.2.and.drflag(doy)) then
c         call pesterr (appday, degrad, doy,NPout(nlayr)+NPout(tilel-1),
c     +                 nlayr, opsys, pestin, spec, tpest, tpesty,
c     +                 uptake)
c      Else
c         call pesterr (appday, degrad, doy, NPout(nlayr), nlayr,
c     +                 opsys, pestin, spec, tpest, tpesty, uptake)
c      Endif
c
cc     Save total amount of pesticide for next day's error check
c
c      tpesty = tpest
c
cc     Write outnut:
c      WRITE (10, 1500) DOY, TPlcht, (spec(L), CT(L), CL(L), L=1,NLAYR)
1500  FORMAT ('DOY = ', I3 , ' TPlcht = ', F10.6, /,
     &        '      MASS, CT, CL IN EACH LAYER',
     &        10(/, 3(2X, F10.4)))
      RETURN
      END
```

UPWARD FLOW

```
C +-----------------------------------------------------------------------+
C | Move water upward                                                     |
C +-----------------------------------------------------------------------+
C | Created by:                                                           |
C | Modified by: aris gerakis, Oct. 1993                                  |
C +-----------------------------------------------------------------------+

      Subroutine UpFlow (Ad, Dlayr, Doy, Dul, Eos, Es, Flowu, LL,
     &                   layr, Pond, Sat, Sw)

c   Layr is the last layer you want to calculate upward flow for

      Implicit None
      Real Ad(*),Dlayr(*),Dsw(3), DUL(*), flowu(0:*), Sat(*), Sw(*),
     &     Ll(*), Eos, Es,Diff, Pond
      Integer Doy, L,layr,K,M

      ES = 0.0                                                          !AG
C
C     Evaporate water from ponding (if exists) and alter ponding amount
C

      IF(POND.GT.EOS)THEN
         ES=EOS
         POND=POND-EOS
      ELSE
```

```
c        Reduce pot. evaporation by the amount that evaporated from pond.
c        This is the effective EOS now for the rest of the routine      !AG
         EOS = EOS - POND
         ES = POND   !we know actual evaporation is at least that much  !AG
c
c     Compute Maximum water loss from top three layers as a function
c     of their moisture contents

         IF (SW(1).GT.DUL(1) - 0.02) THEN
            DSW(1) = (SW(1) - 0.02 - AD(1)) * 0.80
         ELSE
            Dsw(1)=0.5*(0.5+Eos)*(Sw(1)-Ad(1))**1.4
         ENDIF

         IF (SW(2).GT.DUL(2) - 0.02) THEN
            DSW(2) = (SW(2) - 0.02 - AD(2)) * 0.12
         ELSE
            Dsw(2)=0.075*(Sw(2)-Ad(2))**1.4
         ENDIF

         IF (SW(3).GT.DUL(3) - 0.02) THEN
            DSW(3) = (SW(3) - 0.02 - AD(3)) * 0.032
         ELSE
            Dsw(3)=0.04*(Sw(3)-Ad(3))**1.4
         ENDIF

c
c        Soil evaporation is the sum of these
c
         Es= Es + Dsw(1)*dlayr(1) + Dsw(2)*dlayr(2) + Dsw(3)*dlayr(3)   !AG
c
c        Ensure ES does not exceed EOS - if so scale back DSW
c
         If(Es-pond.Gt.EoS)Then                                         !AG
           Do L=1,3
              Dsw(L)=Dsw(L)*Eos/(Es-pond)                             !AG
           Enddo
           Es=Eos + pond                                              !AG
         Endif
c
c        Compute a temporary change in water content of layer 3
c
         Sw(3)=Sw(3)-Dsw(3)
         Flowu(2)=0.0

         IF (SW(3).LT.DUL(3)) THEN
c
c           Calculate diffusivities and fluxes for layers 4 to layr
c
            Do L=3,layr
                K=L-1
                M=L+1
                Diff=0.5*Exp(40.0*((Sw(M)-LL(M))+
     &                (Sw(L)-Flowu(K)/Dlayr(L)-LL(L)))/2.0)
                If(Diff.Gt.50.0)Diff=50.0
                Flowu(L)=((Sw(M)-DUL(M)) - (SW(L)-DUL(L)-
     &                  Flowu(K)/Dlayr(L))) * Diff /
     &                  (Dlayr(L)+Dlayr(M))/2.0
                IF (FLOWU(L).LT.0.0) THEN
                   FLOWU(L) = 0.0
                ENDIF
c
c            Flowu(k) Moves water from L to L-1 , Flowu(L) from L+1 to L
c
                Sw(L)=Sw(L)-Flowu(K)/Dlayr(L)+Flowu(L)/Dlayr(L)
                If (Sw(L).gt.Sat(L)) then                               !AG
```

```
                  Flowu(L) = Flowu(L) - (sw(L) - sat(L))*dlayr(L)      !AG
                  sw(L) = sat(L)                                       !AG
               Endif                                                   !AG
            Enddo
            Flowu(layr+1)=0.0
            Sw(layr+1)=Sw(layr+1)-Flowu(layr)/Dlayr(layr+1)
         ELSE
            DO L=3, layr + 1
               FLOWU(L) = 0.0
            ENDDO
         ENDIF
c
c        Compute moisture content and Flows in top three layers
c

         Flowu(2)=Dsw(3)*dlayr(3)
         Flowu(1)=Flowu(2)+Dsw(2)*dlayr(2)
         Flowu(0)=Flowu(1)+Dsw(1)*dlayr(1)
         Sw(2)=Sw(2)-Dsw(2)
         Sw(1)=Sw(1)-Dsw(1)
         POND = 0.0                                                   !AG
      ENDIF ! End if ponding .lt. eos
C   Some checking .....
      DO L=1,LAYR
          IF(SW(L).GT.SAT(L)) THEN
             WRITE (*,*) 'SW(', L, ')=',sw(L), ' > SAT(', L,')=',sat(L),
     +                   ' on ', DOY
          ENDIF
      ENDDO
      Return
      End
```

WATER TABLE

```
C +-------------------------------------------------------------------------+
C | Initialize water table at the beginning of the day and adjust           |
C | level after any change in water content.                                |
C +-------------------------------------------------------------------------+
C | Created by: prathapar & a. gerakis, july 1991                           |
C | Modified by: a. gerakis, feb. 1994 [w.t. goes to nearest whole layer]   |
C +-------------------------------------------------------------------------+

      SUBROUTINE WATABLE (Add, DEPWT, DL1, DL2, Dlayr, Doy, Drflag,
     +                    Flowd, Flowu, Iswwt, NLAYR, Readwt, SAT,SW,
     +                      Tilel, WTLAYR)

      Implicit none
      REAL Add, DEPWT(*), DL1(*), DL2(*), Dlayr(*), Flowd(0:*),
     +     Flowu(0:*), SAT(*), SW(*)
      INTEGER Doy, Iswwt, K, NLAYR, Tilel, WTLAYR
      Logical Drflag(*), Readwt

      wtlayr = nlayr + 1
      K = nlayr  ! temporary layer counter

c     Find water table layer

      If (iswwt.eq.2.and.readwt) then
c       Set w.t. to depth read from file.  Subirrigate if necessary.
c       Assumptions:  Water can be pumped at the desired rate & the w.t. is
c       level.  Additions below the tile are positive, otherwise negative.
c       If a layer is more than half into the w.t., move the w.t. to its top.
```

```
        Do while (k.ge.1.and.dl2(k)-depwt(doy).gt.dlayr(k)/2.0)
c        Do while (k.ge.1.and.dl1(k).ge.depwt(doy))
c           If (k.ge.tile1) then
c              Flowd(k) = (sat(k) - sw(k)) * dlayr(k)
c              add = add + Flowd(k)
c           Else
c              Flowu(k) = (sat(k) - sw(k)) * dlayr(k)
c              add = add + Flowu(k)
c           Endif
           add = add + (sat(k) - sw(k)) * dlayr(k)
           SW(K) = SAT(K)
           wtlayr = K
           K = K -1
        Enddo
      ELSE
        DO WHILE (abs(SW(K)-SAT(K)).lt.0.01.AND.K.GE.1)
           WTLAYR = K
           K = K - 1
        ENDDO
      ENDIF

c     Find new water table depth

      If (wtlayr.le.nlayr) then
        depwt(doy) = dl1(wtlayr)
      else
        depwt(doy) = dl2(nlayr)  ! can't let it drop > profile
      endif
      RETURN
      END
```

MASTER WATER BALANCE

```
C +-------------------------------------------------------------------------+
C |    Master water balance program                                         |
C +-------------------------------------------------------------------------+
C |    Calls:                                                                |
C |    DRAWPROF  IRRIGE   ROOTGROW  WATDEF   OXSTRESS                       |
C |    CALEO     NFLUXD   SNOWFALL  WBERROR                                 |
C |    DRAINAGE  NFLUXU   UPFLOW    WSTRSS                                  |
C |    ETRATIO   PONDING  WATABLE   WUPTAKE                                 |
C +-------------------------------------------------------------------------+
C |                 GLOSSARY OF RECENTLY ADDED VARIABLES                    |
C | ADD         : Daily additions as subirrigation (cm)                     |
C | DEPWT(366)  : Depth of water table every day         (cm)               |
C | DOYOUT      : Day of the year to start printing cumulative output       |
C | DRFLAG(366): Flag to denote whether tiles are open today                |
C | EVFLAG      : Evaporation flag, unused at present                       |
C | FLOWD(21)   : Downward flow leaving a layer (cm)                        |
C | FLOWN(21)   : Net      flow leaving a layer (cm)                        |
C | FLOWU(21)   : Upward   flow into    a layer (cm)                        |
C | GRAPHD      : Day to start graphic display of soil water                |
C | IEEE_FLAGS : Variables of IEEE routine                                  |
C | IEEER,      :      "     "   "     "                                    |
C | MOD,OUT,IN :       "     "   "     "                                    |
C | KSOPEN      : Conductivity of the tile layer with tiles open            |
C | JUL         : Date of simulation                                        |
C | LEFTWAT     : Total amount of water left from yesterday (cm)            |
C | NNOUT(21)   : Net Nitrate N out (kg/ha)                                 |
C | NUNOUT(21)  : Net Urea N out (kg/ha)                                    |
C | OPSYS       : Operating System code                                     |
C | OUT         : Variable  of IEEE routine                                 |
```

```
C | OVERFLOW   : Water that can't be held by the soil (cm)                    |
C | READWT     : Flag to read the water table depth or not                    |
C | RUF        : Root Water Uptake Factor?                                    |
C | SHOWGR     : Flag   for graphically showing soil water                    |
C | SHOWGR     : Flag to graphically display profile                          |
C | SNOMLT     : Snow melt (cm)                                               |
C | SWBEFD     : Soil water before drainage (cm3/cm3)                         |
C | TILEL      : Tile layer                                                   |
C | TNlchd     : Total NO3-N leaching deep (kg/ha)                            |
C | TNlcht     : Total NO3-N leaching through tiles (kg/ha)                   |
C | TRU        : Total root water uptake                                      |
C | TSWY       : Total soil water yesterday (cm)                              |
C | Tadd       : Total additions through subirrigation (cm)                   |
C | Tdeepd     : Total deep drainage (cm)                                     |
C | Tep        : Total plant evaporation (cm)                                 |
C | Tes        : Total soil  evaporation (cm)                                 |
C | Tprec      : Total rain + irrigation (cm)                                 |
C | Train      : Total rain   (cm)                                            |
C | Troff      : Total runoff (cm)                                            |
C | Ttildr     : Total tile drainage (cm)                                     |
C | WFPS1      : Alternative water filled porosity                            |
C | WTLAYR     : Water table layer                                            |
C +-------------------------------------------------------------------------+
C |    All water units are cm except precipitation and irrigation that are   |
C |    read as mm and converted to cm before use.     DSOIL (irr. management |
C |    depth) is in m - AG                                                   |
C +-------------------------------------------------------------------------+
C |   Created by:                                                            |
C |   Modified by:  aris gerakis 1991-1992 [structured somewhat]             |
C |   Modified by:  j.t. ritchie & doug godwin sep. 1992 [various changes]   |
C |   Modified by:  jon lizaso   nov. 1992 [added O2 stress]                 |
C |   Modified by:  aris gerakis feb. 1993 [finished SWAN changes]           |
C |   Modified by:  aris gerakis nov. 1993 [added lateral contribution to w.t.]|
C |   Modified by:  aris gerakis dec. 1993 [averaged WFPS during the day]    |
C +-------------------------------------------------------------------------+

      SUBROUTINE WATBAL (crop, DOY, doyout, Drflag, graphd, grort, jul,
     +                   LAI, NNNout, Opsys, phint, plants, ruf, showgr,
     +                   Swbefd, Tadd, Tdeepd, Tep, Tes, Tilel, TNlchd,
     +                   TNlcht,tprec, TPRECP, troff, Ttildr)

      Implicit None
      Include 'enviro.blk'
      Include 'evaptrn.blk'
      Include 'extwater.blk'
      Include 'genetics.blk'
      Include 'irrign.blk'
      Include 'nleach.blk'
      Include 'soildep.blk'
      Include 'soilnit.blk'
      Include 'soilox.blk'
      Include 'soiltemp.blk'
      Include 'switch.blk'
      Include 'temporw.blk'
      Include 'v3water.blk'
      Include 'weather.blk'
      Include 'wstress.blk'

      Integer DOY, doyout, graphd, j, jul, L, Tilel
      Integer  iesar, iees_flags, k, ll, lrtdep
      REAL add, grort, Eeq,  Lai, Leftwat, NNNout(0:20), NUNout(0:20),
     +     Overflow, Phint, Pinf,Plants, Rnfac, Ruf, Snomlt, Swdf,
     +     Swbefd(20), Tadd, Tdeepd, Td, Tep, Tes, TNlchd, TNlcht,
     +     Tprec, Tprecp, Tratio, Troff, Tru, Tswy, Ttildr, wfps1
      Character crop*2, input*1, Opsys*3, Out*16, showgr*1
      Logical Airtest, Drflag(*), Evflag, Readwt
```

```
c     Possible underflows and inexact numbers have to clear - AG

      If (opsys.eq.'UNX') then
         ieeer =  ieee_flags ( 'clear', 'exception', 'inexact', out)
         if (ieeer .ne. 0) then
             print*,' *** ieee_flag can not clear (watbal) ***'
         endif
         ieeer =  ieee_flags ( 'clear', 'exception', 'underflow', out)
         if (ieeer .ne. 0) then
             print*,' *** ieee_flag can not clear (watbal) ***'
         endif
      Endif

C     Initialize variables:

      ADD = 0.0
      DEPIR=0.
      EO = 0.0
      EP = 0.0
      ES = 0.0
      ET = 0.0
      EOS= 0.0
      EOP= 0.0
      EVFLAG = .false.
      ICSDUR=ICSDUR+1
      IDRSW = .FALSE.
      IOFF = 0
      OVERFLOW = 0.0
      PINF = 0.0
      PRECIP=0.
      RAIN = RAIN / 10.0       ! convert to cm
      Readwt = .false.
      RUNOFF = 0.0
      wtlayr = nlayr + 1

      DO 602 L= 0, NLAYR + 1
         FLOWD(L)=0.
         FLOWU(L)=0.
         FLOWN(L)=0.
         NNNOUT(L) = 0.0    ! Net Nitrate Nitrogen leaching
         NUNOUT(L) = 0.0    ! Net Urea Nitrogen leaching
602   CONTINUE

C     Yesterday's water (cm) will be used locally for error checking    !AG

       tswy = 0.0
       do 101, L = 1, nlayr
          TSWY = TSWY + sw(l)*dlayr(l)
101    continue
       LEFTWAT = TSWY + POND     !  Total leftover water from yesterday !AG

*    +-------------------------------------------------------+
*    | If IIRR = 1, no irrigation.  If IIRR = 2 or 3, irrigate.    |     !AG
*    | If IIRR = 4, watbal is not called (water non-limiting)      |     !AG
*    +-------------------------------------------------------+

      IF (IIRR.EQ.2.OR.IIRR.EQ.3) THEN
           CALL IRRIGE (AIRR, AMIMIN, ATHETA, DEPIR, DOY, EFFIRR, IDAY,
     1                  IIRR, IOFF, NIRR, SWDEF, THETAC)
      ENDIF

      DEPIR = DEPIR / 10.0 ! convert to cm because irrigation is in mm

*     Precipitation is rain plus irrigation:
```

```
      PRECIP=RAIN+DEPIR
      SWDEF=0.

*  +-------------------------------------------------------------+
*  |  Add snow:                                                  |  !AG
*  +-------------------------------------------------------------+

      IF (TEMPMX.LE.1..OR .SNOW.GT.0.) THEN
        CALL SNOWFALL (TEMPMX, PRECIP, RAIN, SNOMLT, SNOW)
      ENDIF
      tprecp = precip

*  +-------------------------------------------------------------+
*  |  Estimate depth of the water table                          |  !AG
*  +-------------------------------------------------------------+

      IF (ISWWT.ge.1) THEN
         CALL WATABLE (Add, DEPWT, DL1, DL2, Dlayr, Doy, Drflag,
     +                 Flowd, Flowu, Iswwt, NLAYR, .true., SAT,SW,
     +                  Tilel, WTLAYR)
      ENDIF

c     Before drainage, save SW to calculate mean porosity

      Do j = 1, nlayr
         Swbefd(j) = sw(j)
      Enddo

c     Initial water filled porosity

      DO L=1,Nlayr
         Wfps(L) = amin1 (Sw(L) / Tpore(L), 0.93)
      Enddo

*  +-------------------------------------------------------------+
*  |  Calculate potential evapotranspiration:                    |  !AG
*  +-------------------------------------------------------------+

      CALL CALEO (ALBEDO, EEQ, EO, EOS, LAI, SALB, SOLRAD,
     1                  TD, TEMPMX, TEMPMN )

*  +-------------------------------------------------------------+
*  |  If there has been any precip or if water remains in the pond |
*  |  call the ponding routine.  When it rains, water either     |
*  |  infiltrates, ponds or runs off.                            |
*  +-------------------------------------------------------------+

      If(Pond.Gt.0.0.or.Precip.Gt.0.0)Then
         CALL PONDING (doy, KSMACRO,KSMTRX,PINF,POND,PONDMAX,PRECIP,
     +                 RUNOFF, SAT,SW)
      Endif

C     Mass balance error check:                                     !AG

      CALL WBERROR ('PONDROUT', Add, DLAYR, DOY, 0.0,               !AG
     &              EP, ES, LEFTWAT,                                !AG
     &              NLAYR, Opsys, PINF, POND, PRECIP, RUNOFF, SW)   !AG

*  +-------------------------------------------------------------+
*  |  DRAINAGE calculates soil water content at equilibrium, downward |
*  |  flows, and backs up the water if there is a restricting layer |
*  +-------------------------------------------------------------+

      Call Drainage (Add, Dlayr,doy, Drflag, Dul,Flowd, Idrsw,
     +               Iswwt, Ksmacro, Ksopen, Nlayr,
     +               Overflow, pinf, Sat,Sw, Tilel, Wtlayr)
```

```
c     If there has been overflow generated by backup add this to the pond

      Pond=Pond+Overflow
      If(Pond.gt.Pondmax)Then
         Runoff=Runoff+Pond-Pondmax
         Pond=Pondmax
      Endif

C     Mass balance error check:                                          !AG

      If (iswwt.eq.2.and.drflag(doy)) then                               !AG
         CALL WBERROR ('DRAINRT ', Add, DLAYR, DOY, Flowd(nlayr)+        !AG
     +                 Flowd(tilel-1), EP, ES, LEFTWAT, NLAYR, Opsys,    !AG
     +                 0.0, POND, PRECIP, RUNOFF, SW)                    !AG
      Else                                                               !AG
         CALL WBERROR ('drainrt ', Add, DLAYR, DOY, Flowd(nlayr), EP,    !AG
     +                 ES, LEFTWAT, NLAYR, Opsys, 0.0, POND, PRECIP,     !AG
     +                 RUNOFF,SW)                                        !AG
      Endif                                                              !AG

*  +-------------------------------------------------------------------+
*  |  Leach some Nitrogen                                              |
*  +-------------------------------------------------------------------+

      IF (ISWNIT.NE.0.AND.IDRSW) THEN
         CALL NFLUX (Dlayr, Doy, Drflag, Dul, fac, Flowd, Flowu, 0,2,
     +               Iswwt, Nlayr, NNNout, Sat, SNO3, NO3, sw, Swbefd,
     +               swcon, Tilel)
      ENDIF
      IF (ISWNIT.NE.0.AND.IUON.AND.IDRSW) THEN
         CALL NFLUX (Dlayr, Doy, Drflag, Dul, fac, Flowd, Flowu, 0,1,
     +               Iswwt, Nlayr, NUNout, Sat, Urea, Uppm, sw, Swbefd,
     +               Swcon, Tilel)
      ENDIF

*  +-------------------------------------------------------------------+
*  |  Estimate depth of the water table                                |  !AG
*  +-------------------------------------------------------------------+

      IF (ISWWT.GE.1) THEN
         CALL WATABLE (Add, DEPWT, DL1, DL2, Dlayr, Doy, Drflag,
     +                 Flowd, Flowu, Iswwt, NLAYR, .false., SAT,SW,
     +                 Tilel, WTLAYR)
      ENDIF

*  +-------------------------------------------------------------------+
*  |  Calculate soil evaporation and water redistribution:             |
*  +-------------------------------------------------------------------+

      Call Upflow (Ad, Dlayr, Doy, dul, Eos, Es, Flowu, LL,
     +             min1(Wtlayr-1, nlayr-1), Pond, Sat, Sw)

C     Mass balance error check:                                          !AG

      If (iswwt.eq.2.and.drflag(doy)) then                               !AG
         CALL WBERROR ('UPFLROUT ', Add, DLAYR, DOY, Flowd(nlayr)+       !AG
     +                 Flowd(tilel-1), EP, ES, LEFTWAT, NLAYR, Opsys,    !AG
     +                 0.0, POND, PRECIP, RUNOFF, SW)                    !AG
      Else                                                               !AG
         CALL WBERROR ('upflrout ', Add, DLAYR, DOY, Flowd(nlayr), EP,   !AG
     +                 ES, LEFTWAT, NLAYR, Opsys, 0.0, POND, PRECIP,     !AG
     +                 RUNOFF,SW)                                        !AG
      Endif                                                              !AG

*  +-------------------------------------------------------------------+
```

```
*   |  Move some Nitrogen up                                              |
*   +---------------------------------------------------------------------+

      IF (ISWNIT.NE.0) THEN
         CALL NFLUX (Dlayr, Doy, Drflag, Dul, fac, Flowd, Flowu, 1,2,
     +               Iswwt, Nlayr, NNNout, Sat, SNO3, NO3, sw, Swbefd,
     +               Swcon, Tilel)
      ENDIF
      IF (ISWNIT.NE.0.AND.IUON) THEN
         CALL NFLUX (Dlayr, Doy, Drflag, Dul, fac, Flowd, Flowu, 1,1,
     +               Iswwt, Nlayr, NUNout, Sat, Urea,Uppm, sw, Swbefd,
     +               Swcon, Tilel)
      ENDIF

*    +---------------------------------------------------------------+
*    | Calculate water deficit for automatic irrigation.             |
*    +---------------------------------------------------------------+

      If (Iirr.eq.3) Then
         CALL WATDEF (ATHETA, DLAYR, DSOIL, DUL, LL,
     1                NLAYR,SW,SWDEF)
      Endif

C     Add up PESW throughout the soil profile:

      PESW = 0.0
      DO 300, L = 1,NLAYR
         PESW = PESW + ((SW(L) - LL(L)) * DLAYR(L))
300   CONTINUE

      IF (ISTAGE.lt.6) THEN  ! if plant photosynthetically active

*       +-----------------------------------------------------------------+
*       |  Subroutine to make adj. to water balance for elevated CO2:     |
*       +-----------------------------------------------------------------+

        If(ISWCO2.EQ.1) then
            CALL ETRATIO (LAI,TRATIO)
        Else
            Tratio=1.0
        Endif
2800    Continue

*       Calculate wfps.
*       If flow approached conductivity, that layer was pretty much at
*       max wfps for most of the day.
*       Or, keep initial wfps.  If calculate wfps w/ *final* SW, then
*       O2 stress and denitrification won't show - AG

        DO L=1,Nlayr
           wfps1 = (Flowd(L)-Flowu(L)+dlayr(L)*(Sw(L)-Swbefd(L))) /
     &             (0.80*ksmacro(L))
           wfps(L) = amax1 (wfps(L), wfps1)
           wfps(L) = amin1 (wfps(L), 0.93)
        Enddo

*       +-----------------------------------------------------------------+
*       | Root growth subroutine:                                         |
*       +-----------------------------------------------------------------+

        IF (GRORT.GT.0.0 .OR. (CROP .EQ. 'MZ' .AND. ASD .GT. 0.0) .OR.
     &     (CROP .EQ. 'MZ' .AND. ASD2 .GT. 0.0)) THEN
           CALL ROOTGROW (CROP, CUMDEP, DEPMAX, DLAYR, Doy, DTT, ESW,
     1                    GRORT, ISWNIT, L1, NLAYR, NO3, NH4, PHINT,
     2                    PLANTS, RLV, RLDF, RNFAC, RTDEP, SWDF,
     3                    SWDF1, SWDF3, WR, BD, DEPWT, ISTAGE, LRTDEP,
```

```
     4                    POND, wtlayr, iswwt)
            K = 1
            CUMDEP = DLAYR(K)
            DO WHILE (CUMDEP.LT.RTDEP)
               K = K + 1
               CUMDEP = CUMDEP+ DLAYR(K)
            ENDDO
            LRTDEP = K
          ENDIF
          IF (CROP.EQ.'MZ') THEN
              AIRTEST = .FALSE.
              DO 2000, L = 1,LRTDEP
                  IF (WFPS(L).GT.CWFPS) THEN
                      AIRTEST = .TRUE.
                  ENDIF
2000          CONTINUE
          ENDIF

*         +-------------------------------------------------------------+
*         | Oxygen stress routine                                       |
*         +-------------------------------------------------------------+

          IF ((AIRTEST.OR.ASD.GT.0..OR.ASD2.GT.0.).AND.CROP.EQ.'MZ') THEN
             CALL OXSTRESS (depwt, doy, LRTDEP)
          ENDIF
3300      Continue

*         +-------------------------------------------------------------+
*         | Estimate plant water uptake:                                |  !AG
*         +-------------------------------------------------------------+

           CALL Wuptake (LAI, ruf, rwumx, Rwucon,Sw, Tru, LL,RLV,Dlayr,EO,
     &                   EOP, Ep, ES, Nlayr)

*         +-------------------------------------------------------------+
*         |  Calculate water stress coefficients:                       |
*         +-------------------------------------------------------------+

          CALL WSTRSS (CSD1, CSD2, EP, Tru, SWDF1, SWDF2)

        ENDIF  ! end if plant photosynthetically active

c         Accumulate values of precipitation and evaporation

          ET = ES + EP

c         Cumulative variables after germination

          CEP=CEP+EP
          CES=CES+ES
          CET=CET+ET
          CRAIN=CRAIN+PRECIP

c         Cumulative variables before and after germination

          TEP=TEP+EP
          TES=TES+ES
          TPREC = TPREC + PRECIP
          TROFF = TROFF + RUNOFF
c
c  Calculate net water drainage and net nitrogen leaching.
c
        Do L=0,Nlayr
          Flown(L)=Flowd(L)-Flowu(L)
        Enddo
```

```
c     Update cumulative drainage and N leaching

      If (doy.ge.doyout) then
         Tdeepd = Tdeepd + Flown(nlayr)
         TNlchd = TNlchd + NNNout(nlayr)
         If (iswwt.eq.2.and.drflag(doy)) then
            Ttildr = Ttildr + Flown(tilel-1)
            TNlcht = TNlcht + NNNout(tilel-1)
         Endif
      Endif

      Tadd = Tadd + add

*     Write water balance outputs to file:                              !AG
*     Write headers:                                                    !AG

c      IF (jul.eq.1.or.MOD(DOY, 23).EQ.0.and.doy.le.275) THEN           !AG
      IF (jul.eq.1.and.doy.le.275) THEN                                 !AG
c        write(380, 8001)! write column #s                          !AG
        WRITE(380,8000) '"DOY",',  '"RAI",', '"IRR",', '"PNF",',        !AG
     &                  '"DDR",', '"TDR",',                           !AG
     &                  '"PON",', '"RNF",', '"ES",', '"EP",', '"EO",', !AG
     &                  '"ADD",', '"WTL",'                            !AG
      ENDIF                                                             !AG
c
C     Write daily output:                                               !AG
c
      If (iswwt.eq.2.and.drflag(doy).and.doy.le.275) then               !AG
         WRITE (380, 3000) doy, rain, depir, pinf, flown(nlayr),        !AG
     &                     flown(tilel-1), pond, runoff,                !AG
     &                     es, ep, eo, add, wtlayr                      !AG
      elseif (doy.le.275) then                                          !AG
         WRITE (380, 3000) doy, rain, depir, pinf, flown(nlayr),        !AG
     &                     0.0, pond, runoff,                       !AG
     &                     es, ep, eo, add, wtlayr                      !AG
      endif                                                         !AG

8000  FORMAT (1x, 13(A6))                                           !AG
8001  FORMAT (8('1234567890'))                                          !AG
3000  FORMAT (I5, ',', 11(f5.1, ','), I5)                           !AG

      if ((showgr.eq.'y'.or.showgr.eq.'Y').and.graphd.le.doy) then
         call drawprof (nlayr, dlayr, doy, opsys, wfps)
         write(*,'(a,$)') "Hit return to continue or ""s"" to supress gr
     &aph: "
         read (*,'(a)') input
         if (input.eq.'s'.or.input.eq.'S') then
           showgr = 'n'
         endif
      endif

      RETURN
      END
```

WATER TABLE INITIALIZATION

```
C +--------------------------------------------------------------------+
C | Initialize water table depth                                       |
C +--------------------------------------------------------------------+
C | Created by: aris gerakis, feb. 1993                                |
C | Modified by: aris gerakis, jan. 1994 [also initialized for ISWWT=1]|
C +--------------------------------------------------------------------+
```

```
      Subroutine wtini (Drflag, iswwt, trtno, wtfile)

      implicit none
      Include 'v3water.blk'
      Include 'soildep.blk'

      character wtfile*12
      integer ierr, ierr2, iswwt, itemp, J, L, trtno
      real deptemp
      Logical Drflag(*), drftemp

      If (iswwt.eq.2) then
         OPEN (410, FILE=WTFILE,STATUS='OLD')
         Rewind (410)

C        Position file to beginning of treatment:

         ierr = 0
         itemp = 0
         do while (itemp.ne.trtno.and.ierr.ne.-1)
            Read (410, 1000, iostat=ierr) itemp
1000        format (i2)
         enddo
         if (ierr.eq.-1) then
           write(*, *) ' You don''t have water table information for th
     +is treatment'
            pause
         endif
      Endif

C     Initialize w.t. depth and drain flag array:

      do 130 L = 1, 366
            depwt(L) = dl2(nlayr)
            Drflag(L) = .true.
130   continue

c     Read doy, w.t. depths and drainage flag from file:

      If (iswwt.eq.2) then
         j = 1
         deptemp = 0.0
         drftemp = .false.
         do while (J.ge.1)
            read (410, 9900, iostat=ierr2) J, deptemp, drftemp
9900        format (2x, i3, 1x, f5.1, 1x, L5)
            if (j.ge.1) then
              depwt(J) = deptemp
               drflag(J) = drftemp
            endif
         enddo
      Endif
      return
      end
```

WATER BALANCE ERROR CHECK

```
C +-------------------------------------------------------------------+
C | Mass balance error checking in water subroutines                  |
C +-------------------------------------------------------------------+
C | Created by: aris gerakis , aug. 93                                |
```

```
C | Modified by: aris gerakis, jan. 94                                    |
C +-----------------------------------------------------------------------+

      SUBROUTINE WBERROR (ROUTNAME, Add, DLAYR, DOY, DRAIN, EP, ES,
     +                    LEFTWAT, NLAYR, OPSYS, PINF, POND, PRECIP,
     +                    RUNOFF, SW)

      IMPLICIT NONE
      REAL Add, SW(*), DLAYR(*), LEFTWAT, PRECIP, TSW, RUNOFF,
     +     ES, EP, PINF, POND, DRAIN
      real error
      INTEGER DOY, L, NLAYR
      CHARACTER opsys*3, ROUTNAME*8

      Integer  ieeer, ieee_flags
      Character out*16

c     TSW and possibly ERROR create inexact numbers that have to clear

      IF (opsys.eq.'UNX') then
         ieeer =  ieee_flags ( 'clear', 'exception', 'inexact', out)
         ieeer =  ieee_flags ( 'clear', 'exception', 'underflow', out)
         if (ieeer .ne. 0) then
             print *,' *** ieee_flag can not clear (wberror) ***'
             read(*,*)
         endif
      Endif

      tsw = 0.0
      do 204, L = 1, nlayr
          TSW = TSW + sw(L)*dlayr(L)
204   continue
      ERROR = LEFTWAT + PRECIP + Add - TSW - PINF - RUNOFF - ES -EP -
     +        POND - DRAIN
      IF (abs(ERROR).GT.1e-4) then
         WRITE(*,1246) ROUTNAME, ERROR, DOY, LEFTWAT, PRECIP, Add, TSW,
     1                 PINF, RUNOFF, ES, EP, POND, DRAIN
1246     FORMAT (/, 15X, 1H+, 51(1H-), 1H+ , /, 15X,
     1   '| ERROR IN WATER BALANCE (',(A8),')=',(F8.5),' DOY=',I3,'|' ,
     2   /,15X,  1H+, 51(1H-), 1H+ ,/,
     3   /, 2X, 'LEFTWAT = ', (F13.9),
     3   /, 2X, 'PRECIP  = ', (F13.9),
     3   /, 2X, 'ADD     = ', (F13.9),
     3   /, 2X, 'TSW     = ', (F13.9),
     3   /, 2X, 'PINF    = ', (F13.9),
     3   /, 2X, 'RUNOFF  = ', (F13.9),
     3   /, 2X, 'ES      = ', (F13.9),
     3   /, 2X, 'EP      = ', (F13.9),
     3   /, 2X, 'POND    = ', (F13.9),
     3   /, 2X, 'DDR+TDR = ', (F13.9))
         WRITE(380,1247) ROUTNAME, ERROR, DOY
1247     FORMAT ('ERROR IN WATER BALANCE (',(A8),')=',(F8.5),' DOY=',I3)
         write(*,*) ' Press <return> to continue ...'
         read (*,*)
      ENDIF
      RETURN
      END
```

APPENDIX C

APPENDIX C

SAMPLE INPUT AND OUTPUT FILES

SOIL PROPERTIES INPUT FILE (SPROFILE.MZ2)

```
 01 S71MI-19-1   Capac (Aeric Ochraqualfs; fine-loamy, mixed, mesic)
   .13  9.00    .15  78.00   9.9  27.5 1.0   .27E-02   58.0  6.68   .03 1.00 07.0
271.0 0005.8
    2.   .048   .183   .284   .183  1.000  1.50  1.90  2.3 14.0  7.9  7.0   .10   .00
4.0  0.40
    5.   .048   .183   .284   .183   .900  1.50  1.90  2.6 14.0  7.9  7.0   .10   .00
4.0  0.40
    8.   .058   .194   .286   .194   .750  1.52  1.90  3.2 17.0  7.9  7.0   .10   .00
4.0  0.15
   11.   .103   .234   .291   .234   .700  1.56  1.75  3.6 19.0  7.9  7.0   .10   .00
4.0  0.10
   14.   .148   .273   .297   .273   .300  1.64  1.55  2.4  2.0  7.9  7.0   .10   .00
4.0  0.10
   17.   .164   .279   .288   .279   .300  1.70  1.25  2.0  2.0  8.0  7.0   .10   .00
4.0  0.10
   20.   .182   .277   .295   .277   .050  1.88  0.95  1.9  2.0  8.0  7.0   .10   .00
4.0  0.10
   23.   .196   .278   .292   .278   .025  2.03  0.60  1.8  2.0  8.0  7.0   .10   .00
4.0  0.09
   25.   .209   .278   .292   .278   .025  2.05  0.20  1.7  1.0  8.0  7.0   .10   .00
4.0  0.083
   -1.
DLAYR    LL     DUL    SAT    SWINIT  WR    BD     OC   NH4  NO3  pH  KSMAC  SAND  ROK
KSMT RWUCON
```

WATER TABLE INPUT FILE (MSBF9201.MZW)

```
01 msbf9201
  140  76.9 true
  141  76.9 true
  142  76.9 true
  143  76.9 true
  144  76.9 true
  145  76.9 true
  146  76.9 true
  147  76.9 true
  148  76.9 true
  149  76.9 true
  150  76.9 true
  151  76.9 true
  152  76.9 true
```

```
  153  76.9 true
  154  76.9 false
  155  76.9 false
  156  76.9 false
   -1
```

PESTICIDE INPUT FILE (MSBF9201.MZP)

```
ATRAZINE                <-Species name
0.12                    <- Aging factor for residues, 0-1.0
006.2                   <- Denominator of dispersivity eq.
002.1 002.1 002.1 002.1 001.1 001.1 001.1 001.1 001.1 <- Kd
0248.0                  <- Molal volume (cm3/g-mol)
0033000.0               <-Solubility (ug/L)
060.0 060.0 060.0 060.0 060.0 060.0 120.0 120.0 120.0 <- t1/2 (d)
01 MSBF9201 153 01.135 <- Treatment, exp. code, d of application, amount (Kg/ha)
    2.  250.            <- Layer thickness (cm),init. soil concentration (ug/Kg)
    5.  195.
    8.  130.
   11.  130.
   14.   40.
   17.   50.
   20.   70.
   23.  105.
   25.  115.
   -1.
```

CUMULATIVE LEACHING OUTPUT FILE (OUTLCH.MZ)

```
RUN  1
 "DOY",  "TDRT","TNlcht-%","TPlcht-%.",
  178,     2.2,     1.4,     1.0,
  179,     2.9,     1.8,     1.3,
  180,     3.5,     2.1,     1.5,
  181,     4.1,     2.4,     1.8,
  182,     4.8,     2.7,     2.1,
  183,     5.4,     2.9,     2.3,
  184,     6.0,     3.1,     2.6,
  185,     6.7,     3.3,     2.8,
  186,     7.3,     3.5,     3.1,
  187,     7.9,     3.6,     3.3,
  188,     8.6,     3.8,     3.5,
  189,     9.2,     3.9,     3.8,
  190,     9.8,     4.0,     4.0,
  191,    10.4,     4.1,     4.2,
```

WATER BALANCE OUTPUT FILE (OUTWB.MZ)

```
ISWWT = 2
RUN  1
 "DOY","RAI","IRR","PNF","DDR","TDR","PON","RNF", "ES", "EP", "EO","ADD","WTL",
  140,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.4,  0.0,  0.6,  1.1,   10
  141,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.1,  0.0,  0.6,  0.8,   10
  142,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.1,  0.0,  0.5,  0.8,   10
  143,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.1,  0.0,  0.5,  0.8,   10
```

```
 144,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.1,  0.0,  0.2,  0.8,   10
 145,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.1,  0.0,  0.3,  0.8,   10
 146,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.1,  0.0,  0.3,  0.8,   10
 147,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.0,  0.0,  0.2,  0.8,   10
 148,  1.5,  0.0,  1.5,  0.2,  0.6,  0.0,  0.0,  0.4,  0.0,  0.4,  0.6,   10
 149,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.2,  0.0,  0.5,  0.7,   10
 150,  0.0,  0.0,  0.0,  0.2,  0.6,  0.0,  0.0,  0.1,  0.0,  0.6,  0.8,   10
```

PESTICIDE OUTPUT FILE (OUTP.MZ)

```
RUN  1
DOY = 140 TPlcht =   0.000000
      MASS, CT, CL IN EACH LAYER
      0.0057      28.1250       8.7660
      0.0129      25.8750       7.8070
      0.0173      21.6600       6.4053
      0.0278      25.2720       7.2012
      0.0169      12.0540       5.8037
      0.0225      13.2600       6.1703
      0.0254      12.6900       5.4113
      0.0520      22.8375       9.0699
      0.0636      25.5225      10.0482

DOY = 141 TPlcht =   0.000000
      MASS, CT, CL IN EACH LAYER
      0.0058      29.1331       9.1050
      0.0128      25.5755       7.7552
      0.0173      21.6130       6.3983
      0.0278      25.2591       7.1994
      0.0169      12.0542       5.8041
      0.0225      13.2595       6.1701
      0.0254      12.6926       5.4123
      0.0514      22.3559       8.8787
      0.0635      25.3818       9.9928
      0.0110       4.3863       1.7269
```

CONCENTRATIONS INPUT FILE (INCONC.MZ)

```
999          P1
132 5.9   9.4
133
134
135 4.3   7.5
136
137
138
```

CARBON-NITROGEN BALANCE OUTPUT FILE (OUTCNB.MZ)

```
Run  1
 Beginning Nitrogen and Carbon Balance
 Nitrate - N           151.18
```

```
Ammonium- N              48.26
Fertilizer N            152.00
Denitrification           0.00
Mineralized N             0.00
Leached N                 0.00
Soil Organic N        21998.36
Total  N              22349.80
Soil Organic C       218983.81
CO2 Evolved               0.00
Total C              218983.81
Final Nitrogen and Carbon Balance
Nitrate - N              18.12
Ammonium- N              17.34
Fertilizer N              0.00
Denitrification         201.06
Mineralized N            63.40
Leached N                15.48
Soil Organic N        21935.30
Total  N              22187.29
Soil Organic C       218337.28
CO2 Evolved             646.36
Total C              218983.64
```

CONCENTRATIONS OUTPUT FILE (OUTCONC.MZ)

```
RUN  1
 "DOY",  "NO3-N-ppm","Pest-ppb",
  140,        5.1,        6.0,
  141,        5.2,        6.0,
  142,        5.1,        5.9,
  143,        5.0,        5.9,
  144,        5.0,        5.8,
  145,        4.9,        5.8,
  146,        4.8,        5.7,
  147,        4.7,        5.7,
  148,        4.7,        5.7,
  149,        4.7,        5.6,
  150,        4.2,        5.6,
```

EXPERIMENT DIRECTORY FILE (MZEXP.DIR)

```
msbf9201 msu box farm subirrigation facility      msbf0505.w92 sprofile.mz2
msbf9201.mz4 msbf9201.mz5 msbf9201.mz6 msbf9201.mz7 msbf9201.mz8 genetics.mz9
msbf9201.mza msbf9201.mzb out1.mz out2.mz out3.mz out4.mz
msbf9201.mzw inconc.mz    msbf9201.mzp outwb.mz     outlch.mz    outconc.mz
outp.mz      outcnb.mz
```

LIST OF REFERENCES

LIST OF REFERENCES

Adriano, D. C., and H. E. Doner. 1982. Bromine, chlorine, and fluorine. p. 449–483. *In* A. L. Page, R. H. Miller, and D. R. Keeney (ed.) Methods of soil analysis, part 2. Chemical and microbiological properties. Agron. Monogr. 9. 2nd ed. ASA-SSSA, Madison, WI.

ASA, CSSA, and SSSA. 1988. Publications handbook and style manual. ASA, CSSA, and SSSA, Madison, WI.

Baker, R. S., and D. Hillel. 1991. Observations of fingering behavior during infiltration into layered soils. p. 87–99. *In* T. J. Gish and A. Shirmohammadi (ed.) Preferential flow. Proc. National Symposium, Chicago, IL. 16–17 Dec. 1991. ASAE, St. Joseph, MI.

Barriuso, E., U. Baer, and R. Calvet. 1992. Dissolved organic matter and adsorption-desorption of dimefuron, atrazine, and carbetamide by soils. J. Environ. Qual. 21:359–367.

Behki, R. M., and S. U. Khan. 1986. Degradation of atrazine by *Pseudomonas*: N-dealkylation and dehalogenation of atrazine and its metabolites. J. Agric. Food Chem. 34:746–749.

Belcher, H. W. 1988. Regional approach to subirrigation planning. p. 1–5. *In* F. D'Itri (ed.) The Saginaw Bay, Michigan subirrigation/drainage project: 1987–1988. Institute of Water Research, E. Lansing, MI.

Beven, K. 1991. Modeling preferential flow: An uncertain future? p. 1–11. *In* T. J. Gish and A. Shirmohammadi (ed.) Preferential flow. Proc. National Symposium, Chicago, IL. 16–17 Dec. 1991. ASAE, St. Joseph, MI.

Beven, K., and P. Germann. 1981. Water flow in soil macropores. II. A combined flow model. J. Soil Sci. 32:15–29.

Beven, K., and P. Germann. 1982. Macropores and water flow in soils. Water Resour. Res. 18:1311–1325.

Bhattacharyya, G. K., and R. A. Johnson. 1977. Statistical concepts and methods. Wiley, New York.

Biggar, J. W., and D. R. Nielsen. 1976. Spatial variability of the leaching characteristics of a field soil. Water Resour. Res. 12:78–84.

Binford, G. D., A. M. Blackmer, and N. M. El-Hout. 1990. Tissue test for excess nitrogen during corn production. Agron. J. 82:124–129.

Blumhorst, M. R., and J. B. Weber. 1992. Cyanazine dissipation as influenced by soil properties. J. Agric. Food. Chem. 40:894–897.

Boll, J., T. S. Steenhuis, and J. S. Selker. 1992. Fiberglass wicks for sampling of water and solutes in the vadose zone. Soil Sci. Soc. Am. J. 56:701–707.

Bollag, J. M., and S. Y. Liu. 1990. Biological transformation processes of pesticides. p. 169–211. *In* H. H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA book series: 2. SSSA, Madison, WI.

Boote, K. J., J. W. Jones, G. Hoogenboom, G. G. Wilkerson, and S. S. Jagtap. 1989. PNUTGRO V1.02: Peanut crop growth simulation model. User's guide. University of Florida, Gainsville, and International Benchmark Sites Network for Agrotechnology Transfer, Honolulu, HI.

Bouma, J. 1981. Soil morphology and preferential flow along macropores. Agric. Water Management 3:235–250.

Bromilow, R. H., and M. Leistra. 1980. Measured and simulated behaviour of aldicarb and its oxidation products in fallow soil. Pestic. Sci. 11:389–395.

Burrough, P. A. 1986. Principles of geographical information systems for land resources assessment. Oxford University Press, Oxford.

Burrough, P. A. 1989. Modelling land qualities in space and time: The role of Geographical Information Systems. p. 45–59. *In* J. Bouma and A. K. Bregt (ed.) Land qualities in space and time. Proc. Symposium ISSS, Wageningen, Netherlands. 22–26 Aug. 1988. PUDOC, Wageningen, the Netherlands.

Bushway, R. J., B. Perkins, S. A. Savage, S. J. Lekousi, and B. S. Ferguson. Determination of atrazine residues in water and soil by enzyme immunoassay. Bull. Environ. Contam. Toxicol. 40:647–654.

Calvet, R. 1980. Adsorption-desorption phenomena. p. 1–30. *In* R. J. Hance (ed.) Interactions between herbicides and the soil. Academic Press, London.

Campbell, G. S. 1991. Simulation of water uptake by plant roots. p. 273–285. *In* J. Hanks and J. T. Ritchie (ed.) Modeling plant and soil systems. ASA-CSSA-SSSA, Madison, WI.

Carsel, R. F., C. N. Smith, J. D. Dean, and P. P. Jowise. 1984. User's manual for the pesticide root zone model: Release 1. EPA-600/3-84-109. USEPA, Athens, GA.

Childs, E. C., N. Collis-George, and J. W. Holmes. 1957. Permeability measurements in the field as an assessment of anisotropy and structure development. J. Soil Sci. 8:27–41.

Chiou, C. T., T. D. Shoup, and P. E. Porter. 1985. Mechanistic roles of soil humus and minerals in the sorption of nonionic organic compounds from aqueous and organic solutions. Org. Geochem. 8:9–14.

Chou, T. -Y. 1990. Modeling infiltration using time-to-ponding and a storm generator approach. Ph.D. diss. Michigan State Univ., E. Lansing.

Corey, J. C. 1968. Evaluation of dyes for tracing water movement in acid soils. Soil Sci. 106:182–187.

Czapar, G. F., and R. S. Kanwar. 1991. Field measurement of preferential flow using subsurface drainage tiles. p. 122–128. *In* T. J. Gish, and A. Shirmohammadi (ed.) Preferential flow. Proc. National Symposium, Chicago, IL. 16-17 Dec. 1991. ASAE, St. Joseph, MI.

Davis, S. N., G. M. Thompson, H. W. Bentley, and G. Stiles. 1980. Ground-water tracers—a short review. Ground Water 18:14–23.

Devitt, D., J. Letey, L. J. Lund, and J. W. Blair. 1976. Nitrate-nitrogen movement through soil as affected by soil profile characteristics. J. Environ. Qual. 5:283–288.

Dunigan, E. P., and T. H. McIntosh. 1971. Atrazine-soil organic matter interactions. Weed Sci. 19:279–282.

Durand, G., and D. Barceló. 1992. Environmental degradation of atrazine, linuron and fenitrothion in soil samples. Toxicol. Environ. Chem. 36:225–234.

Eisen, M. M. Mathematical methods and models in the biological sciences. Linear and one-dimensional theory. Vol. 1. Prentice Hall, Englewood Cliffs, NJ.

Enfield, C. G., and S. R. Yates. 1990. Organic chemical transport to groundwater. p. 271–302. *In* H. H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA book series: 2. SSSA, Madison, WI.

Erickson, L. E., and K. H. Lee. 1989. Degradation of atrazine and related s-triazines. Critical Reviews in Environmental Control 19:1–14.

Ervin, J. L., and K. M. Kittleson. 1988. Assessment of rural groundwater contamination by agriculture chemicals in sensitive areas of Michigan. Rep. G1429-03. Institute of Water Research, East Lansing, MI.

Everts, C. J., and R. S. Kanwar. 1990. Estimating preferential flow to a subsurface drain with tracers. Trans. ASAE 33:451–457.

Everts, C. J., R. S. Kanwar, E. C. Alexander, Jr., and S. C. Alexander. 1989. Comparison of tracer mobilities under laboratory and field conditions. J. Environ. Qual. 18:491–498.

Feddes, R. A., P. J. Kowalik, and H. Zaradny. 1978. Simulation of field water use and crop yield. Centre for Agricultural Publishing Documentation, Wageningen, the Netherlands.

Germann, P., and K. Beven. 1981. Water flow in soil macropores. I. An experimental approach. J. Soil Sci. 32:1–13.

Germann, P., and K. Beven. 1981. Water flow in soil macropores. III. A statistical approach. J. Soil Sci. 32:31–39.

Ghodrati, M., and W. A. Jury. 1990. A field study using dyes to characterize preferential flow of water. Soil Sci. Soc. Am. J. 54:1558–1563.

Gilliam, J. W., R. W. Skaggs, and S. B. Weed. 1979. Drainage control to diminish nitrate loss from agricultural fields. J. Environ. Qual. 8:137–142.

Godwin, D. C., and C. A. Jones. 1991. Nitrogen dynamics in soil-plant systems. p. 287–321. *In* J. Hanks and J. T. Ritchie (ed.) Modeling plant and soil systems. ASA-CSSA-SSSA, Madison, WI.

Green, R. E., and J. C. Corey. 1971. Pesticide adsorption measurement by flow equilibration and subsequent displacement. Soil Sci. Soc. Am. Proc. 35:561–565.

Green, R. E., and S. W. Karickhoff. 1990. Sorption estimates for modeling. p. 79–101. *In* H. H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA book series: 2. SSSA, Madison, WI.

Grover, R., and R. J. Hance. 1970. Effect of ratio of soil to water on adsorption of linuron and atrazine. Soil Sci. 109:136–138.

Hach Company. 1992. Combination nitrate electrode model 44430. Hach Company, Loveland, CO.

Haith, D. A. 1980. A mathematical model for estimating pesticide losses in runoff. J. Environ. Qual. 9:428–433.

Haith, D. A. 1986. Simulated regional variations in pesticide runoff. Soil Sci. Soc. Am. J. 15:5–8.

Hartley, G. S., and I. J. Graham-Bryce. 1980. Physical principles of pesticide behaviour. Vol. 1. Academic Press, London.

Hartmann, H. T., A. M. Kofranek, V. E. Rubatzky, and W. J. Flocker. 1988. Plant science. Prentice Hall, Englewood Cliffs, NJ.

Hassall, K. 1982. The chemistry of pesticides. Verlag Chemie, Weinheim, Basel.

Hill, D. E., and J.-Y. Parlange. 1972. Wetting front instability in layered soils. Soil Sci. Soc. Am. J. 36:697–702.

Hillel, D. 1982. Introduction to soil physics. Academic Press, San Diego, CA.

Hoogenboom, G., J. W. White, J. W. Jones, and K. J. Boote. 1991. BEANGRO V1.01: Bean crop growth simulation model. User's guide. University of Florida, Gainsville, The University of Georgia, Griffin, International Benchmark Sites Network for Agrotechnology Transfer, Honolulu, HI, and CIAT, Cali, Colombia.

Hornberger, G. M., K. J. Beven, and P. F. Germann. 1990. Inferences about solute transport in macroporous forest soils from time series models. Geoderma 46:249–262.

Huang, P. M., R. Grover, and R. B. McKercher. 1984. Components and particle size fractions involved in atrazine adsorption by soils. Soil Sci. 138:20–24.

IBSNAT. 1986. Decision Support System for Agrotechnology Transfer (DSSAT). Documentation for IBSNAT crop model input and output files, version 1.0. IBSNAT technical report 5. IBSNAT, Honolulu, HI.

Iowa State University of Science and Technology. 1989. How a corn plant develops. Spec. Rep. 48. Iowa State University of Science and Technology Cooperative Extension Service, Ames, IA.

Jardine, P. M., G. V. Wilson, and R. J. Luxmoore. 1990. Unsaturated solute transport through a forest soil during rain storm events. Geoderma 46:103–118.

Jones, C. A., and J. R. Kiniry. 1986. *In* C. A. Jones, and J. R. Kiniry (ed.) CERES-Maize: A simulation model of maize growth and development. Texas A&M Press, College Station, TX.

Jones, C. A., W. L. Bland, J. T. Ritchie, and J. R. Williams. 1991. Simulation of root growth. p. 91–123. *In* J. Hanks and J. T. Ritchie (ed.) Modeling plant and soil systems. ASA-CSSA-SSSA, Madison, WI.

Jones, J. W., K. J. Boote, S. S. Jagtap, and J. W. Mishoe. 1991. Soybean development. p. 71–90. *In* J. Hanks and J. T. Ritchie (ed.) Modeling plant and soil systems. ASA-CSSA-SSSA, Madison, WI.

Kalita, P. K., and R. S. Kanwar. 1990. Pesticide mobility as affected by water table management practices. Int. Summer Meeting ASAE, Columbus, OH. 24-27 June 1990. ASAE paper 90-2089. ASAE, St. Joseph, MI.

Kaspar, T. C., J. B. Zahler, and D. R. Timmons. 1989. Soybean response to phosphorus and potassium fertilizers as affected by soil drying. Soil Sci. Soc. Am. J. 53:1448–1454.

Kaufman, D. D., and P. C. Kearney. 1970. Microbial degradation of *s*-triazine herbicides. p. 235-265. *In* F. A. Gunther and J. D. Gunther (ed.) Residue reviews. Vol. 32. Springer-Verlag, New York.

Keeney, D. R., and D. W. Nelson. 1982. Nitrogen-inorganic forms. p. 643–698. *In* A. L. Page, R. H. Miller, and D. R. Keeney (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. Agron. Monogr. 9. 2nd ed. ASA-SSSA, Madison, WI.

Kenig, A., J. W. Mishoe, K. J. Boote, P. W. Cook, D. C. Reicosky, W. T. Pettigrew, and H. F. Hodges. 1993. Development of soybean fresh and dry weight relationships for real time model calibration. Agron. J. 85:140–146.

Kennedy, P. 1989. A guide to econometrics. 2nd ed. MIT Press, Cambridge, MA.

Kissel, D. E., J. T. Ritchie, and E. Burnett. 1973. Chloride movement in undisturbed swelling clay soil. Soil Sci. Soc. Am. Proc. 37:21–24.

Klint, M., E. Arvin, and B. K. Jensen. 1993. Degradation of the pesticides mecoprop and atrazine in unpolluted sandy aquifers. J. Environ. Qual. 22:262–266.

Kluitenberg, G. J., and R. Horton. 1990. Effect of solute application method on preferential transport of solutes in soil. Geoderma 46:283–297.

Knisel, W. G. (ed.). 1980. CREAMS: A field-scale model for chemicals, runoff, and erosion from agricultural management systems. USDA-SEA Conserv. Res. Rep. 26. U.S. Gov. Print. Office, Washington, D.C.

Knisel, W. G., R. A. Leonard, and D. A. Still. 1986. GLEAMS user manual, version 1.8.52. Agric. Res. Service, SE Watershed Research Center, Tifton, GA.

Koskinen, W. C., and S. S. Harper. 1990. The retention process: Mechanisms. p. 51–78. *In* H. H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA book series: 2. SSSA, Madison, WI.

Kuester, J. L., and J. H. Mize. 1973. Optimization techniques with Fortran. McGraw-Hill, New York.

Kung, K-J. S. 1990a. Preferential flow in a sandy vadose zone: 1. Field observation. Geoderma 46:51–58.

Kung, K-J. S. 1990b. Preferential flow in a sandy vadose zone: 2. Mechanism and implications. Geoderma 46:59–71.

Larson, W. E., and P. C. Robert. 1991. Farming by soil. p. 103–112. *In* R. Lal and F. J. Pierce (ed.) Soil management for sustainability. Soil and Water Cons. Soc. Am., Ankeny, IA.

Lavy, T. L., F. W. Roeth, and C. R. Fenster. 1973. Degradation of 2, 4-D and atrazine at three soil depths in the field. J. Environ. Qual. 2:132–137.

Lavy, T. L., J. D. Mattice, J. H. Massey, B. W. Skulman, and S. A. Senseman. 1993. Dissipation of herbicides in surface and subsurface soils. p. 38. *In* Agronomy abstracts. ASA, Madison, WI.

LeCureux, J. P. 1991. Profitability of a crop rotation on a subirrigation/drainage system: 1990. p. 219–256. *In* F. D'Itri (ed.) The Saginaw Bay, Michigan subirrigation/drainage project: 1989-1990. Institute of Water Research, E. Lansing, MI.

LeCureux, J., and J. Booms. 1988a. Subirrigation/drainage water monitoring for nutrients and pesticides. p. 241–259. *In* F. D'Itri (ed.) The Saginaw Bay, Michigan subirrigation/drainage project: 1987-1988. Institute of Water Research, E. Lansing, MI.

LeCureux, J., and K. Booms. 1988b. Corn production management for subirrigation. p. 203–220. *In* F. D'Itri (ed.) The Saginaw Bay, Michigan subirrigation/drainage project: 1987-1988. Institute of Water Research, E. Lansing, MI.

LeCureux, J., and K. Booms. 1988c. Subirrigation management for sugar beet production. p. 221–240. *In* F. D'Itri (ed.) The Saginaw Bay, Michigan subirrigation/drainage project: 1987-1988. Institute of Water Research, E. Lansing, MI.

Leick, A. 1990. GPS satellite surveying. Wiley, New York.

Leistra, M., and J. H. Smelt. 1981. Movement and conversion of ethoprophos in soil in winter: 2. Computer simulation. Soil Sci. 13:296–302.

Leistra, M., R. H. Bromilow, and J. J. T. I. Boesten. 1980. Measured and simulated behaviour of oxamyl in fallow soils. Pestic. Sci. 11:379–388.

Leonard, R. A. 1990. Movement of pesticides into surface waters. p. 303–349. *In* H. H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA book series: 2. SSSA, Madison, WI.

Lizaso, J. I. 1993. Flooding and field grown maize: Above- and below-ground responses and a simulation model. Ph.D. diss. Michigan State Univ., E. Lansing.

Lupi, C., A. R. Bucchi, A. Piccioni, and G. A. Zapponi. 1988. The environmental behavior of chemicals in soil: Atrazine as an example. Ecotoxicol. Environ. Safety 16:133–142.

Maas, S. J. 1993. Within-season calibration of modeled wheat growth using remote sensing and field sampling. Agron. J. 85:669–672.

Manetsch, T. J., and G. L. Park. 1990. System analysis and simulation with applications to economic and social systems. Part I—methodology, modeling and linear system fundamentals. 7th ed. Michigan State Univ., E. Lansing.

Marble, D. F., and D. J. Peuquet. 1983. Geographic Information Systems and Remote Sensing. p. 923–958. *In* R. N. Colwell (ed.) Manual of Remote Sensing. Vol. 1. 2nd ed. Am. Soc. Photogrammetry, Falls Church, VA.

Marshall, T. J., and J. W. Holmes. 1988. Soil physics. 2nd ed. Cambridge University Press, Cambridge.

Mc Lean, E. O. 1982. Soil pH and lime requirement. p. 199–224. *In* A. L. Page, R. H. Miller, and D. R. Keeney (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. Agron. Monogr. 9. 2nd ed. ASA-SSSA, Madison, WI.

McCall, P. J., D. A. Laskowski, R. L. Swann, and H. J. Dishburger. 1981. Measurement of sorption coefficients of organic chemicals and their use in environmental fate analysis. p. 89–109. *In* Test protocols for environmental fate and movement of toxicants. Proc. Symp. AOAC 94th Annu. Meet., Washington, DC. 21-29 Oct. 1980. Assoc. Off. Anal. Chem., Arlington, VA.

McGlamery, M., and F. W. Slife. 1966. The adsorption and desorption of atrazine as affected by pH, temperature and concentration. Weeds 14:237–239.

McLaughlin, M. J. 1982. A review of the use of dyes as soil water tracers. Water SA 8:196–201.

Melancon, S. M., J. E. Pollard, and S. C. Hern. 1986. Evaluation of SESOIL, PRZM, and PESTAN in a laboratory column leaching experiment. Environ. Toxicol. Chem. 5:865–878.

Michigan Department of Agriculture. 1992. Michigan agricultural statistics. Michigan Department of Agriculture, Lansing.

Mingelgrin, U., and Z. Gerstl. 1983. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. J. Environ. Qual. 12:1–11.

Mortimer, C. E. 1986. Chemistry. 6th ed. Wadsworth, Belmont, CA.

Mortland, M. M. 1970. Clay-organic complexes and interactions. Adv. Agron. 22:75–117.

Mulla, D. J. 1991. Using geostatistics and GIS to manage spatial patterns in soil fertility. p. 336–345. *In* Proc. Symp. Autom. Agric. for the 21st Century. Int. Winter Meeting ASAE, Chicago, IL. Dec. 15-17, 1991. ASAE, Chicago, IL.

Myers, V. I., M. E. Bauer, H. W. Gausman, W. G. Hart, J. L. Heilman, R. B. MacDonald, A. B. Park, R. A. Ryerson, T. J. Schmugge, and F. C. Westin. 1983. Remote sensing applications in agriculture. p. 2111–2228. *In* R. N. Colwell (ed.) Manual of Remote Sensing. Vol.2. 2nd ed. Am. Soc. Photogrammetry, Falls Church, VA.

Nations, B. K., and G. R. Hallberg. 1992. Pesticides in Iowa precipitation. J. Environ. Qual. 21:486–492.

Nicholls, P. H., A. Walker, and R. J. Baker. 1982. Measurement and simulation of the movement and degradation of atrazine and metribuzine in a fallow soil. Pestic. Sci. 12:484–494.

Nielsen, D. R. 1992. Global agronomic opportunities. Presidential address. Agron. J. 84:131–132.

Omoti, U., and A. Wild. 1979a. Use of fluorescent dyes to mark the pathways of solute movement through soils under leaching conditions: 1. Laboratory experiments. Soil Sci. 128:28–33.

Omoti, U., and A. Wild. 1979b. Use of fluorescent dyes to mark the pathways of solute movement through soils under leaching conditions: 2. Field experiments. Soil Sci. 128:98–104.

Orion. 1991. Model 94-35 and 94-53 halide electrodes instruction manual. Orion Research Inc., Laboratory Products Group, Boston, MA.

Perkin-Elmer. 1982. LS-5 luminescence spectrometer operator's manual. Rev. 2. Perkin-Elmer, Beaconsfield, England.

Piekielek, W. P., and R. H. Fox. 1992. Use of a chlorophyll meter to predict sidedress nitrogen requirements for maize. Agron. J. 84:59–65.

Pignatello, J. J. 1989. Sorption dynamics of organic compounds in soils and sediments. p. 45–80. *In* B. L. Sawhney, and K. Brown (ed.) Reactions and movement of organic chemicals in soils. SSSA Spec. Publ. 22. SSSA and ASA, Madison, WI.

Protasiewicz, L. J. 1990. Water table management impacts on water quality. M. Sc. thesis. Michigan State Univ., E. Lansing.

Protasiewicz, L., H. Belcher, and G. E. Merva. 1988. Water table management water quality study. Final report to the Michigan Dept. of Natural Resources. Dept. of Agric. Eng., Michigan State Univ., E. Lansing.

Rao, P. S. C., and J. M. Davidson. 1980. Estimation of pesticide retention and transformation parameters required in nonpoint source pollution models. p. 23–67. *In* M. R. Overcash and J. M. Davidson (ed.) Environmental impact of nonpoint source pollution. Ann Arbor Science, Ann Arbor, MI.

Renner, K. A., and J. J. Kells. 1994. 1994 weed control guide for field crops. Michigan extension bulletin E-434.

Ritchie, J. T. 1986. The CERES-Maize model. p. 3-6. *In* C. A. Jones and J. R. Kiniry (ed.) CERES-Maize: A simulation model of maize growth and development. Texas A&M Press, College Station, TX.

Ritchie, J. T., and B. S. Johnson. 1990. Soil and plant factors affecting evaporation. p. 363–390. *In* B. A. Stewart and D. R. Nielsen (ed.) Irrigation of agricultural crops. Agron. Monogr. 30. ASA-CSSA-SSSA, Madison, WI.

Ritchie, J. T., and J. I. Lizaso. 1991. Assessment of the influence of the water table management on corn performance and the loss of agricultural chemicals. Rep. for the Subirrigation Annual Meeting. Dept. of Crop and Soils Sci., Michigan State Univ., E. Lansing.

Ritchie, J. T., D. E. Kissel, and E. Burnett. 1972. Water movement in undisturbed swelling clay soil. Soil Sci. Soc. Am. Proc. 36:874–879.

Ritchie, J. T., E. C. Alocilja, U. Singh, and G. Uehara. 1986. IBSNAT and the CERES-Rice model. Proc. Workshop on Impact of Weather Parameters on Growth and Yield of Rice. International Rice Research Institute, Manila, Philippines.

Ritchie, J. T., U. Singh, D. Godwin, and L. Hunt. 1989. A user's guide to CERES-Maize--v.2.10. International Fertilizer Development Center, Muscle Shoals, AL.

Ritchie, T. J., and M. Amato. 1990. Field evaluation of plant extractable soil water for irrigation scheduling. Acta Horticulturae 278:595–615.

Robinson, V. B., A. U. Frank, and H. A. Karimi. 1987. Expert systems for geographic information systems in natural resource management. AI Applications in Natural Resource Management 1:47–57.

Ross, P. J. 1990. SWIM—a simulation model for soil water infiltration and movement. Reference manual. CSIRO Division of Soils, Townsville, Australia.

Rubio, F. M., J. A. Itak, A. M. Scutellaro, M. Y. Selisker, and D. P. Herzog. 1991. Performance characteristics of a novel magnetic-particle-based enzyme-linked immunosorbent assay for the quantitative analysis of atrazine and related triazines in water samples. Food & Agric. Immunology 3:113–125.

Satterfield, C. N. 1970. Mass transfer in heterogeneous catalysis. MIT Press, Cambridge, MA.

Scheunert, I. 1992. Physical and physico-chemical processes governing the residue behavior of pesticides in terrestrial ecosystems. p. 2–22. *In* W. Ebing (ed.) Chemistry of plant protection. 8. Terrestrial behavior of pesticides. Springer-Verlag, Berlin.

Schrap, S. M., and A. Opperhuizen. 1992. On the contradictions between experimental sorption data and the sorption partitioning model. Chemosphere 24:1259–1282.

Sichani, S. A., B. A. Engel, E. J. Monke, J. D. Eigel, and E. J. Kladivko. Validating GLEAMS with pesticide field data on a Clermont silt loam soil. Trans. ASAE 34:1732–1737.

Skidmore, E. L., and J. R. Williams. 1991. Modified EPIC wind erosion model. p. 457–469. *In* J. Hanks and J. T. Ritchie (ed.) Modeling plant and soil systems. ASA-CSSA-SSSA, Madison, WI.

Smart, P. L., and I. M. S. Laidlaw. 1977. An evaluation of some fluorescent dyes for water tracing. Water Resour. Res. 13:15–33.

Smettem, K. R. J., and S. T. Trudgill. 1983. An evaluation of some fluorescent and non-fluorescent dyes in the identification of water transmission routes in soils. J. Soil Sci. 34:45–56.

Smettem, K. R. J., S. T. Trudgill and A. M. Pickles. 1983. Nitrate loss in soil drainage waters in relation to by-passing flow and discharge on an arable site. J. Soil Sci. 34:499–509.

Soil Conservation Service. 1979. Soil survey of Ingham county, Michigan. USDA-SCS.

Soil Conservation Service. 1980. Soil survey laboratory data and descriptions for some soils of Michigan. Soil survey investigations Rep. 36. USDA-SCS.

Stearman, G. K. 1992. Atrazine degradation and sorption-desorption using enzyme immunoassay analysis. p. 60. *In* Agronomy abstracts. ASA, Madison, WI.

Stumm, W. 1987. Aquatic surface chemistry: Chemical processes at the particle-water interface. Wiley, New York.

Swanson, R. A., and G. R. Dutt. 1973. Chemistry and physical processes that affect atrazine movement and distribution in soil systems. Soil Sci. Soc. Am. Proc. 37:872–876.

Taylor, A. W., and W. F. Spencer. 1990. Volatilization and vapor transport processes. p. 213–269. *In* H. H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA book series: 2. SSSA, Madison, WI.

Thurman, E. M., M. Meyer, M. Pomes, C. A. Perry, and A. P. Schwab. 1990. Enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water. Anal. Chem. 62:2043-2048.

Troiano, J., C. Garretson, C. Krauter, J. Brownell, and J. Hutson. 1993. Influence of the amount and method of irrigation water application on leaching of atrazine. J. Environ. Qual. 22:290–298.

Trojan, M. D., and D. R. Linden. 1992. Microrelief and rainfall effects on water and solute movement in earthworm burrows. Soil Sci. Soc. Am. J. 56:727–733.

Trought, M. C., and M. C. Drew. 1980. The development of waterlogging damage in wheat seedlings (*Triticum aestivum* L.). II. Accumulation and redistribution of nutrients by the shoot. Plant Soil 56:187-199.

Trudgill, S. T. 1987. Soil water dye tracing, with special reference to the use of Rhodamine WT, Lissamine FF, and Amino G Acid. Hydrol. Process. 1:149–170.

U.S. Congress, Office of Technology Assessment. 1984. Protecting the nation's groundwater from contamination. Vol 2. OTA-O-276. U.S. Gov. Print. Office, Washington, DC.

Van Emon, J. M., J. N. Seiber, and B. D. Hammock. 1989. Immunoassay techniques for pesticide analysis. p. 217–263. *In* J. Sherma (ed.) Analytical methods for pesticides and plant growth regulators. Vol. 17. Advanced analytical techniques. Academic Press, San Diego, CA.

van Keulen, H., and N. G. Seligman. 1987. Simulation of water use, nitrogen nutrition and growth of a spring wheat crop. Pudoc, Wageningen, the Netherlands.

Wagenet, R. J., and J. L. Hutson. 1986. Predicting the fate of nonvolatile pesticides in the unsaturated zone. J. Environ. Qual. 15:315–322.

Wagenet, R. J., and J. L. Hutson. 1990. Quantifying pesticide behavior in soil. Annu. Rev. Phytopathol. 28:295–319.

Wagenet, R. J., and P. S. C. Rao. 1990. Modeling pesticide fate in soils. p. 351–399. *In* H. H. Cheng (ed.) Pesticides in the soil environment: Processes, impacts, and modeling. SSSA book series: 2. SSSA, Madison, WI.

Warner, G. S., and R. A. Young. 1991. Measurement of preferential flow beneath mature corn. p. 150–159. *In* T. J. Gish and A. Shirmohammadi (ed.) Preferential flow. Proc. National Symposium, Chicago, IL. 16-17 Dec. 1991. ASAE, St. Joseph, MI.

Wauchope, R. D., and R. S. Myers. 1985. Adsorption-desorption kinetics of atrazine and linuron in freshwater-sediment aqueous slurries. J. Environ. Qual. 14:132–136.

Weed Science Society of America. 1983. Herbicide handbook. Weed Sci. Soc. Am., Champaign, IL.

White, R. E. 1985. The influence of macropores on the transport of dissolved and suspended matter through soil. p. 95-120. *In* B. A. Stewart (ed.) Advances in soil science. Springer-Verlag, New York.

Wienhold, B. J., and T. J. Gish. 1993. Effect of formulation and tillage practice on volatilization of atrazine and alachlor. p. 53. *In* Agronomy abstracts. ASA, Madison, WI.

Williams, J. R. 1991. Runoff and water erosion. p. 439–455. *In* J. Hanks and J. T. Ritchie (ed.) Modeling plant and soil systems. ASA-CSSA-SSSA, Madison, WI.

Wu, S., and P.M. Gschwend. 1986. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. Environ. Sci. Technol. 20:717-725.