



**Agricultural
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**United States
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National Sedimentation Laboratory

Oxford, Mississippi 38655

GROUND WATER RESEARCH

RESEARCH PROGRESS REPORT - 1989/1990

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Gentlemen:

Enclosed are 3 program reports on investigation of ground water quality. Specifically, this research is directed to determining the best conservation tillage practices for minimizing the potential contamination of ground and surface water with plant nutrients and pesticides.

Several years will be required to complete research for publication in a scientific journal. Hopefully, this preliminary information will be helpful. Please call me or the authors for further information.

Sincerely,

CALVIN K. MUTCHLER
Laboratory Director

Enclosures

cc:

P. A. Putnam
D. A. Farrell
W. D. Kemper
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FORWARD

This research progress report is the compiling of three separate manuscripts for the purpose of technology transfer in water quality research. This enclosed reports give results of ground and surface water quality research conducted during 1989/1990 by the USDA - Agricultural Research Service - National Sedimentation Laboratory - Water Quality/Ecology Research Unit. The first two reports "Plant Nutrients in Shallow Ground Water and Surface Runoff of a North Mississippi Soybean Watershed" and "Herbicide Concentrations in Shallow Ground Water and Surface Runoff for Land Cropped to No-till Soybeans" represent research conducted at the Ed Nelson Research Farm located in Tate County near Como, Mississippi. The third report "Instrumentation to Quantify and Sample Surface Runoff and Shallow Ground Water" illustrates the establishment of small plots for ground and surface water quality research at the North Mississippi Branch Experiment Station at Holly Springs, Mississippi. These research plots were established in the summer of 1990 with 1991 to be the first cropping year.

These research projects are designed to last several years so that a range in environmental conditions will make the results more reliable. Also, the data will require more analysis before formal publication.

The scientists wish to acknowledge the technical assistance and quality service of Kenneth Dalton, Steve Smith, Blake Sheffield, and James Hill.

We also appreciate the assistance of our cooperators in these projects - the Soil Conservation Service and the Mississippi Agricultural and Forestry Experiment Station. We hope these reports are helpful.

EXECUTIVE SUMMARY

The USDA Research Plan for Water Quality has as its general goal the protection and enhancement of quality of the Nation's surface and ground waters while sustaining agricultural activities. Emphasis is on effects of conservation tillage practices on surface and ground water quality, with the objective to develop economically and environmentally sound crop production systems. Specific objectives of the research reported here are to (1) determine the effect of conventional, conservation, and no-tillage soybeans on potential ground and surface water contamination by pesticides and fertilizers applied to small watersheds and (2) evaluate in conservation tillage systems the effects of different application methodologies including timing, placement, and formulation on the mobility and transport of pesticides and nutrients to surface and ground water.

As a part of the Interagency Demonstration Erosion Control Project (DEC) in the Yazoo Basin, northern Mississippi, the USDA National Sedimentation Laboratory initiated a study of cost-effective practices for control of upland erosion on the Ed Nelson Farm located in Tate County, Mississippi. Assessment of erosional characteristics includes land areas ranging from specialty plots and rainfall simulator tests to standard sized runoff/erosion plot studies to field-sized (watershed) evaluations of runoff and soil loss. During 1989 this research was expanded to include water quality studies of shallow ground water and surface runoff. Perched ground water (0.15 to 1.52 m) and surface runoff from a 2.14-ha watershed planted to no-till soybeans were sampled during the 1990 water year (WY) and analyzed for plant nutrients and pesticides. Surface runoff was measured with a Parshall flume and sampled with an ISCO composite sampler. Ground water samples were collected using observation wells (sampling piezometers) and soil water suction tubes. Total precipitation for the 1990 WY was 1276 mm compared with a total runoff of 330 mm, most of which occurred during the winter and spring months. Subsequent paragraphs summarize nutrient and pesticide content of ground water and surface runoff.

The annual mean ortho-phosphorus ($\text{PO}_4\text{-P}$), ammonium-nitrogen ($\text{NH}_4\text{-N}$), and nitrate-nitrogen ($\text{NO}_3\text{-N}$) concentrations for all ground water sites were 0.05, 0.08, and 11.56 mg/L, respectively. Ground water $\text{NO}_3\text{-N}$ concentrations for some storms exceeded the U. S. Drinking Water Standard by as much as a factor of 2.7, and are of interest since no N fertilizers were applied after 1987. Soybean residues were suspected as the source of $\text{NO}_3\text{-N}$. In general, $\text{NO}_3\text{-N}$ concentrations during the winter at depths < 0.46 m were greater than those deeper in the soil profile. However, these higher $\text{NO}_3\text{-N}$ concentrations decreased during the spring due to continued leaching of the soil profile and nutrient uptake by a prolific growth of native vegetation. In runoff, the annual mean $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ concentrations were 0.56, 0.15, and 0.28 mg/L, respectively. However, only 8-days after a broadcast application of 0-20-20, soluble $\text{PO}_4\text{-P}$ concentrations exceeded 4 mg/L. Compared with ground water, concentrations of soluble $\text{NO}_3\text{-N}$ in the runoff were considerably lower, and no $\text{NO}_3\text{-N}$ was detected during March, April, and May. Soluble $\text{PO}_4\text{-P}$ and N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) losses were estimated to be 1.21 and 1.60 kg/ha, respectively, and most likely

represented almost all of the total nutrient losses since sediment concentrations were low.

Metribuzin (0.42 kg/ha) and metolachlor (2.24 kg/ha) were applied in early May 1990 for preemerge weed control to a 2.14-ha no-till soybean watershed on the Nelson Farm in Tate County, Mississippi. In mid June 1990, this watershed was treated with acifluorfen (0.28 kg/ha) and bentazon (0.56 kg/ha) for postemerge weed control and with chlorpyrifos (0.56 kg/ha) for soil insect control. Mean concentrations of metribuzin and metolachlor in ground water 6 days after application were 23 and 67 $\mu\text{g/L}$, respectively; and were 1 and 3 $\mu\text{g/L}$ 27 days after application (last ground water-producing rainfall). No measurable ground water resulted from rainfall events that occurred after acifluorfen, bentazon, and chlorpyrifos application. Concentrations of metribuzin and metolachlor in the water phase of runoff 6 days after application were 110 and 535 $\mu\text{g/L}$ (ppb), respectively. By 85 days after application (last runoff event), these values had decreased to 0.3 and 1.2 $\mu\text{g/L}$. No metribuzin and metolachlor residues were found in the sediment phase of runoff. No residues of acifluorfen, bentazon, and chlorpyrifos were detected in runoff from the single event which occurred 48 days after their application. Total seasonal losses of metribuzin and metolachlor in runoff were 0.017 and 0.085 kg/ha, respectively, or about 4% each of that applied.

This 1-yr of study suggests that no-till soybeans are nondetrimental to surface water quality. Additional research is needed to define the movement of shallow ground water that may contain high $\text{NO}_3\text{-N}$ concentrations. The rapidly decreasing pesticides concentrations observed to date in this ongoing study do not appear to present water quality problems. In a related study, an adjacent soybean conventional-till watershed was instrumented for ground and surface water quality research in the fall of 1990, and sample collection has begun.

In an unrelated study, standard-size erosion plots were established to study the quality of surface and ground water with corn grown by conventional, minimum, and no-tillage methods. The plots were constructed during the summer of 1990 with 1991 to be the first cropping year. For conducting such water quality research on the smaller standard-sized erosion plots a field acquisition system was developed to sample and quantify surface runoff and shallow ground water. Included in the system to evaluate runoff were collectors, approaches, H-flumes equipped with liquid-level recorders, water separators, dataloggers, and composite water samplers. Pump samplers are activated by dataloggers. The components for ground water include hydrologically-isolated plots with subsurface drains (installed via horizontal drilling) into sumps.

PLANT NUTRIENTS IN SHALLOW GROUND WATER AND SURFACE RUNOFF OF A NORTH MISSISSIPPI SOYBEAN WATERSHED¹

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INTRODUCTION

Maintaining and/or improving crop production efficiency without adversely affecting environmental quality is a major challenge for U. S. Agriculture. Pesticide and nitrate-N contamination of ground water is a national problem that needs timely and rational solutions. Research worldwide has shown that the most extensive source of pesticides and nutrients delivered to ground and surface waters is agriculture. There is a great public concern about ground water quality since it is the source of drinking water for half of the U. S. In rural communities nearly 95% of the population depend upon wells for drinking water. The emphasis during the 1960's and 1970's was on point source pollution and surface water; at this time, there is a great public concern about ground water quality which will probably be a primary water quality issue of the 1990's.

In Mississippi, ground water constitutes 54% of all freshwater and is the water supply for 93% of the population (10). Ground water contamination is not yet considered to be a major problem. However the State's ground water is very susceptible to contamination because of the permeable soils, shallow depth to ground water, and high average annual rainfall (10). Water quality information for most of the State is limited to a very few organic and inorganic compounds and is considered inadequate for the principal aquifers. Data are lacking on any potential agrichemical contamination of ground water underlying agricultural areas of the State, particularly the Delta along the Mississippi River and the uplands to the north. Evaluation of farm management (tillage practices, pesticide and fertilizer application technology) on surface and subsurface agrichemical transport and on water quality is essential to conserving and protecting the State's and the Nation's soil and water resources.

The three basic nutrients applied to crops are nitrogen, phosphate, and potassium. The only fertilizer nutrient believed to create significant ground water contamination problems is N fertilizer as K and P are not highly soluble and are easily adsorbed to soil particles which prevents leaching. Nitrogen fertilizer accounts for half of the U. S. fertilizer usage. Fertilizer use in the U. S. has grown rapidly, increasing by 300% between 1960 and 1980, with the use of nitrogen increasing most rapidly at over

¹Names of commercial products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the U. S. Department of Agriculture.

400%. Across the U. S. average fertilizer N rates to corn increased from 65 lbs. per acre in 1967 to 135 lbs. per acre in 1982 (2). In the past, crops removed more N than was applied as commercial fertilizer; however, because of increased N fertilization rates in recent times, this trend has reversed. Now only about 60% or less of the N fertilizer applied is used by the crop in the year of application (5). The remainder is lost through leaching, washoff, volatilization, or stays in the soil profile. The highly soluble nitrate form of nitrogen is easily transported through the soil by percolating water to ground water. The best known health problem caused by nitrates is methemoglobinemia, or blue baby disease. The current U. S. Drinking Water Standard for nitrates is based on protecting against this disease, and that standard is 10 mg nitrate-N per liter. Other health effects that may be associated with nitrates, but not well documented, include impairments of the nervous system, cancer (conversion of nitrates to nitrosamines), and birth defects. The type of land tillage, as well as fertilizer N usage, may also influence the movement of agrichemicals through the soil profile.

By the year 2,000, it has been estimated that 60 - 70% of all U. S. cropland will employ some type of conservation tillage. For much farm land, conservation tillage may be the only way to reduce soil erosion to acceptable limits by 1990 as provided by the Food Security Act of 1985. Conservation tillage has proven to minimize nonpoint contamination of surface water by reductions in runoff and erosion, but it also increases infiltration, and hence the potential for increased leaching of pesticides and fertilizers. The objective of this research is to determine the effect of no-tillage soybeans on plant nutrient concentrations in shallow (perched) ground water and surface runoff during the 1990 water year.

MATERIALS AND METHODS

Research directed toward the development of cost-effective methods of row crop production in DEC (Demonstration Erosion Control) watersheds was initiated during the fall of 1987 on the Nelson farm in Tate County, Mississippi. Included in the study area are three small watersheds about 2.09 to 3.17 ha in size. Soils belong to the Loring-Grenada series and are loessial. There is a genetic fragipan 0.3 to 1.0 m below the soil surface depending upon location within the watershed.

This study concerns watershed number one (Fig. 1) which is 2.14 ha in size. During the 1988/90 cropping years the watershed was in minimum-till soybeans; for the 1990 cropping year it was planted to no-till soybeans. In the fall of 1987 the three watersheds received a one time N fertilizer application of 44.8 kg-ha^{-1} as $\text{NH}_4\text{-NO}_3$ and were planted to winter wheat. No N fertilizers have been applied since that time. For the 1988-90 cropping years 0-20-20 fertilizer was broadcast applied each spring before planting at a rate of 224 kg-ha^{-1} .

Runoff from the watershed was measured with a 0.61 m Parshall flume equipped with a FW-1 recorder. Potentiometer output from the FW-1 was converted to discharge and the resultant discharge logged in an Omnidata Easy Logger (Version 3.0) every N

minutes. The Omnidata Easy Logger was also used to activate an ISCO composite sampler. Sampling times were specified increments of runoff, resulting in one discharge-weighted sample per storm event. Samples were collected in a stainless steel container and stored at 4C until analysis. During the 1990 water year (WY), sample collection of runoff for plant nutrients was not begun until February 10, 1990.

For ground water sampling, 3 sites (Fig. 1) were established along the northern edge of the watershed. Sites 1, 2, and 3 were located 12.5, 40.7, and 83.3 m, respectively, from the uppermost edge (eastern boundary) of the watershed. The elevation above sea level of sites 1, 2, and 3 are 98.8, 97.6, and 94.8 m respectively. Instrumentation for ground water sampling at each site consisted of observation wells (sampling piezometers) and soil water suction tubes at 0.15, 0.30, 0.46, 0.61, 0.91, 1.22, and 1.52 m depths into the soil profile. Observation wells and soil water suction tubes were located about 4.56 m from edge of the watershed, within crop rows, with a 0.91 m spacing between each observation well or soil water suction tube. Within 24 hrs of each storm event the depth of ground water in each observation well was measured, and all ground water evacuated. Similarly, all water was removed from the soil water suction tubes and tension set at 0.03 megapascal. Approximately 24 hours later, the depth of ground water in each observation well was again measured, and samples obtained from the observation wells and soil water suction tubes. Samples were placed in amber glass containers and transported to the laboratory where they were stored at 4C until chemical analysis. Unless otherwise indicated, all chemistry data reported in this manuscript are from ground water obtained from the observation wells. At planting time, those portions of a crop row containing instrumentation were hand planted. All ground water sampling instrumentation was covered during fertilizer or pesticide applications. The ground water sampling equipment was installed during October 1989, with the first ground water samples obtained in January 1990, after the soil profile had become saturated.

Prior to chemical analysis, all samples were filtered using a 0.45 μm Millipore filter. Runoff and ground water samples were analyzed for $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ using a Dionex HPLC equipped with an AS4A anion column, an anion micromembrane suppressor, and a conductivity detector. Samples were analyzed for $\text{NH}_4\text{-N}$ using the automated colorimetric phenate method (13). As runoff sampling did not begin at the start of the 1990 WY, the discharge weighted nutrient concentration from February 10, 1990 through April 27, 1990 was used to estimate nutrient losses for the unsampled storms of October 16, 1989 through February 3, 1990. For this period, the storms showed seasonal similarities in plant nutrient concentrations. Sediment concentrations in runoff samples were determined gravimetrically.

Nutrient concentrations were usually not normally distributed in the runoff and ground water as determined by Lilliefors's test (1). Therefore, nonparametric Kolmogorov-Smirnov two-sample and two-sided test statistic, T_1 , the greatest distance between two empirical cumulative distribution functions, was used to test the hypothesis that each nutrient concentration distribution was the same for all treatments. All statistical comparisons were conducted at the 0.05 probability level.

RESULTS AND DISCUSSIONS

Nutrients in Surface Runoff

The mean discharge-weighted concentrations of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ in runoff for all measured storm events of the 1990 WY were 0.56, 0.15, 0.28, 2.33, and 0.92 $\text{mg}\cdot\text{L}^{-1}$, respectively (Table 1). Based upon the total runoff of 330 mm for the 1990 WY, total losses of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ were 1.21, 0.54, 1.06, 4.98, and 2.21 $\text{kg}\cdot\text{ha}^{-1}$, respectively. Total precipitation for the 1990 WY was 1,276 mm. Other water quality research in north Mississippi has shown total N and P losses (solution plus sediment) from no-till soybeans at 4.7 and 2.8 $\text{kg}\cdot\text{ha}^{-1}$, respectively (9).

Cumulative frequency distributions of runoff and $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ losses provided additional information on the losses of nutrients in runoff. For example, considering $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, and $\text{NO}_3\text{-N}$ for only the storms analyzed, 44, 36, and 22 percent of the runoff, respectively, had concentrations that exceeded the discharge-weighted mean concentration, and produced about 81, 62, and 94 percent of the losses.

Single storm events can contribute a significant portion of the total (measured plus estimated) yearly losses. For example, a single storm event on May 21, 1990 (Table 1), contributed about 40% of the yearly $\text{PO}_4\text{-P}$ losses. This high P loss was the result of both a relatively high P concentration (0.81 $\text{mg}\cdot\text{L}^{-1}$) and runoff (59.94 mm). Similarly, the largest $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ losses for a single storm event were 38 and 39 percent, respectively, of the total yearly losses.

The largest nutrient concentrations for $\text{PO}_4\text{-P}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ in runoff were 4.21, 2.30, 27.59, and 14.30 $\text{mg}\cdot\text{L}^{-1}$, respectively, which occurred on June 3, 1990 (Fig 2). These high nutrient concentrations are attributed to a broadcast application of 0-20-20 on May 26, 1990. As the fertilizer should not have contained any nitrogen compounds, the increase in $\text{NO}_3\text{-N}$ may have resulted from a stimulation of microbiological activity. It should be noted that no $\text{NO}_3\text{-N}$ was detected in surface runoff for the period March 9, 1990 through May 21, 1990. While the $\text{NH}_4\text{-N}$ concentration in runoff increased relative to previous storms on June 3, 1990, the largest increase was not observed until one storm later on July 31, 1990, and may also reflect an increase in microbiological activity. Smaller increases in $\text{PO}_4\text{-P}$ and Cl concentrations in runoff occurred on May 23, 1990, which may be the result of nutrients leached from desiccated vegetation due to a herbicide application on May 8, 1990.

Most likely, these solution losses of nutrients represent almost all of the total nutrient losses since sediment concentrations were low. For the 1990 WY, the mean discharge-weighted sediment concentration in runoff was only 319 $\text{mg}\cdot\text{L}^{-1}$; sediment yield was 1,050 $\text{kg}\cdot\text{ha}^{-1}$.

Nutrients in Shallow Ground Water

Once the soil profile became saturated about mid-January, 1990, ground water samples were easily obtained, particularly at observation well depths greater than 0.61 m. A typical distribution of water in the observation wells after a storm event is shown in Figure 3. These data show the tendency of ground water to pond above the fragipan located 0.61 to 0.91 m below the soil surface. Nearly equal amounts (level) of water in all observation wells at site 3 may be an indication of water movement down slope across the fragipan surface. Finally, the data indicate an abundance of ground water within the fragipan itself. Research has indicated that a common characteristic of fragipan soils is that the material above the fragipan is usually quite porous whereas the fragipans have a much lower saturated hydraulic conductivity than the materials above, hence, low tension water accumulates at the top of the fragipan and moves laterally (4, 11).

The annual mean $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ concentrations for all ground water sites and depths were 0.05, 0.08, 11.56, 14.70, and 1.56 $\text{mg}\cdot\text{L}^{-1}$, respectively. With the exception of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$, nutrient concentrations in ground water were higher than those in runoff. Shallow ground water $\text{NO}_3\text{-N}$ concentrations for some storms exceeded the U. S. Drinking Water Standard by as much as a factor of 2.7 (Fig. 4), and are of interest since no N fertilizers were applied after 1987. In fact, for all sites and depths, 59% of all $\text{NO}_3\text{-N}$ concentrations exceeded the U. S. Drinking Water Standard of 10 $\text{mg}\cdot\text{L}^{-1}$. Three coastal plain studies indicate that even when recommended nutrient management practices were followed, $\text{NO}_3\text{-N}$ concentrations in shallow ground water were significantly higher than the standard for public drinking water. In one study of conventional-till soybeans, thirty-nine out of forty-four samples exceeded the nitrate-N standard of 10 $\text{mg}\cdot\text{L}^{-1}$ (7). Groundwater at 1.5 m with corn that received N fertilization showed $\text{NO}_3\text{-N}$ concentrations to be about 18 $\text{mg}\cdot\text{L}^{-1}$ (14). Tile drainage from Ohio alfalfa over a two year period average 1.5 $\text{mg}\cdot\text{L}^{-1}$ $\text{NO}_3\text{-N}$, compared with 4.9 to 32.8 $\text{mg}\cdot\text{L}^{-1}$ measured under soybeans (6). In this present study, soybean residues, tops and roots, are suspected as the $\text{NO}_3\text{-N}$ source. As in other research, it would appear that one of the primary factors that determines the magnitude of N leaching losses to groundwater is the availability of soluble N forms, especially nitrate, in the upper soil profile after the soybean harvest (12). In addition, legumes may cause a greater availability of $\text{NO}_3\text{-N}$ in the root zone and hence can promote significant nitrification and $\text{NO}_3\text{-N}$ leaching (3). Furthermore, the use of conservation tillage may result in increased infiltration rates due primarily to the formation of macropores in the soil, and thus increasing the likelihood of chemicals leaching beyond the root zone (8).

In general (sites 2 and 3), $\text{NO}_3\text{-N}$ concentrations during the winter at depths <0.46 m were greater than those deeper in the soil profile (Fig. 4 and Fig. 5). However, these higher ground water $\text{NO}_3\text{-N}$ concentrations at the shallow depths in the soil profile decreased dramatically (Fig. 5) during the spring due to 1) continual leaching of the soil profile, 2) nutrient uptake by a prolific late winter-early spring growth of native

vegetation, and 3) denitrification. For much of this same time period no $\text{NO}_3\text{-N}$ was detected in runoff.

In contrast to sites 2 and 3, winter $\text{NO}_3\text{-N}$ concentrations at site 1 were greater at the 1.52 m depth than at shallower depths in the soil profile. These higher $\text{NO}_3\text{-N}$ concentrations may be attributed to a combination of biological and hydrological factors. For example, site 1 has less slope than sites 2 and 3 that may result in a greater accumulation of surface residues and hence a larger earthworm population to incorporate residues into the soil profile. Furthermore, the flatter slope would promote a greater amount of downward water movement (leaching) and perching above the fragipan. Additional research is needed to verify this hypothesis. The initially high $\text{NO}_3\text{-N}$ concentrations at the 1.52 m depth decreased continuously during the winter/spring months, such that by late spring $\text{NO}_3\text{-N}$ concentrations were similar to those at the shallower depths (Fig. 4).

In general, with only a few exceptions, distribution functions of $\text{NO}_3\text{-N}$ concentrations in ground water for individual storm events differed significantly (5 percent level) at observation well depths 0.61 m or greater, but were similar (5 percent level) at well depths 0.46 m or less. Distribution functions of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ concentrations were the same (5 percent level) across study sites at all well depths. No trends in $\text{PO}_4\text{-P}$ or $\text{NH}_4\text{-N}$ concentrations were observed with season or well depth.

Ground water samples were collected and analyzed from both observation wells and soil water suction tubes, all at the same sites and depths. The annual mean $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Cl , and $\text{SO}_4\text{-S}$ concentrations in ground water collected by soil water suction tubes (for all sites and depths) were 0.05, 0.08, 9.94, 10.16, and 12.43 $\text{mg}\cdot\text{L}^{-1}$, respectively. At all sites, for individual storm events, distribution functions of Cl and $\text{NO}_3\text{-N}$ concentrations, collected by these two techniques, generally differed significantly (5 percent level) at depths greater than 0.46 to 0.61 m. The $\text{SO}_4\text{-S}$ concentrations differed significantly (5 percent level) at all depths. In contrast (except for a few depths and sites), $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ concentration distribution functions did not differ between the two sampling methods.

SUMMARY AND CONCLUSIONS

While the results presented within this manuscript represent only 1-year of research, and should be considered preliminary, they do provide the following insights regarding the quality of ground and surface water of a no-till soybean watershed:

1. Most plant nutrient concentrations, except $\text{NO}_3\text{-N}$, in shallow ground water are relatively low and present no environmental problems.
2. Even though no nitrogen was applied to the no-till soybeans, $\text{NO}_3\text{-N}$ concentrations in shallow ground water at times exceeded U. S. Drinking Water Standards. Crop residues are the suspected N source.

3. Plant nutrient concentrations and yields in surface runoff from a no-till soybean watershed are relatively low, and should pose no environmental problem.
4. Once the soil profile becomes saturated, free water is easily perched above the fragipan, and is suspected to move down-slope laterally across the fragipan surface.

The results of this 1-year study have also helped to define additional research areas which include:

1. Research is needed to define ground and surface water quality under conventional-till soybeans as compared with the no-till soybeans of this present study (This research was initiated at the start of 1991 WY).
2. Additional research is needed to define and quantify the movement of shallow ground water that may contain high $\text{NO}_3\text{-N}$ concentrations.
3. A more detailed sampling and chemical analysis of soil and crop residues is needed to better define N cycling. The role of soybean residues as a N source needs to be determined, and related to environmental factors such as rainfall intensity and duration.
4. Deeper observation wells are needed to determine if plant nutrients, specifically $\text{NO}_3\text{-N}$, are moving below the fragipan.
5. Research is needed to define the role of cover crops and application of fertilizers below ground as a means of reducing plant nutrient concentrations in ground water and surface runoff, respectively.

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Table 1. Nutrient concentration in runoff of individual storm events from a no-till soybean watershed during the 1990 water year.

| STORM DATE | RUNOFF (mm) | PO ₄ -P | | NH ₄ -N | | NO ₃ -N | |
|---------------------|----------------|----------------------------|-----------------------------|----------------------------|-----------------------------|----------------------------|-----------------------------|
| | | CONC mg·L ⁻¹ | LOSS kg·ha ⁻¹ | CONC mg·L ⁻¹ | LOSS kg·ha ⁻¹ | CONC mg·L ⁻¹ | LOSS kg·ha ⁻¹ |
| 10-16-89 THROUGH | | | | | | | |
| 2-3-90 | 159.36 | nd | nd | nd | nd | nd | nd |
| 2-10-90 | 30.73 | 0.27 | 0.08 | 0.14 | 0.04 | 0.95 | 0.29 |
| 2-15-90 | 7.11 | nd | nd | nd | nd | nd | nd |
| 2-22-90 | 3.81 | 0.12 | 0.01 | 0.01 | 0.00 | 0.77 | 0.03 |
| 3-2-90 | 5.16 | 0.59 | 0.03 | 0.30 | 0.02 | 0.02 | 0.00 |
| 3-9-90 | 2.79 | 0.09 | 0.00 | 0.19 | 0.01 | 0.00 | 0.00 |
| 3-10-90 | 0.58 | nd | nd | nd | nd | nd | nd |
| 3-15-90 | 11.66 | 0.00 | 0.00 | 0.20 | 0.02 | 0.00 | 0.00 |
| 3-20-90 | 2.44 | 0.03 | 0.00 | 0.22 | 0.01 | 0.00 | 0.00 |
| 4-5-90 | 5.61 | 0.11 | 0.01 | 0.23 | 0.01 | 0.00 | 0.00 |
| 4-21-90 | 18.62 | 0.09 | 0.02 | 0.21 | 0.04 | 0.00 | 0.00 |
| 4-27-90 | 8.79 | 0.15 | 0.01 | 0.22 | 0.02 | 0.00 | 0.00 |
| 5-2-90 | 0.86 | 0.14 | 0.00 | 0.34 | 0.00 | 0.00 | 0.00 |
| 5-12-90 | 5.41 | 1.06 | 0.06 | 0.08 | 0.01 | 0.00 | 0.00 |
| 5-21-90 | 59.94 | 0.81 | 0.48 | 0.06 | 0.04 | 0.00 | 0.00 |
| 6-3-90 | 4.22 | 4.21 | 0.18 | 0.22 | 0.01 | 2.30 | 0.10 |
| 7-31-90 | 2.46 | 1.12 | 0.03 | 0.99 | 0.02 | 1.50 | 0.04 |

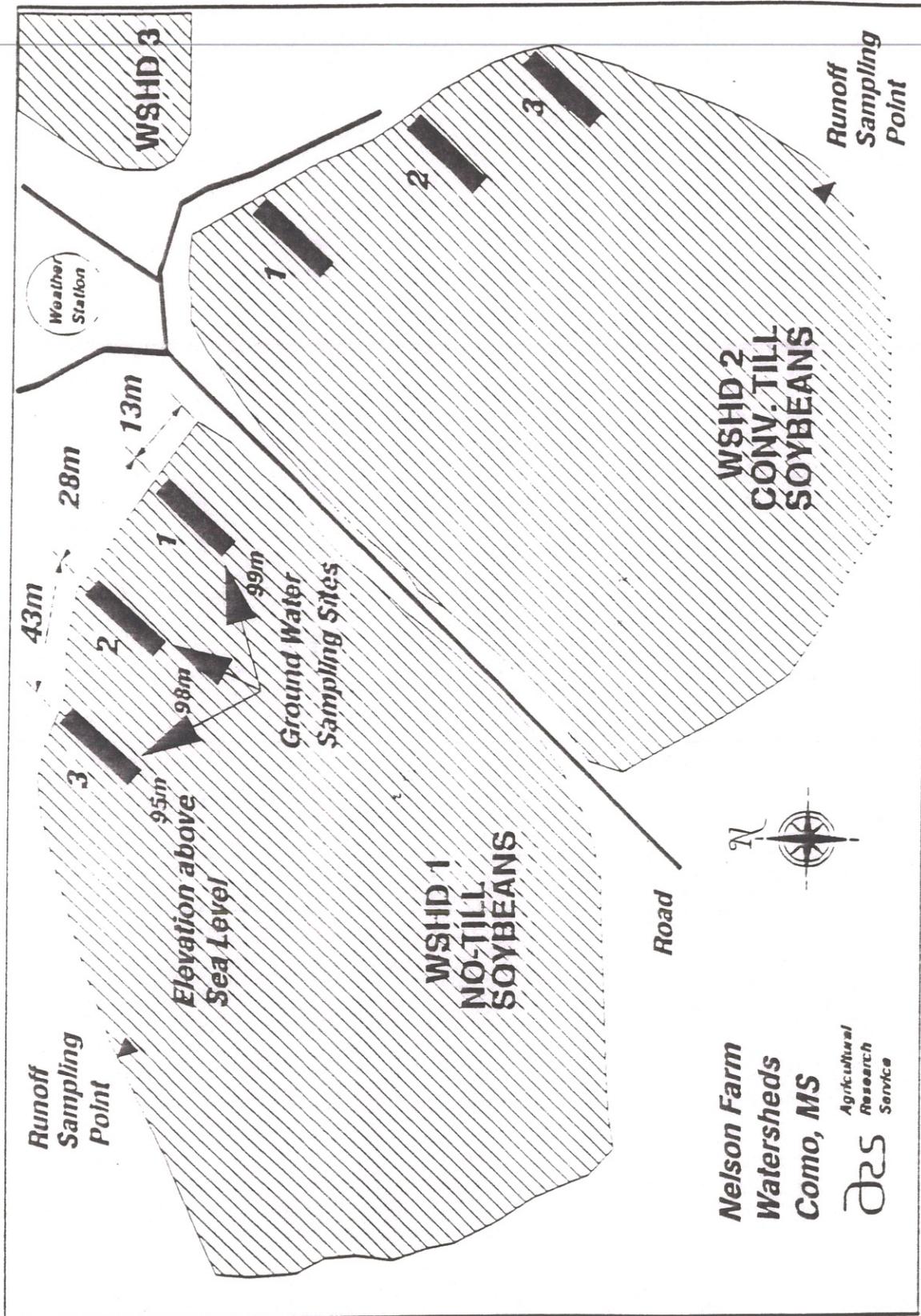


Figure 1. Location of runoff and ground water sampling sites.

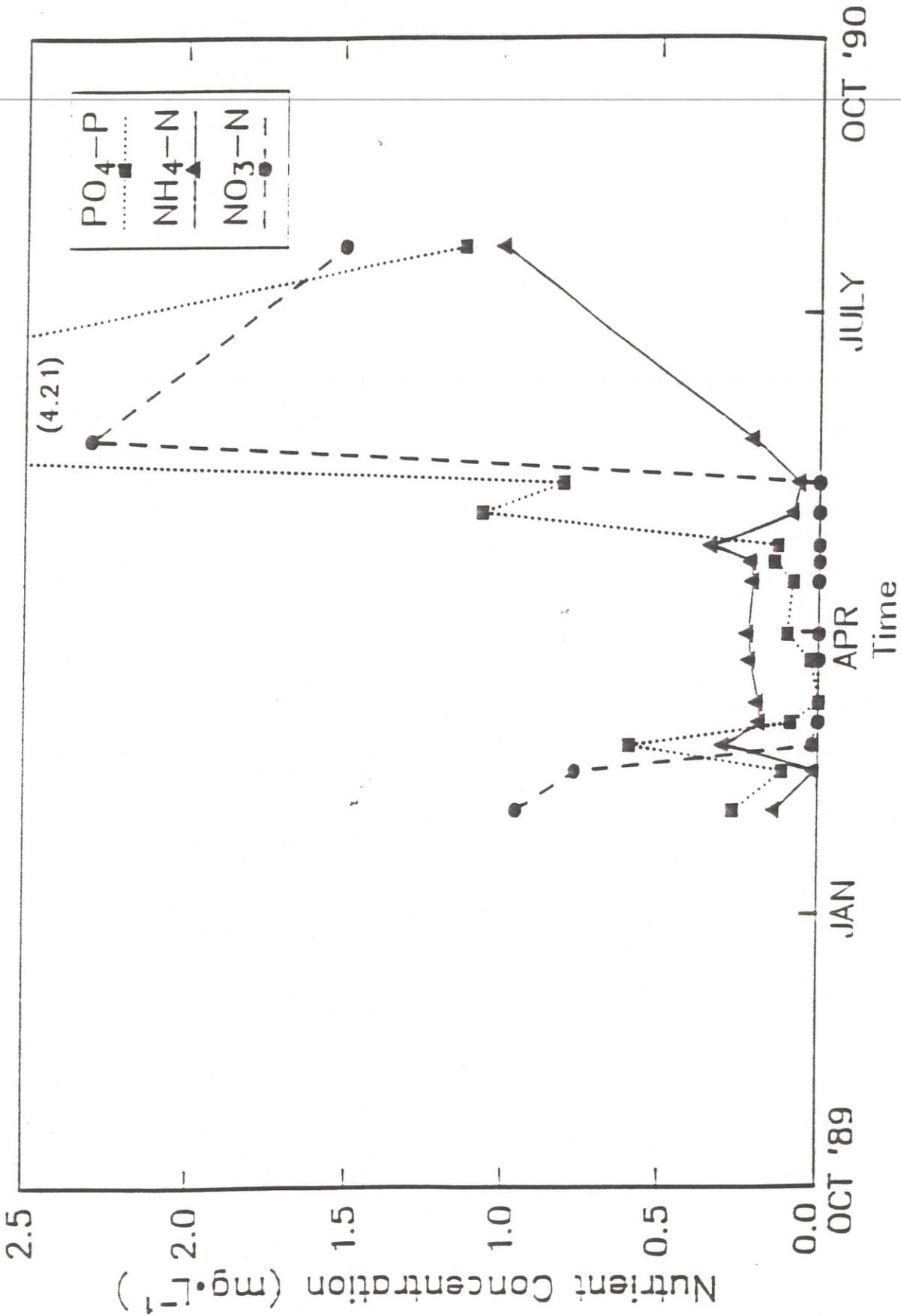
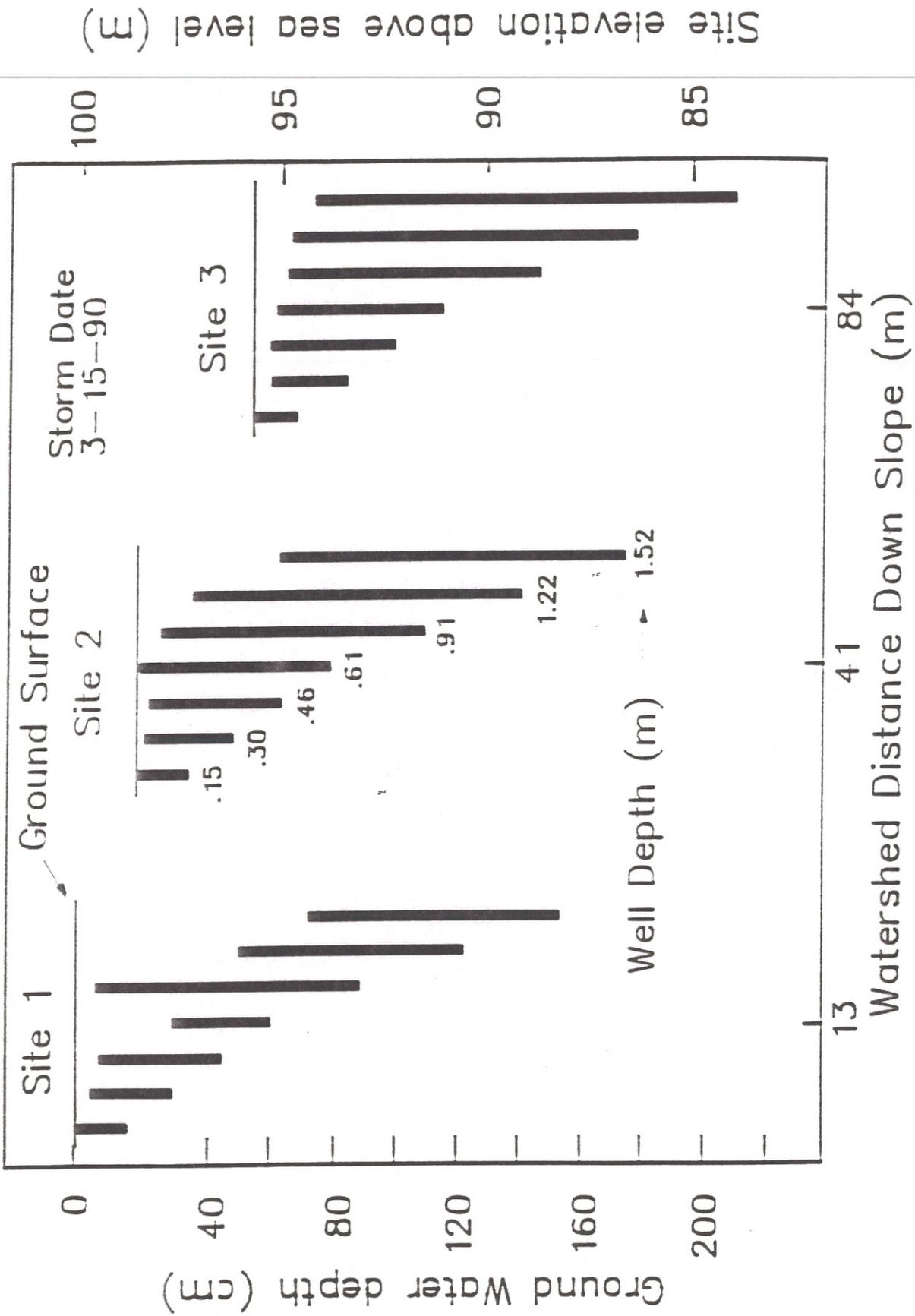


Figure 2. Nutrient concentrations in runoff from a no-till soybean watershed.



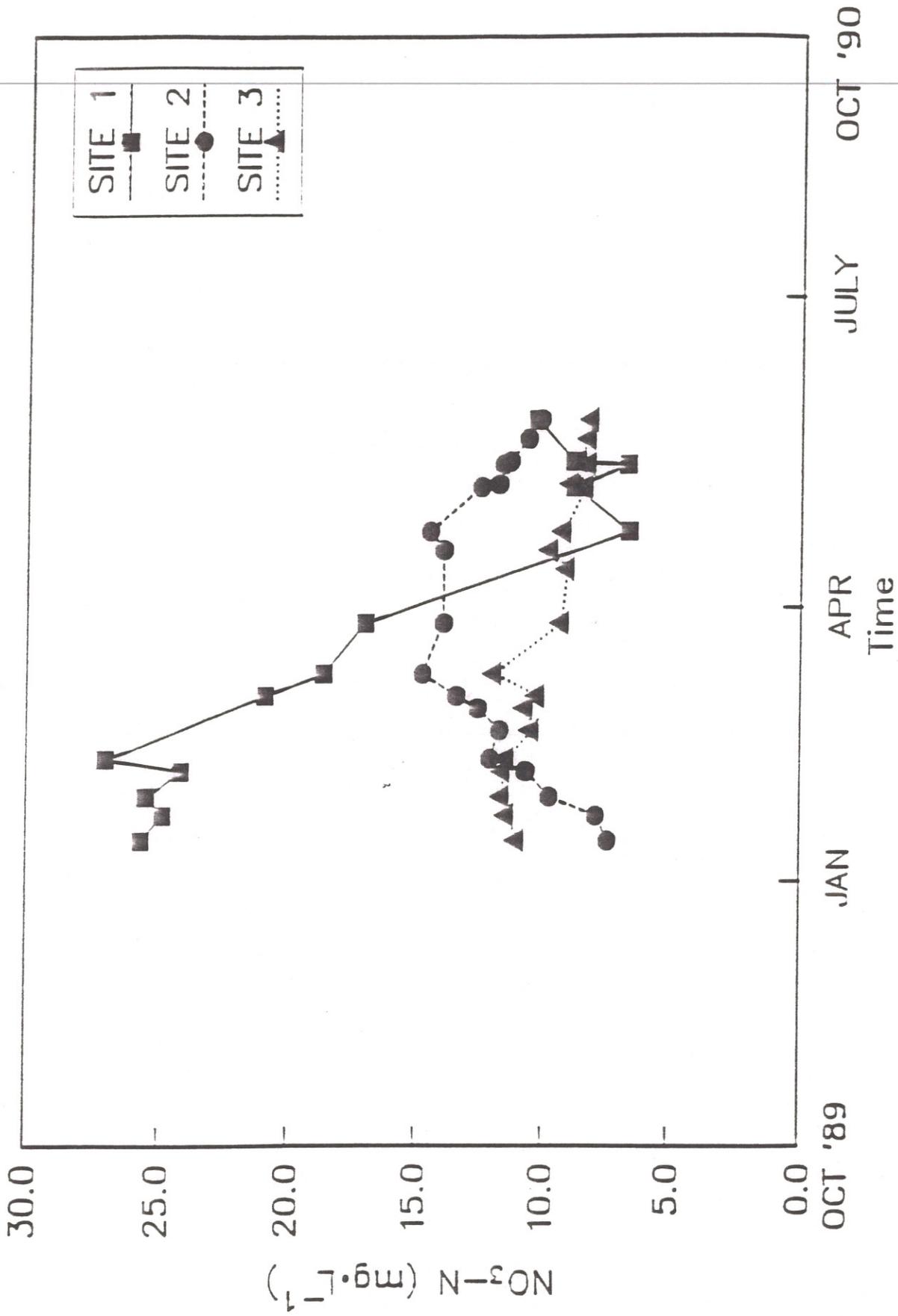


Figure 4. Nitrate-N concentrations in ground water of a no-till soybean watershed at the 1.52 m depth.

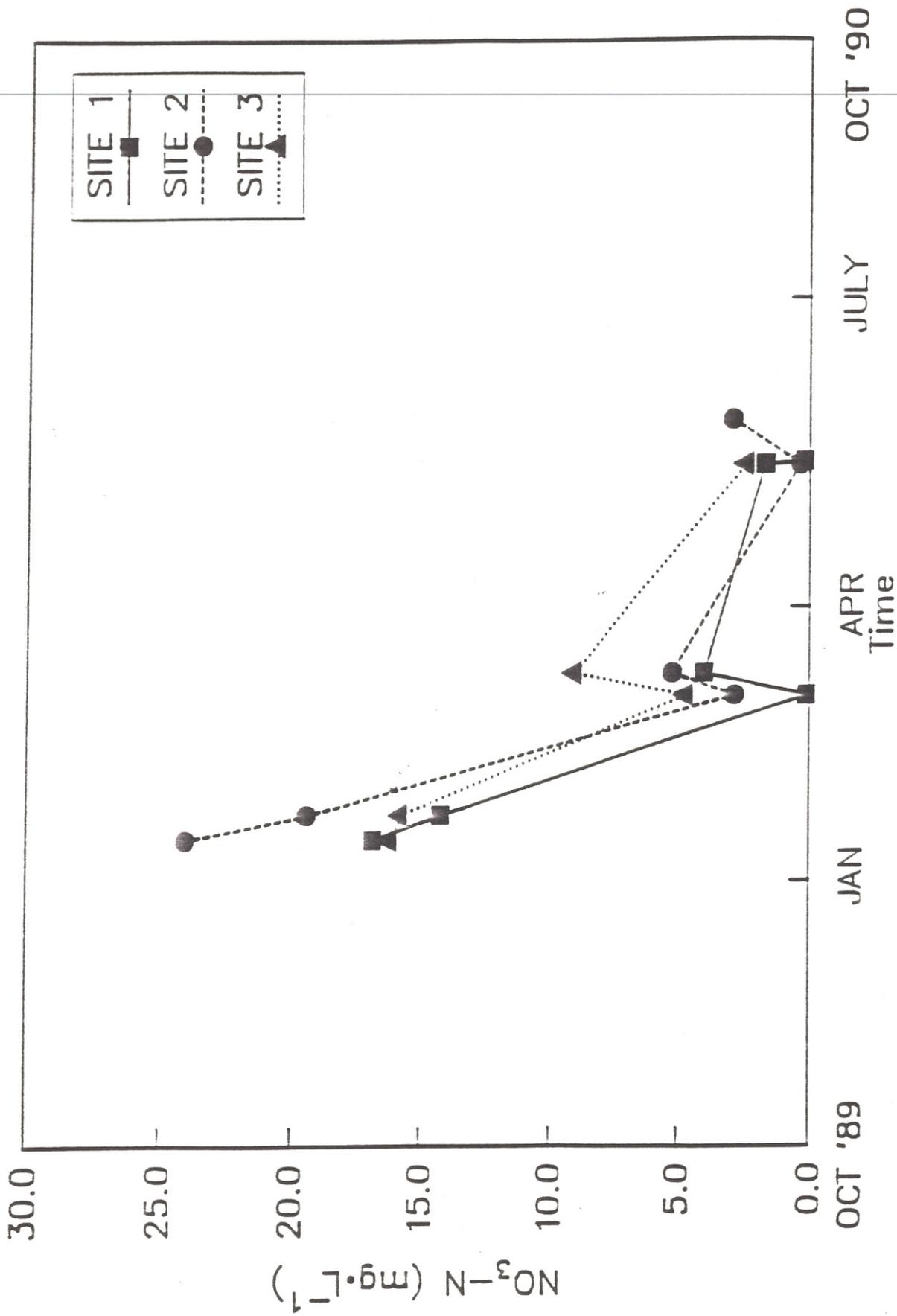


Figure 5. Nitrate-N concentrations in ground water of a no-till soybean watershed at the 0.30 m depth.

HERBICIDE CONCENTRATIONS IN SHALLOW GROUND WATER AND SURFACE RUNOFF FOR LAND CROPPED TO NO-TILL SOYBEANS²

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INTRODUCTION

Tremendous progress has been made in the last decade in biological pest control methodology such as using pest-resistant crop varieties, promoting the enhancement of natural pest predators and parasites, using pheromone traps, releasing sterilized pest insects, and applying microbial insecticides and herbicides (*Bacillus thuringiensis* and *Phytophthora palmivora* are examples) (Schweizer, 1988; Smith et al., 1983). However, since the late 1940's, synthetic organic chemicals have been and still are used as the primary means for pest control to sustain agricultural production. The amount of active ingredients applied to croplands increased 170% between 1964 and 1982 (Moody, 1990). Currently over 300,000 tons of chemical pesticides are annually applied to 330 million acres of cropland in the U.S. (U.S. Department of Agriculture, 1988; U.S. Bureau of Census, 1989).

Ground water surveys conducted during the last few years have revealed the contamination of some of the Nation's aquifers with both inorganic and organic compounds, several of which are used in agriculture. As better and more sensitive pesticide analytical methods were developed, the number and frequency of occurrence of different pesticides detected increased. Cohen et al. (1984) reported the occurrence of 12 pesticides in ground water in 18 states; and just 2 years later, this had increased to at least 17 pesticides in 23 states (Cohen et al., 1986). A recent report indicates the presence of 46 different pesticides in ground water samples from 26 states as a result of "normal" agricultural practices (Williams et al., 1988).

Since ground water is the source of drinking water for about half the population of the U.S., these increasing detections of pesticides in our aquifers have raised questions regarding the environmental costs of farming practices such as chemigation and conservation tillage. The impact on ground water quality of USDA decisions that promote the use of conservation tillage to control soil erosion is of major national interest and concern because a) conservation tillage practices initially require an increased use of pesticides, particularly herbicides to control weeds that conventional

²Mention of a pesticide in this paper does not constitute a recommendation for use by the U. S. Department of Agriculture nor does it imply registration under FIFRA as amended. Names of commercial products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the U. S. Department of Agriculture.

tillage had previously controlled and b) the higher infiltration rates generally associated with conservation tillage increase the potential of these pesticides to leach below the root zone to ground water (U.S. Department of Agriculture, 1989; Leonard, 1988). The USDA Research Plan for Water Quality has as its general goal the protection and enhancement of quality of the Nation's surface and ground waters while sustaining agricultural activities. Emphasis is on effects of conservation tillage practices on surface and ground water quality, with the objective to develop economically and environmentally sound crop production systems. This information is lacking for most of Mississippi, particularly the uplands of northern Mississippi. This paper discusses the National Sedimentation Laboratory's initial and ongoing efforts in this very critical research area and presents the pesticide data obtained thus far (i.e., for the 1990 crop year). Nutrient results and details of field instrumentation are presented in companion papers (Schreiber et al., 1991; Cullum et al., 1991).

MATERIALS AND METHODS

The study was conducted on the Nelson Research Farm located in the loess hills of northern Mississippi near the town of Como. These fragipan soils are of the Grenada, Loring, and Memphis series. In the fall of 1989, runoff and shallow ground water sampling sites were established on a 2.14-ha watershed (WSHD 1 in Figure 1, mean slope about 4%) which had been in minimum-till soybeans during 1988 and 1989. The runoff sampling site was instrumented for automatic data and discharge-weighted composite sample collection as described elsewhere (Grissinger and Murphree, 1991; Cullum et al., 1991). The three shallow ground water sampling sites were located along one edge of the watershed so as to minimize disturbance to the watershed surface via foot traffic during sampling. Each ground water sampling site consisted of seven porous ceramic-cup samplers (Soilmoisture Equipment Corp. model 1920) and seven observation wells (sampling piezometers) each at soil depths of 0.15, 0.30, 0.46, 0.61, 0.91, 1.22, and 1.52 m (i.e., 0.5, 1, 1.5, 2, 3, 4, 5 ft) placed within the crop row and spaced 0.9 m apart. The sampling interval in each well was from the bottom upward about 7.5 cm.

Metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one, trade name Lexone) at 0.42 kg/ha and metolachlor [2-chloro-6'-ethyl-*N*-(2-methoxy-1-methyl-ethyl)acet-*o*-toluidide, trade name Dual] at 2.24 kg/ha were applied broadcast by ground equipment in early May 1990 for preemerge weed control over the entire watershed. In late May, 0-20-20 fertilizer was applied broadcast at 224 kg/ha, followed 3 days later by no-till planting of soybeans [*Glycine max* (L.) Merr., Delta Pine 415] at 50-56 kg/ha. In mid-June, the watershed was treated with a broadcast application of acifluorfen-sodium [sodium 5-(2-chloro- α,α,α -trifluoro-*p*-tolylloxy)-2-nitrobenzoate, trade name Blazer] at 0.28 kg/ha and bentazon [3-isopropyl-(1*H*)-benzo-2,1,3-thiadiazin-4-one 2,2-dioxide, trade name Basagran] at 0.56 kg/ha for postemerge weed control and with chlorpyrifos (*O,O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate, trade name Lorsban) at 0.56 kg/ha for soil insect control. Ceramic-cup samplers and observation wells were covered during pesticide applications. Aliquots (about 300 mL) of all tank mixes were obtained for confirmation

of application rates. None of these pesticides had previously been applied to this watershed.

Usually within 12 h of a rainfall event, the composite runoff sample, which was collected, was transported in its stainless steel container (40-L capacity) to the National Sedimentation Laboratory (NSL) and stored at 4°C (usually <72 h) for pesticide and other analyses. Each ceramic-cup sampler was pumped dry, the water being discarded; and 30 KPa tension was applied to the sampler. Each observation well was also pumped dry and the water, discarded. About 12-16 h later, the water (usually 0.1-0.3 L) in each ceramic-cup sampler was collected (by applying pressure to the sampler with a small hand pump) in a 1-L amber glass bottle with teflon-lined screw cap. At about the same time, the depth to water in each observation well was measured and recorded; a 1-L sample was collected from each well (using a small, hand-operated vacuum pump with teflon intake line) in a 1-L bottle as just described. Excess well water was discarded. Shallow ground water samples were immediately transported to the NSL and also stored at 4°C (usually <72 h) for pesticide and other analyses.

Runoff and ground water samples were allowed to come to room temperature (about 25°C) and Millipore filtered at 0.45 µm. For metribuzin, metolachlor, and chlorpyrifos analyses, a 100-mL aliquot of the water phase was removed from each by volumetric pipette. To each aliquot was added 1 g reagent-grade KCl and 25 mL pesticide-grade EtOAc. Pesticide extraction was accomplished by sonification for 1 min, partitioning in a separatory funnel, and discarding the water phase. The EtOAc phase was dried over anhydrous Na₂SO₄ and brought to an appropriate volume for gas chromatographic analysis. The sediment (in runoff samples) from Millipore filtration was oven-dried (105°C, 16 h), weighed, and extracted with 100 mL distilled water, 1 g reagent-grade KCl, and 25 mL pesticide-grade hexane by sonification for 1 min. The mixture was partitioned in a separatory funnel and the water phase was discarded. The hexane phase was dried over anhydrous Na₂SO₄ and brought to an appropriate volume for gas chromatographic (gc) analysis.

Pesticide extracts were analyzed using a Tracor Model 540 gc equipped with Ni63 electron capture detector, a Hewlett-Packard model 3396A integrator, and a 15 m X 0.53 mm J & W Scientific DB 210 (1.0 µm film thickness) column. The carrier gas was ultra-high purity helium at 12.7 cc/min and the column makeup and detector purge gas was ultra-high purity nitrogen at 60 and 10 cc/min, respectively. Column oven, inlet, and detector temperatures were 180, 240, and 350°C, respectively. Under these conditions, retention times were 1.54, 2.02, and 3.17 min for metribuzin, chlorpyrifos, and metolachlor, respectively. Mean extraction efficiencies, based on fortified samples, were >90% for all three pesticides from both water and sediment. Pesticide residues were confirmed with a Tracor model 702 nitrogen-phosphorus detector.

Acifluorfen-sodium was extracted from acidified water and/or sediment with ethyl ether and determined as its methyl derivative according to the method of Adler et al. (1978). Mean recoveries, based on fortified samples, were 83-85%.

Bentazon was extracted from water and/or sediment with pesticide-grade EtOAc and determined as its pentafluorobenzyl derivative according to the method of Gaynor and MacTavish (1981). Mean recoveries, based on fortified samples, were 85-88%.

RESULTS AND DISCUSSION

Pendimethalin [*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylidine, trade name Prowl] and fluazifop-butyl {butyl (*RS*)-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate, trade name Fusilade} had been applied to WSHD 1 in late spring of 1989, prior to our study, but no residues of either of these herbicides or of any other pesticides could be detected in runoff and shallow ground water samples collected between the fall of 1989 and early May of 1990 when metribuzin and metolachlor were applied. For the 1990 crop year, shallow ground water samples for pesticide analyses were obtained from wells only.

There were only 4 runoff-producing rainfall events after metribuzin and metolachlor application in early May and prior to soybean harvest in early October (Table 1). The highest herbicide concentrations observed in discharge-weighted runoff samples were 111 and 535 $\mu\text{g/L}$ (ppb) metribuzin and metolachlor, respectively, and occurred in the water phase of the first runoff only 6 d after application. These water-phase concentrations decreased rapidly for the first 30 d after herbicide application, and by 85 d (last runoff-producing rainfall event) were only 0.3 and 1.2 $\mu\text{g/L}$, respectively, each equivalent to <1% of the concentrations observed on day 6 (Figure 3). The next runoff occurred after harvest, but no herbicide residues could be detected (data not shown). The greatest runoff losses of metribuzin and metolachlor were about 11 and 56 g/ha, respectively, and occurred 13 d after application as a result of the largest runoff event (about 60 mm). These losses were solely in the water phase and represent 63% and 65%, respectively, of the total runoff losses of about 17 and 85 g/ha for the crop year. The total runoff losses of metribuzin and metolachlor, expressed as % of applied, were about the same, i.e. about 4%. Individual storm losses, expressed as % of applied, were also about the same for the two herbicides and result from a combination of factors. The water solubility of metribuzin (1200 mg/L) is 2.26 times that of metolachlor (530 mg/L) (Royal Society of Chemistry, 1987). However, metolachlor was applied at 5.33 times the application rate at which metribuzin was applied. For recommended application rates, the average field persistence of metolachlor ($t_{1/2}$ =15-25 d) is about one-half that of metribuzin ($t_{1/2}$ =30-60 d) (Weed Science Society of America, 1983).

Another factor to consider is the organic carbon partition coefficient (K_{oc}) for each compound. The K_{oc} is an adsorption constant based on the fraction of organic carbon in the soil and is calculated from the adsorbed pesticide mass per unit mass of soil (C_s , usually in g/g) divided by the product of the pesticide concentration in solution in

equilibrium with the soil mass (C_w , usually in g/cc) and the fraction of organic carbon in the soil (OC) (Leonard and Knisel, 1988). The reported K_{oc} 's of 24 cc/g for metribuzin and 181 cc/g for metolachlor indicate a greater tendency for metribuzin to be partitioned toward the soil solution than metolachlor (Jury et al., 1987).

No metribuzin and metolachlor residues were found in the sediment phase of runoff probably because of their relatively high water solubilities and relatively low K_{oc} 's compared to other pesticides which tend to partition more toward the soil/sediment mass. Also, sediment concentrations in runoff from this no-till watershed were relatively low (< 200 mg/L) for each of the 4 runoff events. No residues of acifluorfen-sodium, bentazon, or chlorpyrifos were detected in runoff from the single event which occurred 48 d after their application. In addition to having been applied at reduced rates, acifluorfen-sodium ($t_{1/2}$ =30-60 d) and bentazon (persistence < 6 w) had probably undergone extensive degradation by the time runoff occurred (Weed Science Society of America, 1983). Chlorpyrifos, with its low water solubility (2 mg/L) and high K_{oc} (6070 cc/g), would not be detectable in runoff with very low sediment loads (Royal Society of Chemistry, 1987; Jury et al., 1987).

Only 3 ground water-producing rainfall events occurred after metribuzin and metolachlor application (Table 2). No ground water resulted from the rainfall that produced the last runoff event in Table 1. On 5/14/90, only 9 of the 21 wells contained sufficient ground water for sampling. Metribuzin and metolachlor concentrations were highest at site 1 at the 1.52-m depth, indicating significant movement of the herbicides into the fragipan, possibly in the polygonal seams. Herbicide concentrations at sites 2 and 3 were highest at the 0.61-m and 0.91-m depths, respectively, and may have resulted from water accumulating at the top of the fragipan after lateral movement downslope (Grossman and Carlisle, 1969). On 5/21/90, all 21 wells contained sufficient water for sampling but no pattern of herbicide distribution in the wells was apparent. At site 1, herbicide concentrations were higher at the 0.15-m, 0.30-m, 0.61-m, and 1.52-m depths, with relatively small amounts at the other 3 depths. At site 2, the higher herbicide concentrations were found at the 0.15-m, 0.46-m, 0.61-m, and 0.91-m depths; and at site 3, at the 0.15-m, 0.91-m, and 1.52-m depths. On 6/4/90, sufficient water for sampling was found in 15 wells, and the highest herbicide concentrations were at the 1.52-m depth at site 1, the 0.61-m depth at site 2, and the 1.52-m depth at site 3.

Metribuzin concentrations in shallow ground water for each sampling date, site, and well depth, were always lower than metolachlor concentrations. Therefore, relative application rate must be more important than relative water solubility and relative average field persistence, at least in this study. Nothing more should be said about distribution patterns of these two herbicides in the shallow ground water until several more years of data are collected for this no-till soybean watershed and for a companion conventional-till watershed nearby. Hopefully, more complete sets of samples for each sampling date will be obtainable.

Both metribuzin and metolachlor rapidly disappeared from the shallow ground water (Figure 4). The mean ground water concentrations for all sampled sites and depths on 5/14/90 (6 d after application) were 23 and 67 $\mu\text{g/L}$ of metribuzin and metolachlor, respectively. On 6/4/90 (27 d after application), these mean concentrations had decreased to 1 and 3 $\mu\text{g/L}$, respectively. The most likely cause was extensive biodegradation. Other factors contributing to this rapid disappearance may have been a) movement of the herbicides out of the watershed in lateral subsurface flow across the top of the fragipan and b) movement of the herbicides deeper into or possibly through the fragipan. Herbicides moving across the top of the fragipan could manifest themselves in surface flow at some point downslope. Herbicides moving deeper into the soil profile have a higher potential for contaminating permanent ground water because of reduced microbial activity and biodegradation rates at greater depths (Federle, et al., 1986; Moorman and Harper, 1989). In order to discern this, deeper ground water and extensive soil sampling, quantitation of subsurface water flow, and mapping of the fragipan surface by ground-penetrating radar are planned for the 1991 and succeeding crop years.

No measureable ground water resulted from rainfall events which occurred after acifluorfen-sodium, bentazon, and chlorpyrifos application in mid-June.

Thus far in this research, none of the herbicide concentrations found in surface runoff and shallow ground water appear to present any water quality problems. The ten-day health advisory for drinking water is defined as "the concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects up to 14 consecutive days of exposure, within a margin of safety," and for metribuzin and metolachlor, respectively, is 5000 and 2000 $\mu\text{g/L}$ (U. S. Environmental Protection Agency, 1989). The analogous lifetime health advisories are 200 and 100 $\mu\text{g/L}$, respectively, and are based on a 70-kg adult human drinking 2 L water per day over a lifetime, within a margin of safety (i.e., considering uncertainty and relative source contribution factors).

In summary, metribuzin and metolachlor concentrations in runoff water and shallow ground water were initially relatively high but decreased rapidly to almost undetectable levels. The importance of rainfall timing relative to pesticide application is re-emphasized. The inconclusiveness of the results of this 1-crop-year study reinforces the need for additional years of data for this and other tillage systems and the need for deeper ground water sampling, quantitation of shallow ground water movement, and comprehensive soil sampling. Information about the effects of conservation tillage practices on pesticide transport in surface runoff and percolation to shallow ground water is needed for development of improved agrichemical transport models and resulting agrichemical management systems.

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Table 1

*Herbicide concentrations and losses in runoff
from WSHD 1 during the 1990 crop year*

| Date | Runoff mm | Metribuzin | | Metolachlor | | | |
|---------|--------------|---------------|--------------|---------------|--------------|-------|------|
| | | Conc. ug/L | Loss g/ha | Conc. ug/L | Loss g/ha | | |
| | | | % of applied | | % of applied | | |
| 5/14/90 | 5.41 | 110.7 | 5.95 | 1.41 | 534.6 | 28.74 | 1.28 |
| 5/21/90 | 59.94 | 17.7 | 10.54 | 2.51 | 93.9 | 55.94 | 2.49 |
| 6/04/90 | 4.22 | 2.4 | 0.10 | 0.02 | 16.5 | 0.69 | 0.03 |
| 8/01/90 | 2.46 | 0.3 | 0.01 | 0.00 | 1.2 | 0.03 | 0.00 |

Table 2
Herbicide concentrations in shallow ground water
in WSHD 1 for crop year 1990

| Site | Well depth | | | | | | |
|--------------------|------------|------|-------|-------|-------|------|------|
| | 0.15m | 0.3m | 0.46m | 0.6m | 0.9m | 1.2m | 1.5m |
| 5/14/90 | | | | | | | |
| Metribuzin | | | | ppb | | | |
| 1 | nw | nw | nw | nw | nw | 7.0 | 46.3 |
| 2 | nw | nw | nw | 99.2 | 1.2 | 0.0 | 0.0 |
| 3 | nw | nw | nw | nw | 40.2 | 0.1 | 9.8 |
| Motolachlor | | | | | | | |
| 1 | nw | nw | nw | nw | nw | 11.8 | 72.0 |
| 2 | nw | nw | nw | 219.6 | 2.0 | 0.0 | 0.0 |
| 3 | nw | nw | nw | nw | 270.0 | 1.1 | 28.4 |
| 5/21/90 | | | | | | | |
| Metribuzin | | | | | | | |
| 1 | 13.7 | 10.4 | 0.4 | 12.0 | 0.2 | 1.1 | 15.2 |
| 2 | 13.8 | 0.5 | 9.2 | 21.4 | 8.3 | 0.0 | 0.1 |
| 3 | 5.4 | 0.4 | 0.2 | 0.2 | 9.4 | 1.2 | 2.0 |
| Motolachlor | | | | | | | |
| 1 | 45.7 | 26.6 | 1.0 | 28.0 | 0.0 | 2.3 | 30.4 |
| 2 | 57.6 | 1.0 | 18.6 | 64.6 | 22.7 | 0.0 | 0.0 |
| 3 | 34.8 | 2.3 | 1.0 | 1.1 | 50.8 | 5.3 | 10.6 |
| 6/4/90 | | | | | | | |
| Metribuzin | | | | | | | |
| 1 | nw | nw | 0.0 | nw | 0.1 | 0.6 | 3.6 |
| 2 | nw | 0.0 | 1.4 | 4.8 | 1.1 | 2.7 | 0.0 |
| 3 | nw | nw | 0.0 | 0.0 | 0.4 | 0.3 | 0.5 |
| Motolachlor | | | | | | | |
| 1 | nw | nw | 7.7 | nw | 0.5 | 1.6 | 8.5 |
| 2 | nw | 0.3 | 4.6 | 7.6 | 2.2 | 3.2 | 0.2 |
| 3 | nw | nw | 0.3 | 0.2 | 3.7 | 2.7 | 4.7 |

Application date = 5/08/90
nw = no water in well

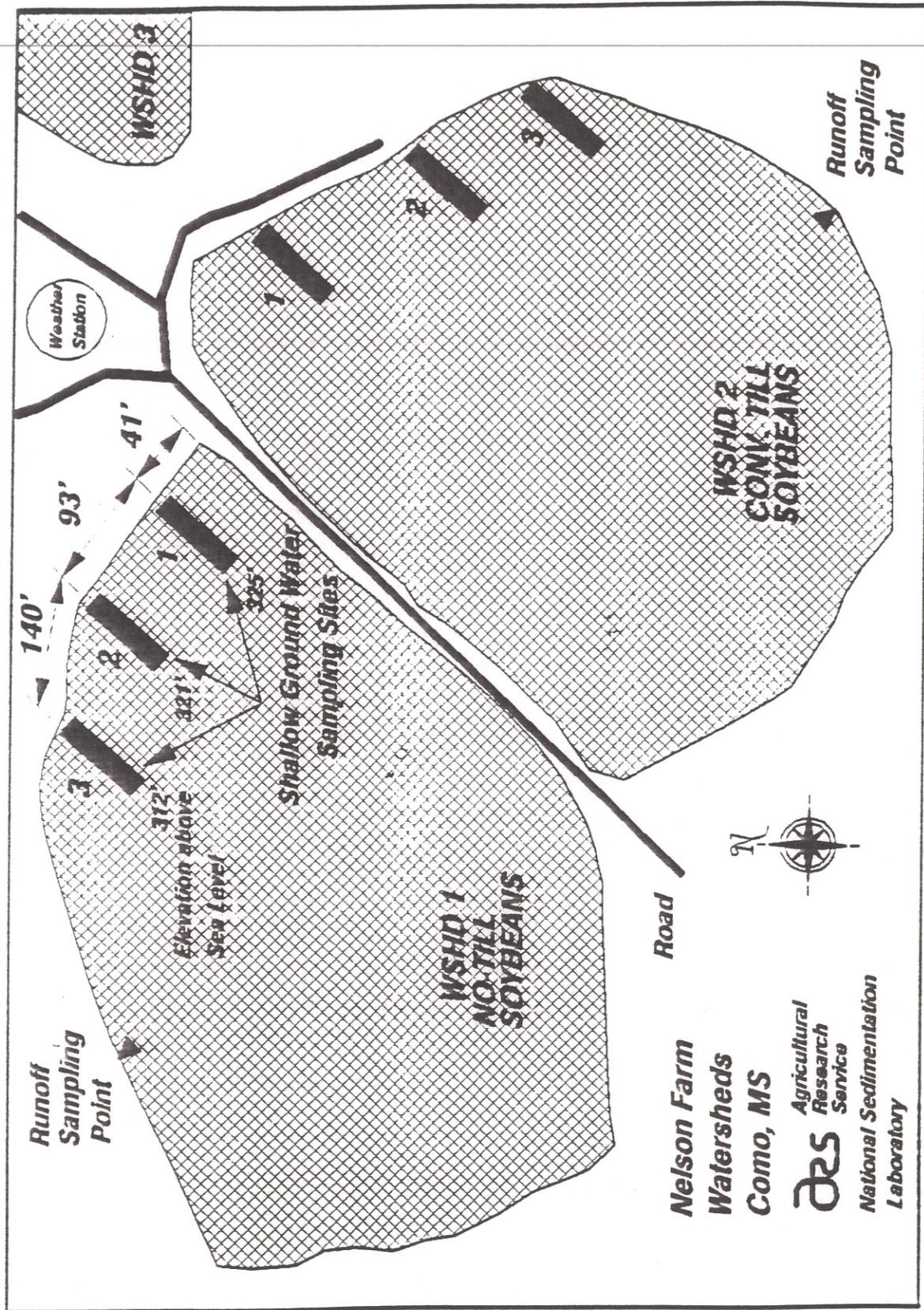
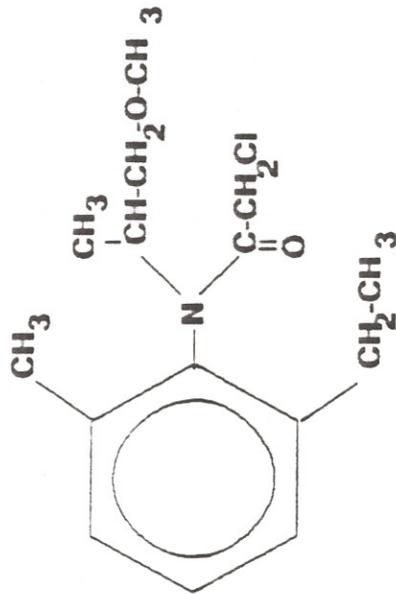


Figure 1. Location of runoff and shallow ground water sampling sites.

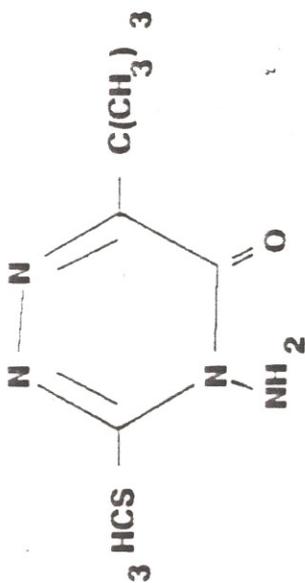


METOLACHLOR

$$S_{H_2O} = 530 \text{ ppm}^*$$

$$K_{OC} = 181 \text{ cc/g}^{**}$$

* Water solubility from *Agrochemicals Handbook 2nd ed.*
 ** Organic carbon partition coefficient from *Jury et al. 1987.*



METRIBUZIN

$$S_{H_2O} = 1200 \text{ ppm}^*$$

$$K_{OC} = 24 \text{ cc/g}^{**}$$

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 Agricultural
 Research
 Service
 National Sedimentation
 Laboratory

Figure 2. Basic structures and selected properties of herbicides found in water.

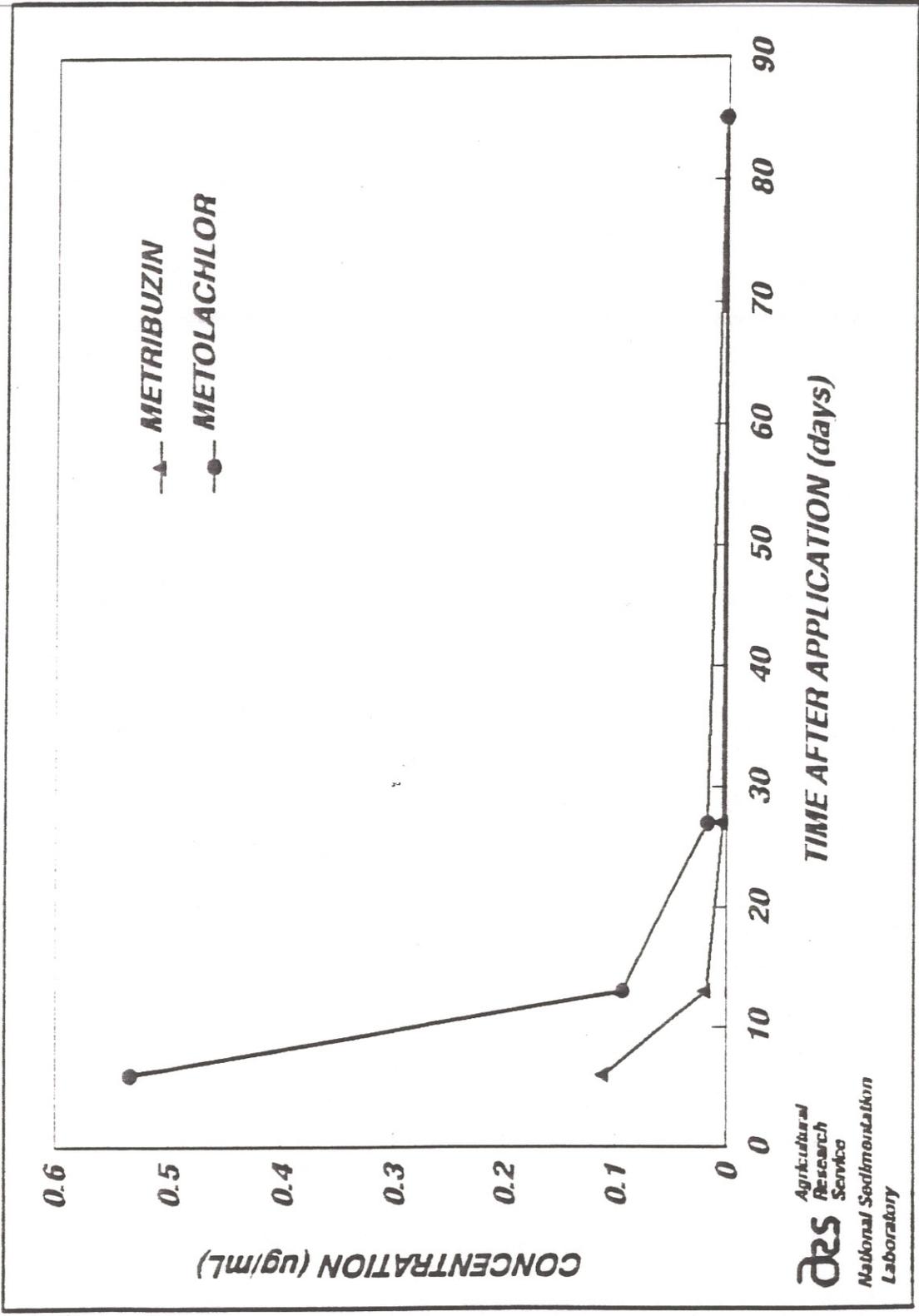


Figure 3. Herbicide concentrations in runoff from WSHD 1, crop year 1990.

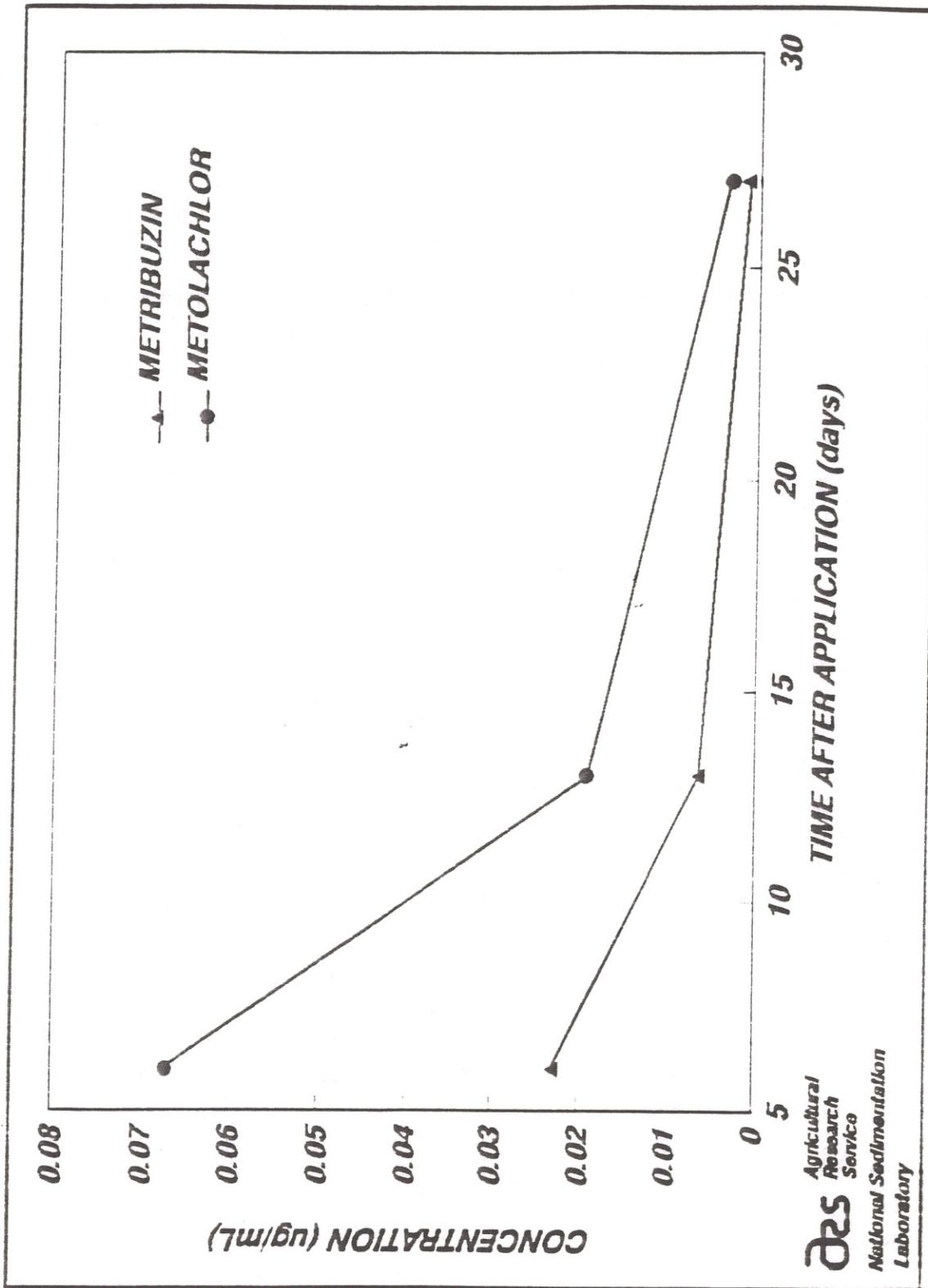


Figure 4. Mean herbicide concentrations in shallow ground water, WSHD 1, crop year 1990.

INSTRUMENTATION TO QUANTIFY AND SAMPLE SURFACE RUNOFF AND SHALLOW GROUND WATER³

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ABSTRACT

A field acquisition system was developed and constructed to sample and quantify surface runoff and shallow ground water. The main components of the system for surface runoff from standard-sized erosion plots cropped to corn were appropriately-sized collectors, approaches, H-flumes equipped with portable liquid-level recorders, runoff splitter, dataloggers, and composite water samplers. The dataloggers recorded rainfall and runoff data every minute during storm events. Pump samplers were activated by the dataloggers when the cumulative discharge volumes equaled or exceeded a predefined value. The components for shallow ground water included hydrologically-isolated erosion plots with subsurface drains (installed via horizontal drilling) and outlets into sumps, wave guides for soil moisture measurements by time domain reflectometry, and a series of ceramic cup samplers, piezometers, and tensiometers ranging from 15-cm to 152-cm depths positioned at the middle section of each plot. Measured variables from surface runoff were incremental discharge rate, cumulative discharge volume, sediment loads, and water quality. Ground water samples were analyzed for specific chemicals introduced as fertilizer or pesticides. Soil moisture contents were measured and depths of free water within each piezometer after major storm events were monitored to determine water movement in the root and vadose zone.

INTRODUCTION

Ground water contamination by chemical fertilizers and pesticides has been documented by various federal and state agencies in the United States (Canter, 1987). Ground water pollution continues to be a major concern in the United States, because over half of the drinking water is from this natural resource. Various studies have found water pollution to be the most damaging and wide spread environmental effect of agricultural production (Brinsfield *et al.* 1987; Kanwar, 1990). Ground water contamination by pesticides and nitrogen fertilizers have been cited in 32 states and Europe from agricultural-related enterprises (National Research Council, 1989; Oakes *et al.*, 1981; Gast *et al.*, 1978; Hall *et al.*, 1989; Kanwar *et al.*, 1988). Over 800 of 1437 counties in the U.S. have reported ground water pesticide contamination. One

³Names of commercial products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the U. S. Department of Agriculture.

billion kg of more than 400 different types of pesticide chemicals are sprayed each year on America's cropland (National Research Council, 1989).

In Mississippi, ground water constitutes 54 percent of all the freshwater and is the water supply of 93 percent of the population (Mississippi Ground-Water Quality, 1986). Due to Mississippi's sparsely populated agricultural areas, ground water contamination has not been considered a major problem. However, Mississippi's ground water is susceptible to contamination due to the very permeable soils, shallow depth to ground water, heavy clay subsoil, and large annual rainfall. Data is lacking on any potential agrichemical contamination of ground water underlying the agricultural areas of Mississippi, particularly the Delta along the Mississippi River and the Uplands to the north (Mississippi Ground-Water Quality, 1986).

Agricultural land areas have varying degrees of potentials for ground water pollution depending on the type of soils, climate, geology, and the agricultural management practices. The use of conservation tillage for production of agriculture may help in developing the Best Management Practices in reducing the ground water pollution problems. Conservation tillage, such as a no tillage practice, is an effective practice for conserving energy and soil. Conservation tillage reduces surface water pollution by contaminants attached to the sediment particles since erosion is significantly reduced. However, conservation tillage may increase the risk of ground water pollution of soluble contaminants because these tillage systems have been found to increase infiltration and subsequently ground water recharge (Kanwar *et al.*, 1988). Conservational tillage (minimum to no tillage) practices leave the structure of surface soil largely intact, which may cause faster movement of pesticides and nitrates due to reduced soil residence time. In contrast, the conventional tillage practices, which include plowing, disking, and harrowing, destroy all the preferential paths which result in reducing the movement of chemical pollutants to the ground water. The combination of mobility and persistence of a chemical pollutant determines whether a compound will be degraded to a harmless form during its residence time in the biologically active vadose zone.

Research is needed to determine the extent of chemical leaching to ground water as a function of tillage practices. Therefore, a field study was started to understand the relationships among agricultural practices (tillage and chemical application), surface runoff (soil erosion), and ground water pollution. The overall objectives of this study were to determine the role of macropore flow under three different tillage systems (conventional, conservational or minimum, and no tillage) on corn, and to quantify the concentrations of pesticides and nitrate found in shallow ground water and in surface runoff so that practices could be developed to improve both ground water quality and surface runoff. The methods used to establish these objectives are discussed below.

DESIGN

The experimental site for this study was located at the North Mississippi Branch of the Mississippi Agricultural and Forestry Experiment Station at Holly Springs, Mississippi.

This study site was on a predominantly Loring silt loam soil (*Typic Fragiudalf*) formed from loess material on sloping uplands. A fragipan occurred 50 to 60 cm under the soil surface that restricted the downward movement of water and caused an intermittent perched water table during months of high rainfall. This fragipan is a naturally occurring subsurface horizon generally characterized by high bulk density, very low hydraulic conductivity, brittleness, and the absence of fine feeder roots in the brittle portion. This site was planted to corn by conventional tillage for several years prior to 1990. In 1990, the site was mechanically fallowed while construction occurred.

The experimental design will consist of growing corn on a randomized block design with three treatments (no-till, minimum till, conventional till) with two replications. Plots were constructed and installed during the summer of 1990 with 1991 being the first cropping year. Each plot was 8.1 m x 38.1 m (0.03 ha) with slopes averaging 2.8 and 4.0% for replications 1 and 2, respectively. Runoff and ground water samples were taken from a subarea of 4.0 m x 22.1 m (0.01 ha) within each 0.03 ha plot (Figure 1).

Ground Water Design

In 1990, six field plots (0.03 ha) were established to obtain shallow ground water and runoff samples from the corn study. These plots were hydrologically isolated by making a 20-cm wide and 122-cm deep trench around three sides (the above-slope side and the two parallel-slope sides) of each plot using a small chain-type trencher. After trenching, a 0.38-mm thick plastic barrier was placed in the trench from the surface to a depth of 122 cm to ensure outside subsurface water from entering into the test plots. The depth of the plastic barrier was approximately 0.61 m into the fragipan to prevent the lateral movement of the perched ground water from the plot and ensure its collection.

Within each plot, a 4.1 m x 22.1 m (USLE plot) (Mutchler *et al.*, 1988) subplot was constructed for sampling runoff and ground water quality (Figure 1). Separation of the USLE plot was achieved by enclosing three sides (above-slope and two parallel-slope) with a 10-cm PVC pipe entrenched 5 cm into the soil. For ground water collection, three 5-cm PVC pipes (Schedule 40), 4.1-m long, were horizontally placed on top of the fragipan (approximately 50 cm below soil surface) perpendicular to the slope (dashed lines in Figure 1). Each lateral was placed 7.31 m apart beginning at 3.65 m from the lowest side of plot. These laterals were installed by horizontally drilling 5.0-cm holes 4.57 m starting 90 cm from the side of plot. The laterals were perforated along the upper two-thirds of the pipe's circumference and 3.65-m length by drilling 0.635-cm holes 5-cm apart. Five lines spaced 2.54 cm along the circumference possessed these perforations with adjacent lines having holes offset by 2.54 cm. Each lateral was plugged with a PVC end cap and was inserted into the 5-cm holes with the center line of perforations toward the soil surface and all the perforated length (3.65 m) within the plot allowing for the remaining 0.45 m to tie into the main. No traffic was allowed on the plots which would alter infiltration and hydraulic conductivities due to compaction. Quantities of runoff and ground water would be

more representative of true values than would conventional drainage installation techniques. Nylon stockings were placed around the pipes to prevent plugging the drainage system. Each lateral was connected into a main, and adjacent mains from adjacent plots were routed with outlets into a concrete sump. A 37.8-L stainless-steel container was positioned under each outlet to collect the ground water sample. Three sumps were constructed with concrete floors, block walls and aluminum roofs to prevent rainfall contamination into the ground water samples. Inside each sump, the two outlets were draped with a plastic shroud that covered the sampling container to further prevent sample contamination. After major rainfall events that produced ground water samples, the containers were removed and taken to the National Sedimentation Laboratory for water quality measurements. Clean containers were repositioned inside each sump.

Runoff design

The equipment used for measuring runoff and soil loss for each of the six USLE plots included collectors, approaches, end plates, 0.15-m H-flumes, FW-1 water-level recorders with potentiometers, runoff splitters, Isco composite water samplers, and dataloggers. Collectors, approaches, end plates, flumes, and water-level recorders were constructed according to procedures in Agricultural Handbook 224 (Brakensiek *et al.*, 1979) (Figure 2). Due to the advances in microprocessor and electronic controls within the past five years, this manual was unable to provide adequate information to automate this system. Information, from Grissinger and Murphree (1991) of using commercially-available dataloggers in runoff and erosion studies, was used to automate this design. The runoff splitter, which was initially constructed and described as a modified slotted sampler/turbulence box by Murphree (Grissinger and Murphree, 1991), was used for collecting runoff outflow from the H-flume. The intake port for the composite pump sampler was mounted on this box.

A datalogger (Omnidata 516C Polycorder equipped with an analog/digital interface card) was used to collect rainfall and runoff data and to independently control pump sampling equipment. One datalogger was used to collect data from two runoff plots and a tipping-bucket rain gauge. Two Isco (Model 2710) composite water samplers and two potentiometers from the FW-1 water-level recorders were wired into the analog/digital interface card of the datalogger. The datalogger and water samplers were placed in a grounded, insulated instrument shelter positioned at the lower end between the plots (Figure 3). Power for the datalogger and the pumps on the water samplers was supplied from 12-V DC battery which was kept recharged by 12-V solar panels mounted to the roof of the shelter. The rain gauge was wired into an accumulator that was wired into each of the digital inputs of the datalogger's interface card. Two other shelters with duplicate equipment were used for the remaining four plots, except no rain gauge was required.

One datalogger was programmed to continuously monitor the rain gauge. When rainfall was detected, the datalogger recorded the count and processed the count into the converted measurement (1 count = 0.25 mm) and stored for later retrieval.

At the lower end of each plot, an H-flume and stilling well were mounted onto a collector and approach. Inside the stilling well, a potentiometric float and pulley were installed for measuring the water level. The potentiometric output from the FW-1 water-level recorder is proportional to the stage or height of the float in the stilling well. As a backup, the float height was also recorded on the strip chart. The potentiometer was wired to the analog and excitation port of the analog/digital datalogger (Omnidata 516C Polycorder). An Isco composite water sampler was wired to the digital output of the datalogger.

A complete description of the programming of the dataloggers was provided by Grissinger and Murphree (1991). Using a modified version of their program, the three dataloggers read the voltages of the potentiometers every 30 seconds. When runoff was detected, the dataloggers calculated discharge rates using appropriate equations to convert potentiometric voltages to flow depths and flow depths to discharge rates. For each time interval, discharge volumes were calculated. These incremental discharge volumes were summed and compared to a predefined flow limit. When the cumulative discharges (summation of incremental discharges over 30 second intervals) equaled or exceeded the flow limit, a pulse from the dataloggers activated the water samplers that took a preprogrammed quantity of water from the runoff splitter. The cumulative discharge was reset to zero. As the runoff event continued, the incremental discharges were again summed until the cumulative discharges equaled or exceeded the flow limits that again triggered the water samplers and allowed another incremental quantity of water from the runoff splitter into the water samplers. This cycle continued until runoff ceased. The collection of the discharge-weighted composite samples was necessary to reduce the sample analysis load to levels realistic to available resources. The dataloggers stored the incremental discharge rates and cumulative discharge volumes for each runoff event. During post-storm plot servicing, the data was downloaded from the dataloggers into a Polycorder 600 digital unit (from Omnidata) for transfer to the computers at the National Sedimentation Laboratory for further analyses.

Water samples from the Isco samplers were collected in 37.8-L stainless-steel containers positioned under the inflow of the Isco sampler. These containers were removed with the composite water samples and transported to the lab for sediment load and water quality analyses. The number of pumps, which represented the number of times the cumulative discharge equaled the flow limit during the runoff event, was recorded from the LED display of the Isco sampler. The sampler was reset to zero and clean containers were repositioned under the inflow for preparation of the next runoff event.

Further Installation

Outside the USLE plot, but inside the isolated 0.03 ha area, a series of piezometers, suction tubes, tensiometers, and wave guides for time domain reflectometry will be installed near the center of each plot after the 1991 harvest. The devices will be installed at 0.15, 0.30, 0.46, 0.61, 0.91, 1.22 and 1.52-m depths into the soil profile

and 0.91 m spacing within the crop rows. Piezometers will be used to measure hydraulic head gradients and obtain water samples for nitrate, pesticide, and other major plant nutrient analysis. Soil suction cups will be used to collect ground water samples when piezometers remain dry after storm event. Tensiometers will be used to determine unsaturated moisture condition and develop soil matrix potential. Time domain reflectometry will be used to measure unsaturated volumetric water contents and composite dielectric constants.

RECOMMENDATIONS

Several modifications of commercially available equipment were necessary for the use of the dataloggers in this study. The analog/digital interface board did not provide continuous pulse counting that was necessary for the tipping-bucket rain gauge. An accumulator to interface the rain gauge to the datalogger was developed and supplied by Omnidata for this purpose. Also, the dataloggers' power was modified to accept 12-V DC to extend unattended operation in the field. Various dataloggers such as the Basic Data Recorders (BDR) used by U.S. Geological Survey, or the CR10 and 21X from Campbell Scientific (CR10 and 21X) need no modification and provide many of these same capabilities.

A minor problem with the dataloggers was the periodically random renaming of subroutines with an extended character that caused the incomplete performance of the program. Either static electricity or power drain using the same power source for the two Isco pumps and datalogger was suspected to cause the hardware errors. Since this renaming appeared at random among the subroutines, the programming was not a problem. Dataloggers were wrapped in static-free towels as a possible remedy. A separate power source may eventually be necessary to separate the datalogger from the pumps.

SUMMARY

A field acquisition system was developed and constructed to sample and quantify both surface runoff and shallow ground water from erosion plots of a conservation tillage study. Advantages of this system included minimum labor requirements for data reduction due to taking composite water samples, continuous automation of water sampling during runoff events, and uniform time base for all plots. Although not completely satisfactory due to the periodic erroneous renaming of subroutines, the acquisition system provided accurate and reliable results.

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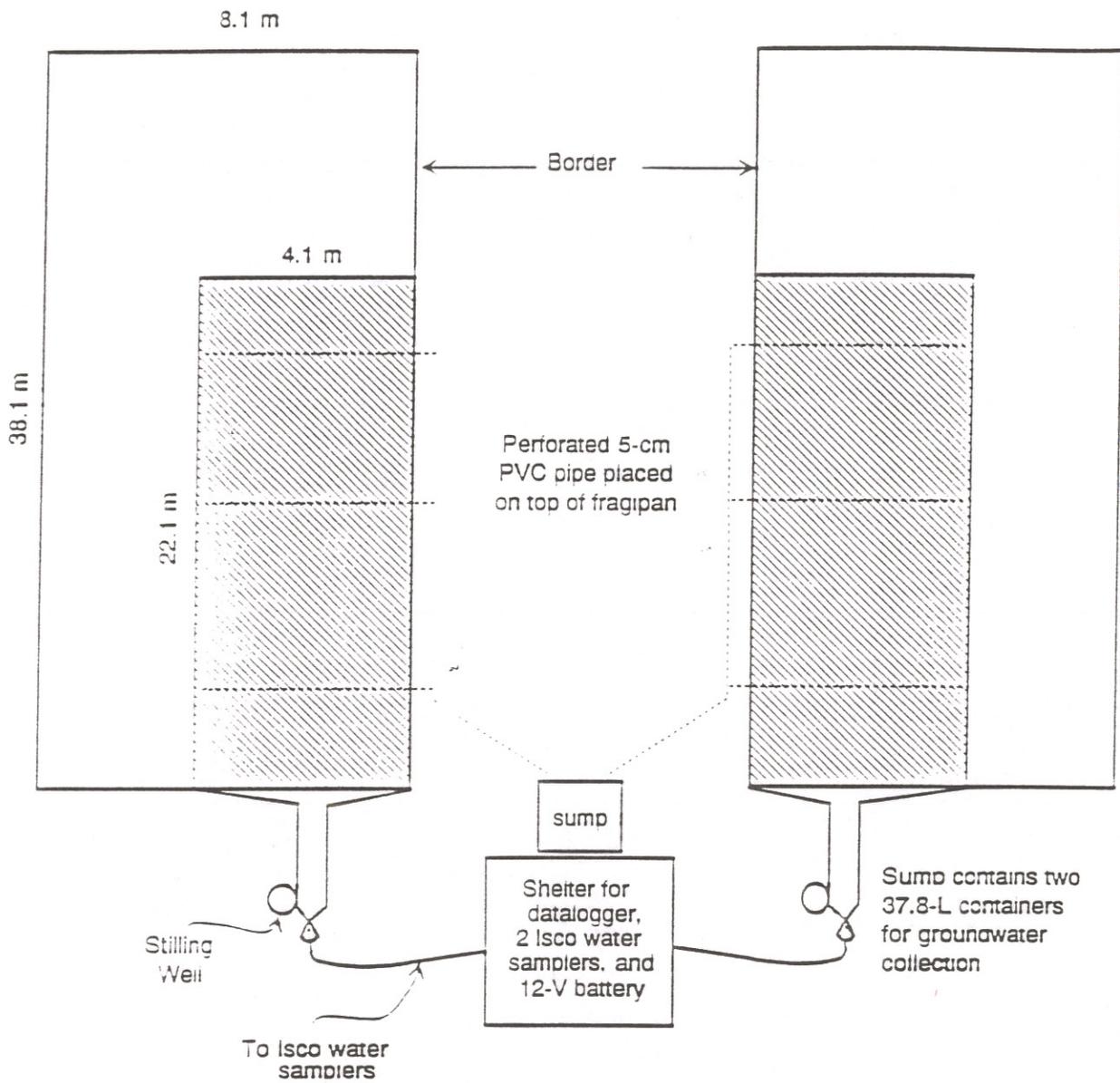


Figure 1. Two of the six water quality plots with locations of sumps, drainage tubes, and runoff samplers.

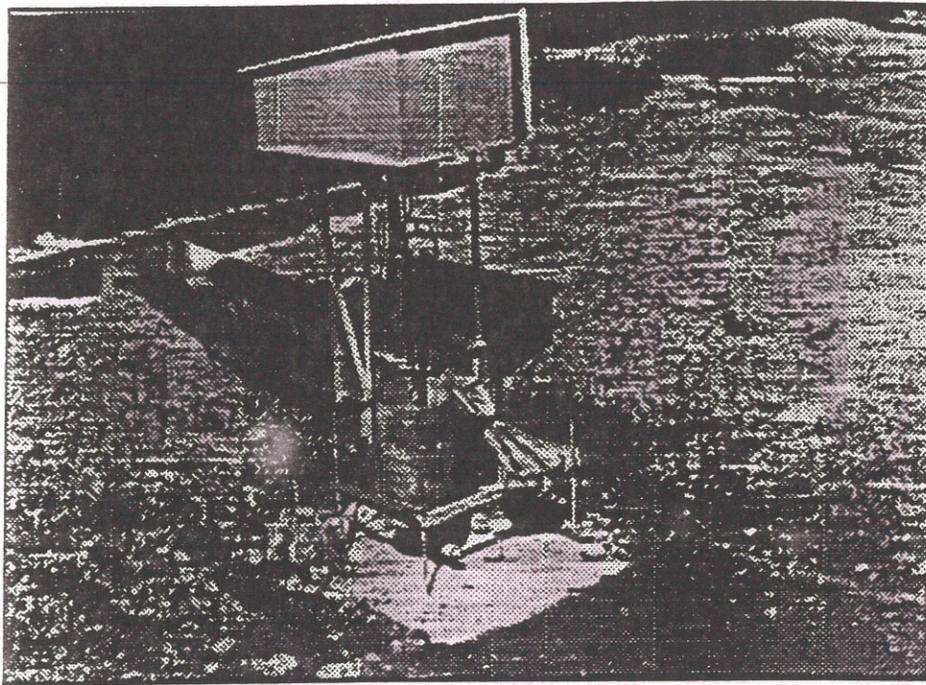


Figure 2. View of the collector, approach, H-flume, stilling well, shelter for FW-1 recorder, and the water splitter with copper tubing routed to Isco composite water sampler.

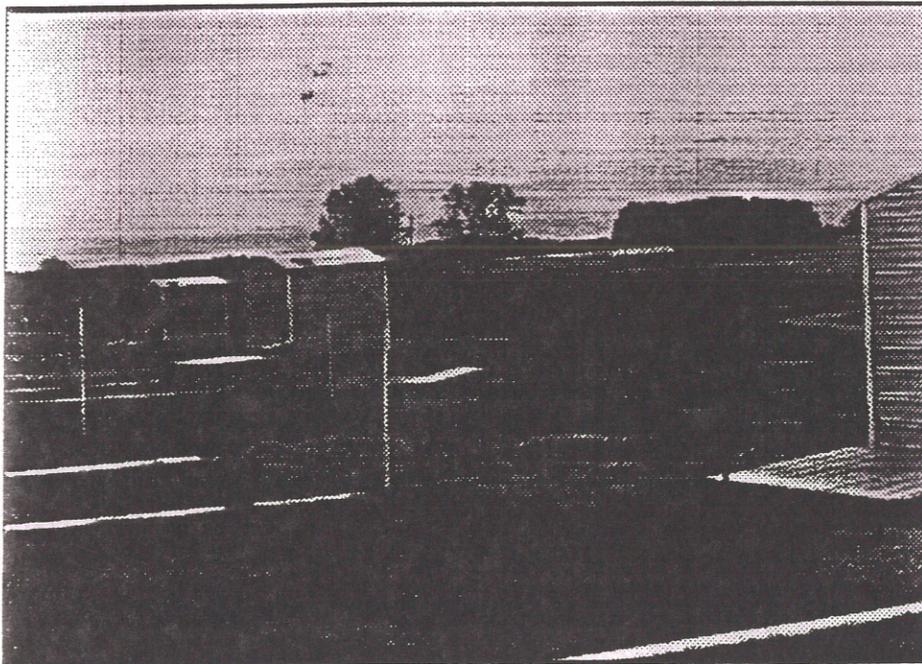


Figure 3. View of the shelters for the dataloggers, water samplers, and batteries with solar panels mounted to the roofs, and the outlets of five of the soil erosion plots.

