

# AGRICHEMICAL TRANSPORT TO GROUNDWATER THROUGH COASTAL PLAIN SOILS

D. D. Bosch, C. C. Truman

**ABSTRACT.** A 1-ha field with Pine Flat loamy sand (coarse-loamy, siliceous, thermic Typic Paleudult) and Troup loamy sand (loamy, siliceous, thermic Grossarenic Kandiudult) surface soils, located near Plains, Georgia, was studied for four years (1993 to 1996) to evaluate potential agrichemical transport to groundwater. The field was managed to produce summer corn and winter wheat. Commercial fertilizer, the herbicide atrazine, and the insecticide carbofuran were applied to the field in 1993, 1994, and 1995. Average annual application rates were 266 kg nitrogen ha<sup>-1</sup>, 2.5 kg atrazine ha<sup>-1</sup>, and 2.4 kg carbofuran ha<sup>-1</sup>. Monthly soil-water and groundwater samples were collected. The samples were analyzed for nitrate nitrogen (NO<sub>3</sub><sup>-</sup>-N), chloride, atrazine, carbofuran, and deethylatrazine (DEA). Soil-water and groundwater samples indicated elevated NO<sub>3</sub><sup>-</sup>-N concentrations (>5 ppm) in the vadose zone at 4.3 m and in the aquifer at 10 m (>4 ppm). Of the studied pesticides, carbofuran and DEA were observed at the greatest concentrations in groundwater.

Both NO<sub>3</sub><sup>-</sup>-N and pesticides were transported during groundwater recharge following periods of excess precipitation. Peak pesticide concentrations in groundwater were observed in late 1994, driven by a large precipitation event in July of 1994 when 565 mm of rain fell over a 4-day period. Atrazine and carbofuran concentrations in groundwater did not exceed the EPA maximum contaminant levels of 3 ppb and 40 ppb, respectively. Spatially averaged concentrations observed in monthly groundwater collected directly below the field were well below these standards. Concentrations of NO<sub>3</sub><sup>-</sup>-N, atrazine, DEA, and carbofuran observed in groundwater from the on-field wells were significantly different from up-gradient and down-gradient concentrations ( $p = 0.05$ ). These data indicate a significant impact to the local groundwater. Nitrate N was transported down-gradient from the field at the largest concentrations. Peak concentrations of atrazine and DEA were simultaneously observed in the groundwater, indicating similar transport rates for both compounds and rapid transformation from atrazine into DEA in the root-zone.

**Keywords.** Water quality, Pesticides, Modeling, Preferential transport.

The Southern Coastal Plain of the U.S. is a physiographic region with a wide range of soil types and crop management systems. The region's abundant rainfall and long growing season are conducive to intense crop production. Production agriculture in this area has significant economic impact on the region. However, the intense use of agricultural chemicals, fertilizer, and pesticides has created concern over possible groundwater contamination.

The Clayton and Claiborne aquifers of Southwestern Georgia are important sources of groundwater, supplying most of the municipal, industrial, agricultural, and domestic

water for the area (McFadden and Perriello, 1983). In this area, the sedimentary deposits in which these aquifers reside gently dip to the southeast from the central portion of Georgia. These aquifers outcrop and are recharged in a belt trending southwest-northeast through the center of the state (Beck et al., 1985). Land use in this area is of great importance to the citizens of South Georgia and North Florida.

The presence of agricultural chemicals in drinking water supplies creates public health concerns. Health risks increase in regions with geologic features conducive to rapid movement of water from the soil surface to aquifers used for drinking water. The types and concentrations of nutrients and pesticides found in streams and groundwater are closely linked to land use and the chemicals applied. In studies completed in 1998 by the National Water-Quality Assessment (NAWQA) program, nitrate and pesticides were most frequently detected in shallow groundwater, less than 30 m below the land surface (USGS, 1999). Along with the concerns this raises over drinking water quality, groundwater contamination can also have implications for surface water. Excess nutrient pollution from surface runoff is believed to be the primary contributor to hypoxia in coastal waters (Rayl, 2000). Reintroduction of nitrogen and pesticides from groundwater into surface drainages through groundwater discharge into the streams can be a significant component of the overall loading to the stream (USGS, 1999) and thus may play a role in the coastal hypoxia problems.

---

Article was submitted for review in November 2001; approved for publication by the Soil & Water Division of ASAE in June 2002. Contribution from the USDA-ARS, Southeast Watershed Research Laboratory, in cooperation with University of Georgia Coastal Plain Experiment Station.

Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the products listed by USDA. All programs and services of the USDA are offered on a nondiscriminatory basis without regard to race, color, national origin, religion, sex, age, marital status, or handicap.

The authors are **David D. Bosch, ASAE Member Engineer**, Research Hydraulic Engineer, and **Clinton C. Truman**, Soil Scientist, USDA-ARS, Southeast Watershed Research Laboratory, Tifton, Georgia. **Corresponding author:** David D. Bosch, USDA-ARS, Southeast Watershed Research Laboratory, P.O. Box 946, Tifton, GA 31793; phone: 229-386-3899; fax: 229-386-7294; e-mail: dbosch@tifton.usda.gov.

Agrichemical leaching is a potential problem in production areas of southern Georgia where sandy soils predominate. High soil hydraulic conductivities, coupled with a water table near the soil surface and large precipitation rates, can lead to rapid percolation from the root zone and to groundwater (Leonard et al., 1979; Leonard et al., 1988). Under these conditions, mobile and persistent compounds are transported by unsaturated flow to shallow water tables (USGS, 1999). In cases where the water table is near the soil surface (<30 m), the potential for groundwater contamination is high. This can be attributed to the short lapse between the time when the chemical is applied at the surface and the time it takes for water to flow from the surface to the water table. Other factors, such as the time between pesticide application and the first major rainfall event after application, soil organic matter content, rainfall volume and intensity, and soil hydraulic conductivity, also affect potential contamination (Kamrin, 1997).

Because of health issues related to nitrate concentrations in drinking water, elevated nitrate concentrations in groundwater in agricultural regions continue to be of concern (USGS, 1999). The NAQWA survey states that some of the highest nitrate concentrations were observed in shallow groundwater in the Atlantic Coastal Plain. Studies in the region indicate that groundwater nitrate nitrogen ( $\text{NO}_3^-$ -N) concentrations can exceed the EPA national primary drinking water maximum contaminant level (MCL) of 10 ppm (Hubbard and Sheridan, 1989). Pesticides in groundwater also warrant public concern. Two pesticides of particular interest because of their widespread use are atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methyl carbamate). Atrazine is used throughout the world to control a variety of weeds. Surveys conducted by Goodrich et al. (1991) and by USEPA (1990) indicated that atrazine is frequently detected in groundwater samples during monitoring studies. Carbofuran is an insecticide used for insect, mite, and nematode control in maize and other crops. Carbofuran is generally considered more mobile but less persistent than atrazine. Both pesticides are mobile in soil, but with fairly rapid decay rates. Measured half lives for atrazine range from 60 to 100 days, with a solubility of  $28 \text{ mg L}^{-1}$  and an adsorption coefficient of 100 (Kamrin, 1997). Half lives for carbofuran range from 30 to 120 days, while its solubility is  $320 \text{ mg L}^{-1}$  and its adsorption coefficient is 22 (Kamrin, 1997). MCLs for atrazine and carbofuran are 3 ppb and 40 ppb, respectively ([www.epa.gov/safewater/](http://www.epa.gov/safewater/)).

Within the soil, pesticides can be degraded and transformed into other compounds (metabolites). Concerns over total pesticide concentrations, parent and metabolite, are increasing. Initial pesticide studies rarely measured pesticide metabolites. This was largely due to less-sensitive analytical instruments and methods, and an inadequate understanding of pesticide transformations. However, we are now aware that health concerns related to the metabolites are often as great or greater than those related to parent compounds. Because of the wide use of atrazine, byproducts of this compound are of particular interest. Conversions of atrazine into deethylatrazine (DEA) (2-amino-4-chloro-6-isopropylanine-s-triazine) and deisopropylatrazine (DIA) (2-amino-4-chloro-6-ethylamino-s-triazine) by soil microorganisms are the main biotic dissipation pathways of atrazine in the soil environment (Jayachandran et al., 1994).

This transformation is expected to take place near the soil surface, where microbial activity is the highest. DEA is about 10 times more soluble than atrazine (Gaynor et al., 1995), and leaching rates of DEA can exceed those of atrazine (Fermanich et al., 1996). Atrazine can also be transformed through hydrolysis into hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine). Chlorinated atrazine metabolites possess a similar health risk to that of atrazine (Belluck et al., 1991), and their presence in groundwater has been documented (Adams and Thurman, 1991; Jayachandran et al., 1994; Gaynor et al., 1995). Hydroxyatrazine is more strongly bound to the soil than atrazine, DEA, and DIA, and therefore is less mobile and of less environmental concern than the other compounds (Jayachandran et al., 1994). Of the two metabolites, DEA and DIA, previous research indicates that DEA is the greatest risk to groundwater (Bosch et al., 2000; Jayachandran et al., 1994).

The objectives of this study were:

- To determine transport rates and pathways of  $\text{NO}_3^-$ -N, chloride, and selected pesticides through the vadose zone and into groundwater below an agriculturally managed field in a Coastal Plain recharge zone.
- To relate transport rate and timing to chemical characteristics, media properties, and climatic patterns.

## METHODS

### SITE DESCRIPTION AND CHARACTERIZATION

A 1-ha field located near Plains, Georgia, was selected for the study (fig. 1). The site is located in the Fall Line Hills geographic province of west-central Georgia (Clark and Zisa, 1976) and is within the Claiborne aquifer recharge area. Surface soils at the site include a Pine Flat loamy sand (coarse-loamy, siliceous, thermic Typic Paleudult) and a Troup loamy sand (loamy, siliceous, thermic Grossarenic Kandudult). The unsaturated zone consists of alternating and intermittent layers of sand, clayey sand, and clay (Hicks et al., 1991). The saturated zone is composed of fine-to-coarse quartz sands with intermittent layers of clay (Hicks et al., 1991). The water table of the Claiborne aquifer begins approximately 10 m below the ground surface and ranges in thickness from 3 to 5 m. The surface aquifer is isolated from the deeper Clayton aquifer by a relatively dense clay with an estimated thickness of 20 m (Hicks et al., 1991). Groundwater flow at the site was from the northwest to the southeast.

The field was fallow for many years prior to the study. The field was surrounded by forested and non-tilled land, minimizing the likelihood of off-site inputs. The surface soil is composed of a highly permeable loamy sand (Bosch and West, 1998; Shaw et al., 2000). Soil cores were collected throughout the field for physical property and hydraulic characterization. Soil texture characterization and classification was done through analysis of samples collected at eight sites located throughout the field (fig. 1). Details of the characterizations are provided in Bosch and West (1998) and Shaw et al. (2000). Mean sea level elevation ranges from 132 m on the north side of the field to 130 m on the south side, with an average ground slope of 1.2%. While surface runoff was expected to be small, a soil berm was constructed around the perimeter of the field to ensure runoff collection and

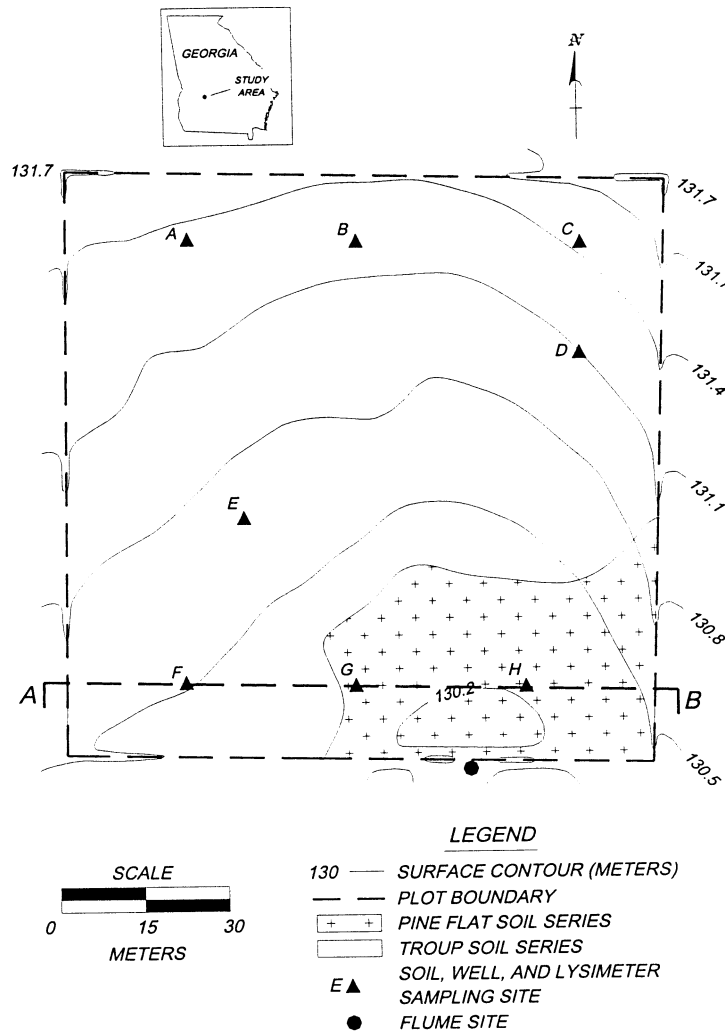


Figure 1. Field configuration, site locations, and soil definitions.

measurement. Surface runoff during the study period was found to be negligible (Bosch et al., 2000).

#### SITE MANAGEMENT

A cropping sequence of summer corn (*Zea mays* L.) and winter wheat was followed from 1993 through 1996. Following corn harvest in August or early September, wheat was planted in late November to early December. While vadose zone and groundwater samples were collected through August 1996, no tillage or chemical application took place after wheat harvest in the spring of 1996. Conventional agricultural management practices were used for tillage,

fertilization, planting, and harvest. The field was fertilized for corn each spring from 1993 to 1995 (table 1).

The herbicide atrazine and the insecticide carbofuran were applied separately by a tractor-mounted sprayer each year prior to planting (table 2). The pesticides were surface applied and incorporated 5 cm into the soil. Irrigation was supplied each year within 4 hrs after planting to minimize pesticide volatilization losses (table 2). During the corn growing season, irrigation was applied as needed to prevent water stress. A 50 m well tapping the Clayton aquifer provided water to the center-pivot irrigation system. The well was screened below the confining unit, which separated the Clayton and Claiborne aquifers. Precipitation measure-

Table 1. Fertilization dates and application rates from 1993 to 1995.

Year	First Application		Second Application		Third Application		Fourth Application		Annual Total N (kg ha <sup>-1</sup> )
	Date	Rate (kg ha <sup>-1</sup> )	Date	Rate (kg ha <sup>-1</sup> )	Date	Rate (kg ha <sup>-1</sup> )	Date	Rate (kg ha <sup>-1</sup> )	
1993	14 April	1045 <sup>[a]</sup>	25 May	500 <sup>[b]</sup>	9 June	140 <sup>[c]</sup>	none	0	231
1994	18 March	840 <sup>[a]</sup>	21 April	675 <sup>[b]</sup>	5 May	235 <sup>[b]</sup>	5 May	145 <sup>[c]</sup>	358
1995	17 March	610 <sup>[a]</sup>	24 April	490 <sup>[b]</sup>	26 April	310 <sup>[a]</sup>	none	0	210

[a] 5-10-15 (N-P-K) formulation.

[b] Ammonium nitrate (33% N).

[c] 10-10-10 (N-P-K) formulation.

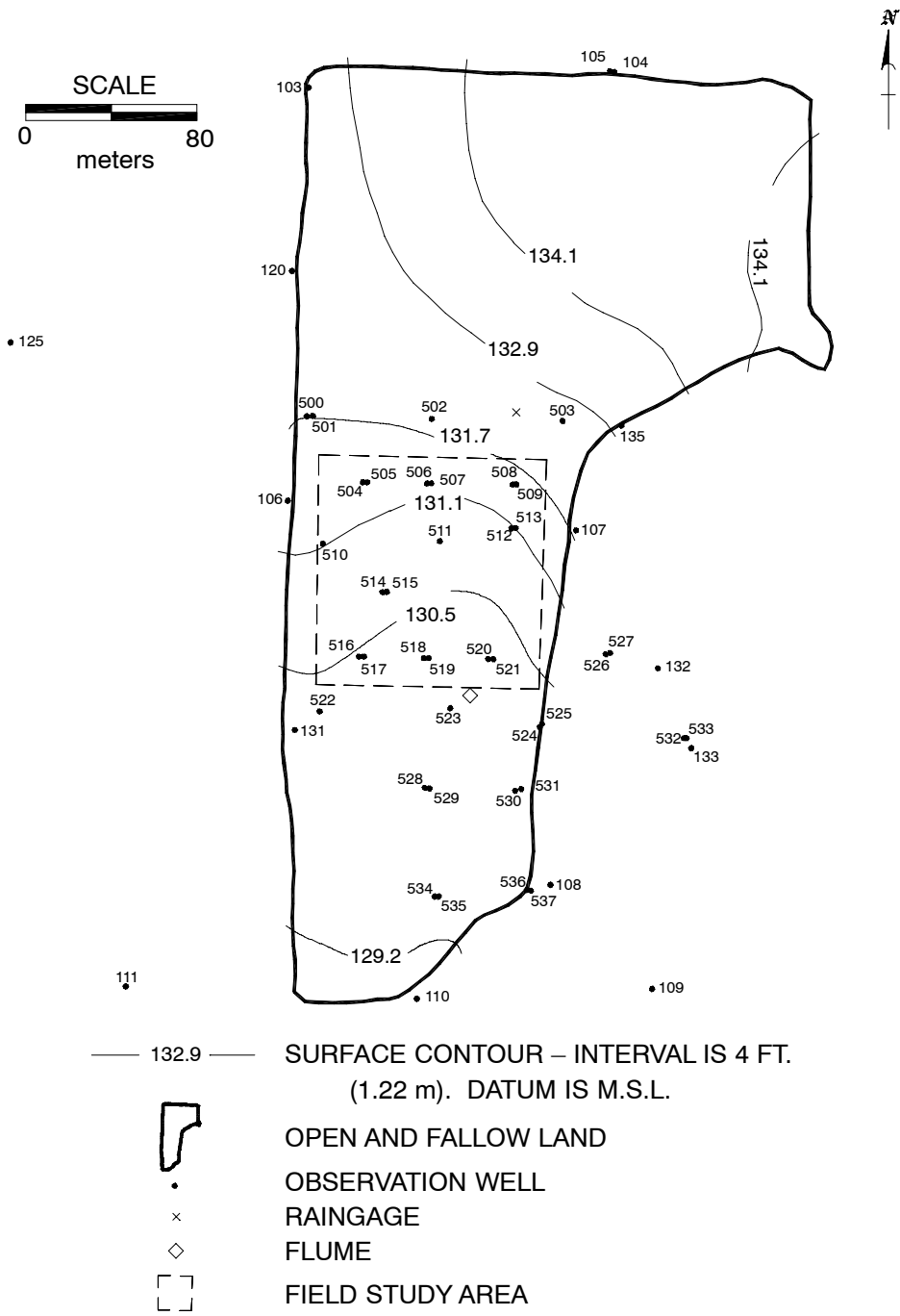


Figure 2. Location of wells within and surrounding the field.

Table 2. Annual pesticide and water inputs from 1993 to 1996.

Year	Application Date	Application Rate		Irrigation After Pesticide Application (cm)	Annual Rainfall (cm)	Annual Irrigation (cm)
		Atrazine (kg ha <sup>-1</sup> )	Carbofuran (kg ha <sup>-1</sup> )			
1993	4 May	2.4	2.2	0.7	149	39
1994	22 March	2.2	2.2	0.7	196	27
1995	21 March	2.8	2.8	5.2	93	41
1996	none	0	0	0	125	20

ments were made using a recording tipping-bucket rain gauge located at the site. The gauge recorded 5-min rainfall totals. Irrigation volumes were measured using eight stan-

dard manual rain gauges evenly distributed throughout the field.

## SAMPLE COLLECTION

Eight permanent monitoring stations were selected within the field (fig. 1). At each site, two 51 mm i.d. PVC wells were installed into the Claiborne aquifer. The screened intervals for the paired wells were from 10.5 to 13 m and from 11 to 14 m from the soil surface. The wells were constructed with sealed interlocking pipe sections, with 10.5 to 11 m of solid monitoring pipe and a 1.5 m screened section for the shallow well and a 3 m screened section for the deeper well. The screened section contained 0.2 mm slots.

The sites were identified based upon soil type in the top 1.5 m of the profile and proximity to other geographical features in the subsurface (Bosch et al., 2000). The transport rate at sites A to F was expected to be more rapid because of a sandier surface soil, while the transport rate at sites G and H was expected to be slower. Additional wells were located around the perimeter of the field to intercept groundwater flowing into and out of the field (fig. 2). Groundwater flow was from the northwest to the southeast. Water samples were collected monthly from April 1993 through August 1996. Because of difficulty in instrumenting the field, the first set of samples from wells located within the field were not collected until 16 June 1993. At each set of paired wells, a 500 mL water sample was collected from the shallowest well containing adequate water. Water was withdrawn from the well until a steady pH and temperature were observed, at which time the sample was collected. The sample was analyzed for atrazine, carbofuran, chloride ( $\text{Cl}^-$ ), and nitrate N ( $\text{NO}_3^-$ -N) concentrations. Samples were collected in glass bottles, sealed, transported to the laboratory on ice in coolers, and refrigerated until analyzed.

Suction lysimeters were installed at each of the eight field sites (A–H) at 0.2, 0.6, 1.2, 1.8, and 2.5 m (fig. 1). The suction lysimeters were tipped with 100 kPa porous ceramic cups. Along with the shallow lysimeters at each of the eight field sites (A–H), 12 additional sites were identified for installation of suction lysimeters within the deeper vadose zone (fig. 3). These lysimeters were located along a transect through sites F, G, and H, labeled line A–B on figures 1 and 3. Prior research at the site indicated the presence of clay lenses within the subsurface, which were believed to influence water flow and chemical transport within the vadose zone (Bosch and West, 1998; Bosch et al., 2000). Ground-penetrating radar and soil sampling were used to identify the horizontal extent and approximate depth of subsurface clay lenses. The suction lysimeters were installed along the upper and lower ends of each sloping lens and at key locations outside of the field. Lysimeters were also installed at equivalent depths within the vadose zone where no clay lenses existed to collect soil–water samples for comparison to those collected along the clay lenses. These lysimeters were installed at various depths: lysimeters 603, 605, 607, 609, and 613 were at 4.3 m; 606 was at 4.5 m; 602, 604, 608, 610, and 611 were at 5.2 m; and 612 was at 6.1 m.

Monthly soil–water samples were collected using both sets of suction lysimeters from May 1993 to August 1996. The first set of lysimeter samples was collected on 20 May 1993, five days prior to the first fertilization. A vacuum of 70 cm was created in the lysimeters 24 hrs prior to collecting the sample. Samples were pumped into sterile glass jars using a vacuum pump. Samples were immediately stored on ice and transported to laboratory facilities for analysis. Attempts were made to collect samples from the shallow lysimeters

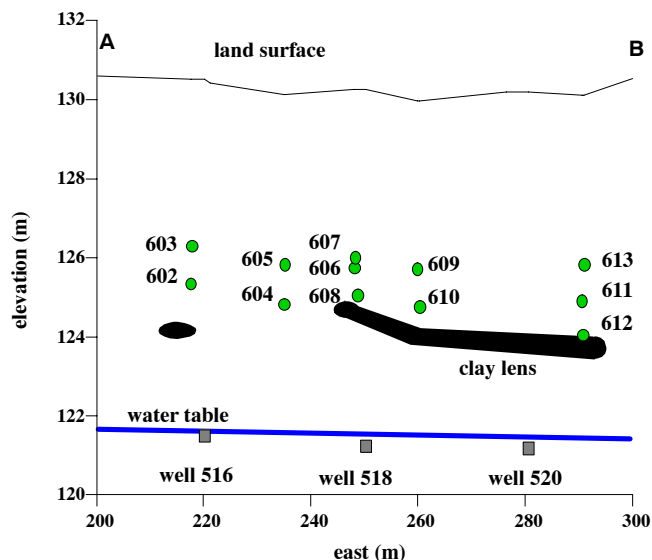


Figure 3. Vadose zone lysimeters and top of the well screen for sample sites located along a transect (A–B) crossing through sites F, G, and H across the south end of the field.

(<2.5 m) throughout 1993 and 1994. However, because of the low water–holding capacity of the sandy soils at the site, very few actual samples were collected from these lysimeters during this time. The majority of the successful attempts to collect samples were from the 0.2 m lysimeters, those most influenced by irrigation and rainfall. Because of the difficulty in collecting samples, regular monthly sampling from the shallow lysimeters was discontinued in 1994. Sampling from the deeper lysimeters (>4.0 m), located in the southern half of the field (fig. 3), was continued on a monthly basis throughout the study period. We were able to collect soil–water from these lysimeters during most sampling attempts.

## ANALYTICAL METHODS

The water samples were analyzed for  $\text{NO}_3^-$ -N,  $\text{Cl}^-$ , atrazine, carbofuran, and DEA. The first 100 mL of each water sample was used for pesticide analysis. If sufficient sample remained, they were also tested for  $\text{NO}_3^-$ -N and  $\text{Cl}^-$ . Nitrate N and  $\text{Cl}^-$  were analyzed using standard colorimetric methods on a Lachat flow injection system. The enzyme-linked immunosorbent assay (ELISA) method was used to screen the water samples for atrazine and carbofuran concentration. The ELISA method used was the magnetic particle–based Rapid Assay manufactured by Ohmicron Corporation. Tests performed by the laboratory that processed the samples for this study found good agreement between ELISA measurements and chromatographic techniques when used for the determination of atrazine between 0.5 and 5 ppb (Marti and Leonard, 1992). Other tests of the atrazine ELISA method have found it to yield results slightly greater than those from capillary column gas chromatography (GC). This can be attributed to the fact that the ELISA test reacts to atrazine metabolites as well as to the parent compound. All samples that tested positive to the atrazine ELISA test were analyzed for atrazine and DEA using GC techniques. Carbofuran was analyzed only with the ELISA method. The ELISA test for carbofuran also reacts to metabolites of carbofuran, but only if the by–products exist

in high concentrations (1.2 to 3000 ppb). Method detection limits for atrazine and carbofuran were 0.05 ppb using the ELISA method, while on the GC they were 0.09 ppb for atrazine and 0.10 ppb for DEA.

## RESULTS

### SOIL CHARACTERIZATION

The two soils identified in the field were a Pine Flat loamy sand (coarse-loamy, siliceous, thermic Typic Paleudult) and a Troup loamy sand (loamy, siliceous, thermic Grossarenic Kandiodult) (fig. 1). The Troup soil occupied approximately 84% of the field area. The Pine Flat soil in the southeast corner of the field contained a well-developed Bt horizon between 50 and 250 cm that contained up to 28% clay (Bosch and West, 1998). The Bt horizon in the Troup loamy sand occurred at greater depth (>100 cm) and typically had less clay (~15%) and a more rapid saturated hydraulic conductivity throughout (Bosch and West, 1998). The saturated hydraulic conductivity of the Troup loamy sand was approximately three times that of the Pine Flat loamy sand in the top 0.5 m of the profile (150 cm hr<sup>-1</sup> vs. 50 cm hr<sup>-1</sup>), while it was approximately fifteen times that of the Pine Flat soil (150 cm hr<sup>-1</sup> vs. 10 cm hr<sup>-1</sup>) in the zone from 1.4 to 2.0 m.

### CLIMATIC CONDITIONS

Precipitation and irrigation patterns from 1993 to 1996 were examined (fig. 4). The average annual precipitation is 1240 mm. Total water (i.e., precipitation + irrigation) exceeded this average each year (table 2). Precipitation patterns in the first 90 days of each year (January through March) were near normal, except in 1993 when the March precipitation was above normal (fig. 4). Total water received from April to June exceeded mean precipitation each year. Total water in June 1993 was almost four times the mean precipitation (418 mm vs. 114 mm), while total water in July 1994 was over five times the normal precipitation (707 mm vs. 130 mm). Most of the water received in July 1994 occurred during a single precipitation event, when 565 mm

of rainfall was received from 3 to 6 July. Total water in May 1996 was three times the normal precipitation (273 mm vs. 91 mm).

Temperature data collected at the University of Georgia Plains Experiment Station indicated air temperatures were consistent with long-term records. Average monthly maximum air temperatures ranged from a high of 33°C in July to a low of 14°C in January, while average monthly minimum air temperatures ranged from a high of 21°C in July to a low of 2°C in January.

### VADOSE ZONE OBSERVATIONS

Over the 4-year study period, 611 lysimeter samples were collected. Of the 611 samples, 233 tested positive for either atrazine or carbofuran, and 569 were analyzed for NO<sub>3</sub><sup>-</sup>-N. Average NO<sub>3</sub><sup>-</sup>-N concentration in the deep lysimeter (>4 m) samples was 6 ppm over the study period. Of these samples, 13% exceeded 10 ppm NO<sub>3</sub><sup>-</sup>-N, while 2% exceeded 20 ppm.

The increase in chemical concentrations in soil-water collected from the shallow (<2.5 m) lysimeters was rapid (within the first month). However, data from these lysimeters was very limited due to the problems previously described. Increases in chemical concentrations in the vadose zone soil-water below 4 m were first observed in January 1994, seven months after the first chemical applications, as illustrated by concentrations observed in lysimeter 605 (fig. 5). Some lysimeter concentrations exhibited a cyclic trend in NO<sub>3</sub><sup>-</sup>-N, likely related to spring fertilization and periods of precipitation excess when rainfall exceeded evapotranspiration demand. Nitrate N concentrations in many of the August 1993 soil-water samples collected from lysimeters below 4 m were above 5 ppm. Samples collected prior to this date were not large enough for both pesticide and nutrient analysis. Because of the large precipitation event in June 1993, the relatively high concentrations observed were likely attributable to the first year's fertilizations. Other possible explanations for the initial NO<sub>3</sub><sup>-</sup>-N include residual N in the profile and mineralization of organic matter. However, it is unlikely that these sources would have led to the concentrations observed.

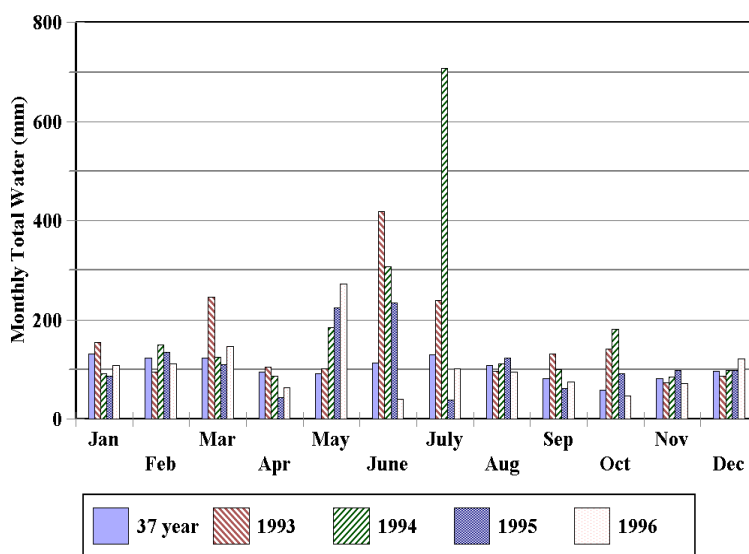


Figure 4. Monthly total field water (precipitation + irrigation), 1993 to 1996, and the 37-year average monthly precipitation from 1959 to 1995.

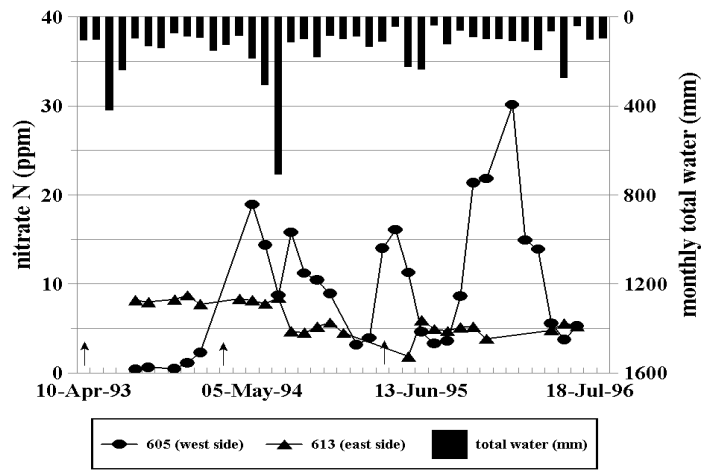


Figure 5. Measured  $\text{NO}_3^-$ -N concentrations in lysimeter 605 on the west side of the field (Troup soil) and in lysimeter 613 on the east side of the field (Pine Flat soil), both at 4.3 m depth, and monthly total water (precipitation + irrigation). The first fertilizer application of each year is marked with arrows on the x-axis.

Several lysimeters exhibited a decrease in  $\text{NO}_3^-$ -N concentration over the study period, beginning at approximately 7 ppm and ending near 5 ppm, similar to the trend shown for 613 (fig. 5). Temporal patterns in  $\text{Cl}^-$  concentrations in the deeper lysimeters were similar to those observed in  $\text{NO}_3^-$ -N.

The first vadose zone observations of pesticide concentrations above the 0.05 ppb ELISA detection limits were made in July 1994 at lysimeters 604 and 609, 15 months after the first application. The following month, atrazine was detected in all lysimeter samples. Peak pesticide concentrations were observed at most lysimeters in the summer of 1994, similar to that observed at 602 (fig. 6). This was likely due to the heavy rain received in July 1994. The greatest observed concentration of carbofuran in the deeper lysimeters was 296 ppb, observed at lysimeter 605, which was at 4.3 m, collected in July 1995. Similar to the  $\text{NO}_3^-$ -N observations, temporal trends in pesticide transport appear to have been driven by excess precipitation. However, annual increases in pesticide concentrations were not observed. Rather, pesticide

transport appeared to be more sensitive to other management and climatic factors such as tillage, organic matter concentration, and soil temperature.

Comparisons were made among lysimeters at equivalent depths across the field to determine if soil differences were affecting agrichemical concentrations in the subsurface. Soil-water samples from lysimeters 603, 605, 607, 609, and 613 (fig. 3) at 4.3 m depth indicated greater concentrations of  $\text{NO}_3^-$ -N,  $\text{Cl}^-$ , atrazine, and carbofuran along the west side of the field. Few samples could be collected at site 603 due to low soil-water conditions. Of the samples that were collected from 603,  $\text{NO}_3^-$ -N ranged between 7 and 18 ppm,  $\text{Cl}^-$  ranged from 5 to 15 ppm, and pesticide concentrations were below detection limits. Of the lysimeters installed at 4.3 m, the greatest  $\text{NO}_3^-$ -N concentrations were observed at 605. Greater  $\text{NO}_3^-$ -N and pesticide concentrations were consistently observed on the west side of the field, as shown for lysimeter 605 (fig. 5). These elevated concentrations appeared to be related to surface soil texture. The surface soil texture (top 2 m) was coarser on the west side of the field than

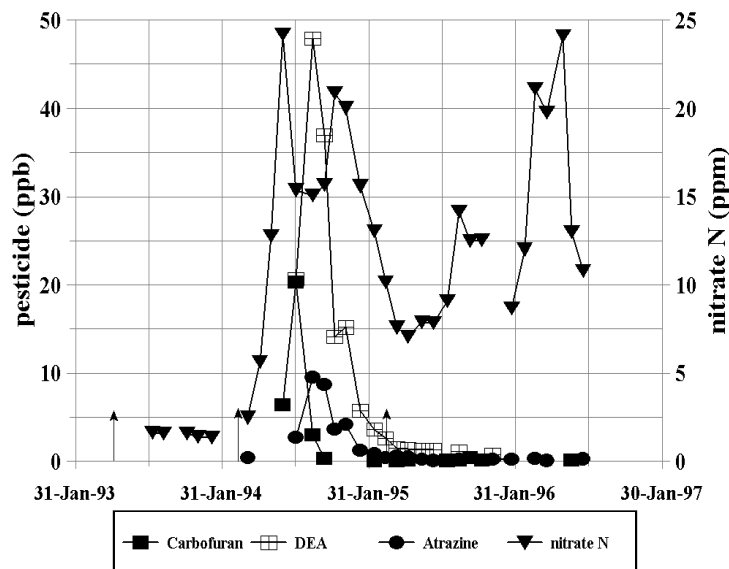


Figure 6. Measured pesticide and  $\text{NO}_3^-$ -N concentration in lysimeter 602 at 5.2 m. The annual pesticide application dates are marked with arrows along the x-axis.

**Table 3. Pesticide and NO<sub>3</sub>-N concentrations for the up-gradient, on-field, and down-gradient wells averaged over the period of study.**

	Atrazine		DEA		Carbofuran		Nitrate N	
	Mean	sd <sup>[a]</sup>	Mean	sd	Mean	sd	Mean	sd
Up-gradient	BD <sup>[b]</sup> a	0.26	BD a	0.11	BD a	0.11	1.8 a	1.6
On-field	0.11 b	0.29	0.57 b	1.14	0.42 b	1.06	4.0 b	1.6
Down-gradient	BD a	0.07	0.15 c	0.42	0.14 c	0.34	3.9 b	1.6

[a] sd = standard deviation.

[b] BD = below detection level; means followed by the same letter were not significantly different at the 5% probability level.

on the east, thus facilitating more rapid transport of agrichemicals. Similar results were found when the samples from lysimeters 602, 604, 608, 610, and 611 at 5.2 m were compared. However, for the 5.2 m lysimeters, elevated carbofuran concentrations were also observed at lysimeter 610 in the transition area between the two soils. Concentrations observed on the east side of the field were not as responsive to rainfall (fig. 5).

Comparisons were also made among lysimeters installed at different depths in vertical transects. In general, higher NO<sub>3</sub>-N concentrations were observed in lysimeters nearest the soil surface, and concentrations decreased with depth. Chloride and pesticide concentrations decreased with depth as well.

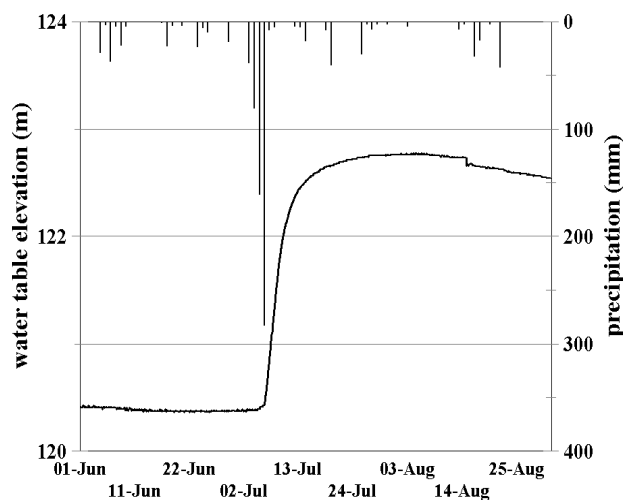
### GROUNDWATER OBSERVATIONS

Over the period of study, 791 groundwater samples were collected, 168 up-gradient from the field, 291 from on-field wells, 254 down-gradient, and 78 east of the field. In some cases, field operations prevented collecting samples from the wells located on the field. For analysis purposes, the wells were grouped as up-gradient, on-field, and down-gradient, according to their position relative to the field and the general direction of groundwater flow. The average groundwater NO<sub>3</sub>-N concentration up-gradient from the field was 1.8 ppm for the entire period of the study, on the field it was 4.0 ppm, and down-gradient it was 3.9 ppm (table 3). Nitrate N concentrations in groundwater from on-field and down-gradient wells were significantly different from up-gradient concentrations ( $p = 0.5$ ) but were not significantly different from one another. Of the samples collected from on-field wells, 12% exceeded 5 ppm, but just 1% exceeded the MCL NO<sub>3</sub>-N of 10 ppm. None of the up-gradient groundwater samples exceeded the MCL, while 1% of the samples from down-gradient wells exceeded the MCL. Nitrate N concentrations in individual samples from the field wells varied from 1 ppm to 16 ppm. The monthly field averages (the means of all of the samples collected from the on-field wells for a given sample date) varied between 3.1 ppm and 6.3 ppm. The greatest monthly field average was observed in December 1995. Interestingly, the spatially averaged NO<sub>3</sub>-N concentration for all of the samples collected from the on-field wells for the first well sampling (June 1993) was 5.2 ppm, in contrast to the 1.8 ppm observed up-gradient. This indicates a rapid impact on groundwater at the site or background concentrations on the field that exceeded up-gradient concentrations. This was consistent with some of the elevated initial concentrations observed in the vadose zone. Water table elevation data collected at the site indicate rapid movement from the surface to the groundwater, particularly during high precipitation events such as those observed in 1994 (fig. 7). Following the 565 mm July 1994 precipitation, the water table rose 2.4 m in a period of

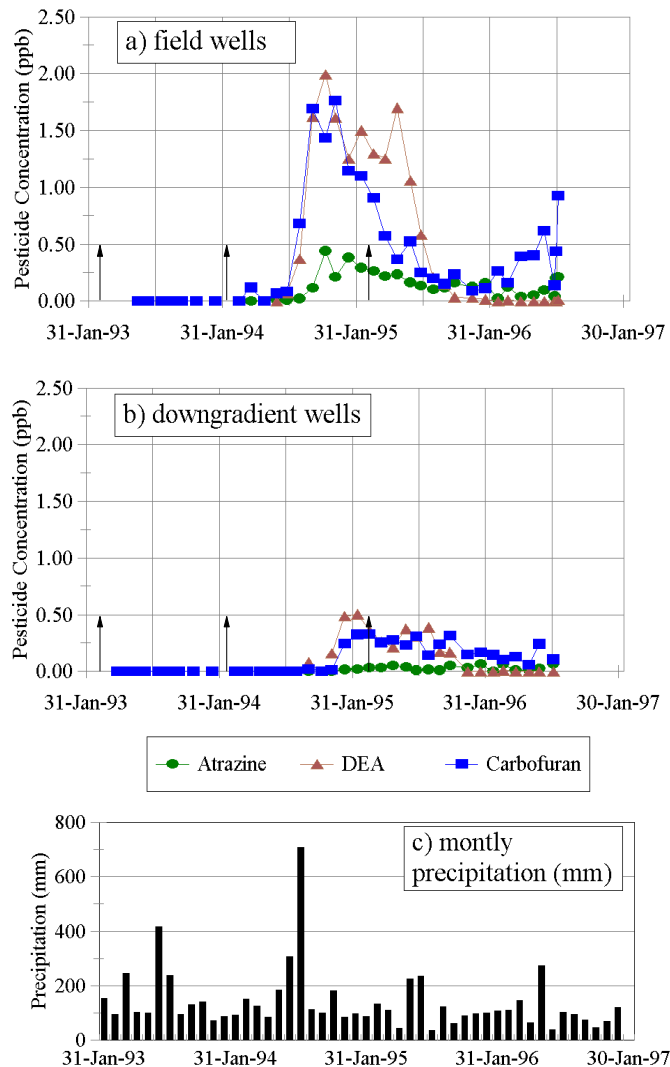
20 days. The water table began to rise just 3 days after rainfall began. These factors indicate the potential for very rapid transport of agrichemicals from the soil surface to groundwater and support the conclusion that we were observing elevated NO<sub>3</sub>-N concentrations due to the first application of fertilizer.

Average concentrations of atrazine, carbofuran, and DEA for each sample date (fig. 8) and for the period of record (table 3) were calculated for the 10 up-gradient wells, 18 on-field wells, and 21 down-gradient wells. The GC analysis data for atrazine and DEA were used for these averages, while ELISA data were used for carbofuran. Mean pesticide concentrations for the entire study period were low (table 3). Of the 791 groundwater samples, 307 tested positive for either atrazine or carbofuran. Up-gradient groundwater pesticide concentrations were generally below detection limits. On-field pesticide concentrations were significantly different from up-gradient concentrations (table 3). The greatest mean concentration observed on the field for the period of record was 0.6 ppb for DEA. For all groundwater samples collected from on the field, none exceeded the MCL for atrazine (3 ppb) or for carbofuran (40 ppb), while 2% exceeded 3 ppb for DEA. As the means indicate (table 3), greater decreases in the pesticide concentrations were observed in down-gradient wells than were observed for NO<sub>3</sub>-N.

The first detectable groundwater pesticide concentrations were observed in April 1994. Average atrazine concentration in the wells on the field increased in 1994, peaking in November 1994 at 0.44 ppb (fig. 8). Average concentrations of DEA increased to 2 ppb on the field in November 1994, while carbofuran increased to 1.8 ppb (fig. 8). A second increase in pesticide concentration was observed in July and



**Figure 7. Water table elevation data from well 500 and daily precipitation for the period from 1 June 1994 to 31 August 1994.**



**Figure 8.** Average groundwater pesticide concentrations observed in the groundwater (a) below the field and (b) down-gradient from the field for each sample date, along with (c) monthly precipitation for the study period (annual pesticide application dates marked by arrows on the x-axis).

August 1996. Since no pesticides were applied in 1996, this increase was due to residual levels of the chemicals applied prior to 1996 coupled with the 273 mm of precipitation that occurred in May 1996. Down-gradient wells showed reduced and delayed increases in mean atrazine concentrations (fig. 8). Overall, down-gradient atrazine groundwater concentrations were relatively unaffected by field activities.

Groundwater pesticide and  $\text{NO}_3^-$ -N concentrations were generally greater in wells placed below the sandier Troup soil than those below the finer textured Pine Flat soil. Comparisons of data from wells 516 and 520 indicate elevated  $\text{NO}_3^-$ -N and pesticide concentrations on the west side of the field (fig. 9). The greatest increases in chemical concentration were observed on the southwest side of the field, in well 516 (fig. 9). Concentrations up to 16 ppm of  $\text{NO}_3^-$ -N and up to 7 ppb of carbofuran were observed in groundwater from this well. This well was found below the region with the sandier Troup soil and on the down-gradient side of the field. Pesticide concentrations at this well peaked in December 1994, while  $\text{NO}_3^-$ -N concentrations did not peak until a year later in December 1995. Increases in  $\text{NO}_3^-$ -N and pesticide concentrations observed in the lysimeters were generally accompanied by increases in groundwater concentrations. In

general, the time delay between when concentration increases were observed in the lysimeters and when they were observed in the wells was less than 6 months. An increase from 3 to 6 ppm  $\text{NO}_3^-$ -N was observed at well 516 in late 1994 (fig. 9), corresponding to the  $\text{NO}_3^-$ -N peak observed in lysimeter 602 in mid-1994 (fig. 6).

More of the carbofuran and DEA were transported to groundwater than was atrazine, indicated by the higher concentrations of these compounds found in groundwater (table 3 and fig. 8). Average concentrations of carbofuran in the groundwater from the on-field wells peaked in January 1994 at 1.8 ppb (fig. 8). A second increase was observed in the monthly average on-field carbofuran concentrations in August 1996. Monthly average concentrations of DEA in wells below the field peaked in November 1994 at 2 ppb and remained high until May 1995. Temporal trends in average on-field carbofuran concentrations were similar to those observed for DEA and atrazine. While the magnitude of the compound transported varied, all three compounds appeared to be transported at approximately the same rate, with each peaking at approximately the same time (fig. 8). This would indicate a rapid transformation of atrazine into DEA and a similar transport rate through the vadose zone.

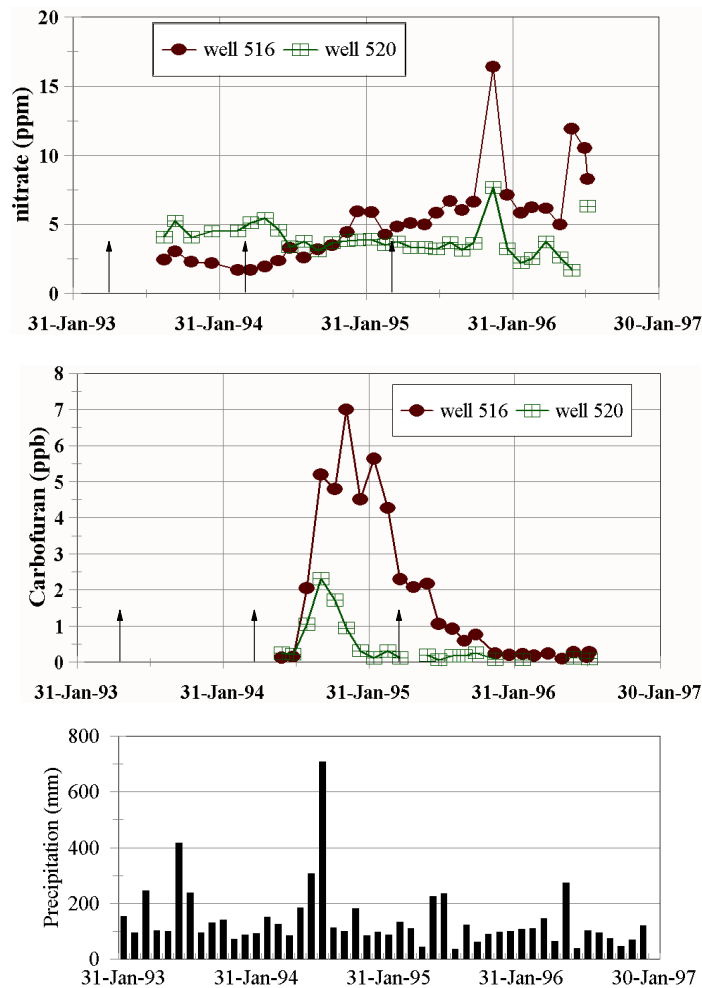


Figure 9. Measured  $\text{NO}_3^-$ -N and carbofuran concentrations at well 516 (west side) and 520 (east side) along with monthly precipitation. The first fertilizer application and the pesticide application dates for each year are marked by the arrows on the x-axis for the nitrate and carbofuran graphs, respectively.

## DISCUSSION

The monitored agrichemicals moved rapidly through the upper 2.5 m of the soil profile. Pesticide movement into the vadose zone below 4 m was detected approximately 7 months after application, while elevated  $\text{NO}_3^-$ -N concentrations in groundwater were observed as early as one month after application. Movement of pesticides into groundwater was not detected until one year after application. While high concentrations of atrazine, DEA, and carbofuran were observed in individual samples, overall concentrations observed in groundwater were generally low (table 3). Average monthly carbofuran concentrations in samples from down-gradient wells ranged from below detection to 1.8 ppb. Average monthly atrazine concentrations ranged from below detection to 0.5 ppb, while average monthly DEA concentrations ranged from below detection to 2.0 ppb. Background concentrations of the pesticides were generally below detection. Up-gradient concentrations of  $\text{NO}_3^-$ -N averaged 1.8 ppm, and down-gradient concentrations averaged 4.0 ppm with a peak down-gradient observation of 16 ppm.

Samples collected from the deep vadose zone lysimeters three months after the first 1993 fertilizer application indicated elevated  $\text{NO}_3^-$ -N concentrations (>5 ppm). Many of these same lysimeters exhibited a decrease in  $\text{NO}_3^-$ -N

concentration in the soil-water over the period of study. Because background vadose zone samples were not collected, the source of the  $\text{NO}_3^-$ -N observed in these initial samples is not known. While it is possible that the elevated  $\text{NO}_3^-$ -N concentrations in these lysimeters were background concentrations, it is more likely that they were an effect of the first year's fertilizations. Elevated  $\text{NO}_3^-$ -N concentrations observed in the groundwater below the field support this conclusion. Water-table data indicate responses to rainfall as rapid as 3 days during high precipitation conditions such as those observed in 1994 (fig. 7). Thus, rapid movement of water from the surface to the water table would not be unusual for these soils. In addition, since the field was unfarmed prior to our study, it is unlikely that the initial soil  $\text{NO}_3^-$ -N was high.

Pesticide transport appears to have been driven by periods of excess precipitation. Continuously elevated  $\text{NO}_3^-$ -N concentrations indicate that  $\text{NO}_3^-$ -N was released more slowly over time. Peak pesticide concentrations in groundwater were observed in late 1994, apparently driven by a large precipitation event in July 1994. Observed increases in groundwater  $\text{NO}_3^-$ -N in 1994 were not as large. It is possible that the majority of the  $\text{NO}_3^-$ -N had been taken up by plants by that time or that it had moved out of the soil profile earlier. In addition, because of the volume of precipitation that

occurred during this event, groundwater concentrations may have been diluted. Larger  $\text{NO}_3^-$ -N concentrations were observed in late 1995, even though less N was applied that year and precipitation was less. The cyclic nature of the  $\text{NO}_3^-$ -N concentrations in the vadose zone and elevated concentrations observed in the spring of 1996 (figs. 5 and 6) indicate excess  $\text{NO}_3^-$ -N remaining in the profile from the 1995 fertilizer application, which later moved out of the vadose zone when precipitation exceeded evapotranspiration. This may indicate why no decrease in groundwater  $\text{NO}_3^-$ -N was observed in 1996, even though no fertilizer had been applied that year. Prior research has indicated that percolation of chemicals into the soil is largely driven by large precipitation events (Leonard et al., 1992; Truman and Leonard, 1991).

The differences in the soils on the field appeared to affect the transport process. Saturated hydraulic conductivity throughout the majority of the field was approximately  $150 \text{ cm hr}^{-1}$ , while in the southeast corner of the field it ranged from 10 to  $50 \text{ cm hr}^{-1}$ . Transport timing did not appear to be as affected by soil differences as did magnitudes (fig. 9). Peak pesticide concentrations were observed at approximately the same time in each section of the field. However, the magnitude of the peak concentrations was higher in the portions of the field with the sandier Troup soil than in the portions with the Pine Flat soil, a consequence of the heavier Bt horizon in the Pine Flat soil. Because of the small size of the field (1 ha), it is possible that we were seeing the effects of mixing from one part of the field to another.

Atrazine and carbofuran observations in groundwater did not exceed the EPA MCLs of 3 ppb and 40 ppb for these compounds, and the average monthly concentrations observed in the field wells were well below these standards (table 3). On-field observations of  $\text{NO}_3^-$ -N, atrazine, DEA, and carbofuran were significantly different from up-gradient concentrations ( $p = 0.05$ ). Down-gradient concentrations were also significantly different from up-gradient concentrations ( $p = 0.05$ ). Only  $\text{NO}_3^-$ -N affected down-gradient concentrations. These data indicate a significant impact on the local groundwater. The impact of the field-applied pesticides appeared to be isolated to the groundwater directly below the field. However,  $\text{NO}_3^-$ -N was transported down-gradient from the field.

Pesticide concentrations observed in groundwater were consistent with other studies conducted in the same area (Bosch et al., 1997; Bosch et al., 1999). Prior studies in the region found that the greatest risk for transport of agrichemicals occurs during periods of high precipitation (Bosch et al., 1997). Bosch et al. (1999) found similar rates of pesticide transport to groundwater. Of the compounds examined, the greatest concentrations in groundwater were of DEA (5.1 ppb) and carbofuran (7 ppb). In prior studies on this same site, atrazine was found to decay in the root zone at about half the rate of carbofuran (Bosch et al., 2000). Thus, more transport of atrazine than of carbofuran would be expected. Transformation of atrazine into DEA and other by-products appears to have occurred below the root zone, leading to lower atrazine concentrations in groundwater. Prior studies in the area also found greater concentrations of carbofuran than atrazine in the groundwater (Bosch et al., 1997).

Adams and Thurman (1991) suggested the DEA-to-atrazine ratio (DAR) could be used as a measure of pesticide

residue age and the amount of interaction between atrazine and soil as the pesticide moves through the soil column. It has been suggested that a DAR greater than 0.4 indicates significant reaction between atrazine and soil (Goolsby et al., 1997). For our study, water samples from lysimeters and wells had concentrations of DEA that were consistently greater than atrazine. Atrazine concentrations were frequently below detection limits, indicating large DARs. This indicates significant interaction between the pesticide and soil, and little if any preferential flow, which is consistent with other observations made at the site. Peak concentrations of atrazine and DEA were observed at the same time in most lysimeters and wells, indicating simultaneous transport of both compounds and rapid root-zone transformation.

## CONCLUSIONS

The results of this study indicate the importance of field management and careful consideration of climatic patterns. During our study, we observed rapid movement of  $\text{NO}_3^-$ -N to groundwater. Total N applications were average for the region. Average monthly  $\text{NO}_3^-$ -N concentrations observed in groundwater below the field and down-gradient from the field exceeded 3.9 ppm, while up-gradient concentrations were approximately 1.8 ppm. Despite split applications of N, it appears that the sandy loam soils studied are still susceptible to substantial losses of  $\text{NO}_3^-$ -N. Fertigation, applying the nitrogen to the crop with the irrigation, may be a very good alternative for these soils. Using this method, the nitrogen can be applied to the crop as needed, reducing the risk for  $\text{NO}_3^-$ -N leaching. However, under all management conditions, it is important not to over-irrigate so that the chemicals stay within the root zone. Large precipitation events occurring over the period of study appeared to transport the  $\text{NO}_3^-$ -N below the root zone, making it unavailable for plant uptake.

While concentrations of the pesticides and pesticide by-products were high in a limited number of samples, the overall observed concentrations were low. Carbofuran and DEA were more readily transported to the groundwater than was atrazine. The greatest risk to pesticide transport occurred in 1994, when approximately half of the expected annual precipitation fell in a 3-day period. This is obviously an extreme case, which is difficult to manage for. Without this event, it appears that the overall pesticide transport to groundwater would have been small. However, little is known about the combined effect of multiple pesticides and their metabolites in drinking water supplies. It may be possible that, despite relatively low concentrations of any one pesticide, there may be health issues related to their cumulative effects.

## ACKNOWLEDGEMENTS

The authors wish to thank Ms. Luz Marti, Ms. Margie Whittle, and Ms. Sally Bellflower for their assistance with the chemical analysis. We also thank Dr. Ralph Leonard, Dr. Woody Hicks, Mr. Shaw Fletcher, Mr. Ricky Fletcher, Mr. George Barfield, and Mr. Homer Allison for their assistance with the project.

## REFERENCES

- Adams, C. D., and E. M. Thurman. 1991. Formation and transport of deethylatrazine in the soil and vadose zone. *J. Environ. Qual.* 20(3): 540–547.
- Beck, B. F., L. Asmussen, and R. Leonard. 1985. Relationship of geology, physiography, agricultural land use, and ground-water quality in Southwest Georgia. *Ground Water* 23(5): 627–634.
- Belluck, D. A., S. L. Benjamin, and T. Dawson. 1991. Groundwater contamination by atrazine and its metabolites. In *Pesticide Transformation Products: Fate and Significance in the Environment*, 254–273. L. Somasundaram and J. R. Coats, eds. ACS Symposium Series No. 459. Washington, D.C.: American Chemical Society.
- Bosch, D. D., and L. T. West. 1998. Hydraulic conductivity variability for two sandy soils. *Soil Sci. Soc. of Am. J.* 62(1): 90–98.
- Bosch, D. D., R. A. Leonard, C. C. Truman, L. T. West, and D. W. Hicks. 1997. Impacts of conventional agricultural practices on aquifer water quality: An overview of the Plains, Georgia water quality study. In *Proc. 1997 Georgia Water Resources Conference*, 504–507. K. Hatcher, ed. Athens, Ga.: University of Georgia.
- Bosch, D. D., R. K. Hubbard, R. A. Leonard, and D. W. Hicks. 1999. Tracer studies of subsurface flow patterns in a sandy loam profile. *Trans. ASAE* 42(2): 337–349.
- Bosch, D. D., C. C. Truman, and R. A. Leonard. 2000. Atrazine and carbofuran transport through the vadose zone in the Claiborne Aquifer recharge area. *Trans. ASAE* 43(6): 1609–1620.
- Clark, W. Z., and A. C. Zisa. 1976. Physiographic map of Georgia. Map SM-4, reprinted 1988, scale 1:2,000,000. Atlanta, Ga.: Georgia Geological Survey.
- Fermanich, K. J., W. L. Bland, B. Lowery, and M. McSweeney. 1996. Irrigation and tillage effects on atrazine and metabolite leaching from a sandy soil. *J. Environ. Qual.* 25(6): 1291–1299.
- Gaynor, J. D., D. C. MacTavish, and W. I. Findlay. 1995. Atrazine and metolachlor loss in surface and subsurface runoff from three tillage treatments in corn. *J. Environ. Qual.* 24(2): 246–256.
- Goodrich, J. A., B. W. Lykins, Jr., and R. M. Clark. 1991. Drinking water from agriculturally contaminated groundwater. *J. Environ. Qual.* 20(4): 707–717.
- Goolsby, D. A., E. M. Thurman, M. L. Pomes, M. T. Meyer, and W. A. Battaglin. 1997. Herbicides and their metabolites in rainfall: Origin, transport, and deposition patterns across the Midwestern and Northeastern United States, 1990–1991. *Environ. Science and Tech.* 31(5): 1325–1333.
- Hicks, D. W., J. B. McConnell, and L. E. Asmussen. 1991. Preliminary geologic and hydrologic evaluation of a small watershed near Plains, Georgia. USGS Water Resources Investigations Report No. 90–4146. Washington, D.C.: U.S. Geological Survey.
- Hubbard, R. K., and J. M. Sheridan. 1989. Nitrate movement to groundwater in the Southeastern Coastal Plain. *J. Soil and Water Conservation* 44(1): 20–27.
- Jayachandran, K., T. R. Steinheimer, L. Somasundaram, T. B. Moorman, R. S. Kanwar, and J. R. Coats. 1994. Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow groundwater. *J. Environ. Qual.* 23(2): 311–319.
- Kamrin, M. A. 1997. *Pesticide Profiles: Toxicity, Environmental Impact, and Fate*. Boca Raton, Fla.: Lewis Publishers.
- Leonard, R. A., G. W. Langdale, and W. G. Fleming. 1979. Herbicide runoff from upland Piedmont watersheds: Data and implications for modeling pesticide transport. *J. Environ. Qual.* 8(2): 223–229.
- Leonard, R. A., A. Shirmohammadi, A. W. Johnson, and L. R. Marti. 1988. Pesticide transport in shallow groundwater. *Trans. ASAE* 31(3): 776–788.
- Leonard, R. A., C. C. Truman, W. G. Knisel, and F. M. Davis. 1992. Pesticide runoff simulations: Long-term annual means vs. event extremes? *Weed Technology* 6(3): 725–730.
- Marti, L. R., and R. A. Leonard. 1992. Comparison of magnetic particle-based enzyme-linked immunosorbent assays (ELISA) with gas chromatography and liquid chromatography for the quantification of atrazine, alachlor, and carbofuran in water. In *Proc. 13th Annual Mtg. SETAC*, 190. Cincinnati, Ohio. Pensacola, Fla.: Society of Environmental Toxicology and Chemistry.
- McFadden, S. S., and P. D. Perriello. 1983. Hydrogeology of the Clayton and Claiborne aquifers in Southwestern Georgia. Information Circular No. 55. Atlanta, Ga.: Department of Natural Resources, Environmental Protection Division, Georgia Geologic Survey.
- Rayl, A. J. S. 2000. Coastal “dead zones” get attention: Strategy sought for combating nitrogen, phosphorous pollution. *The Scientist* 14(13): 12.
- Shaw, J. N., L. T. West, D. E. Radcliffe, and D. D. Bosch. 2000. Preferential flow and pedotransfer functions for transport properties in sandy kandiodults. *Soil Sci. Soc. of Am. J.* 64(2): 670–678.
- Truman, C. C., and R. A. Leonard. 1991. Effects of pesticide, soil, and rainfall characteristics on potential pesticide loss of percolation: A GLEAMS simulation. *Trans. ASAE* 34(6): 2461–2468.
- USEPA. 1990. Findings and results. In *National Survey of Pesticides in Drinking Water Wells: Phase I Report*, 51–88. U.S. Environmental Protection Agency Report No. 570/9–90–015. Washington, D.C.: U.S. Government Printing Office.
- USGS. 1999. The quality of our nation’s waters: Nutrients and pesticides. USGS Circular No. 1225. Reston, Va.: U.S. Geological Survey.