ABSTRACT. A study designed to provide a better understanding of the mechanisms of agrichemical transport to groundwater was conducted on a 0.81-ha agricultural corn field near Plains, Georgia. The objectives were to: (1) characterize vadose zone flow paths of water and agrichemicals under normal climatic and management conditions and evaluate their spatial and temporal variability; and (2) relate spatial and temporal transport patterns to geophysical properties of the soil and climatic conditions. Agrichemical transport was assessed over a five-year period from 1989 to 1994 through analysis of collected soil and groundwater samples. A bromide (Br\(^{-}\)) tracer was applied at 78 kg ha\(^{-1}\) in 1989 and at 105 kg ha\(^{-1}\) in 1991. Chloride (Cl\(^{-}\)) and nitrogen were applied with fertilizer each year except 1994. Soil characterization tests indicated a dramatic decrease in the saturated hydraulic conductivity associated with a large increase in clay content in a zone from 1 to 4 m below the soil surface. As a result of this soil feature, Br\(^{-}\) concentrations in the vadose zone below 4 m were normally less than 2 mg kg\(^{-1}\) throughout the study. Aquifer chemical concentrations indicated nitrate nitrogen (NO\(_3\)– N) and Cl\(^{-}\) applied to the soil surface in the spring were transported to the groundwater at 9 m by that same fall. Bromide concentrations in ground water peaked at 0.65 mg L\(^{-1}\) while NO\(_3\)– N concentrations peaked at 6.9 mg L\(^{-1}\) and Cl\(^{-}\) at 4.0 mg L\(^{-1}\). Agrichemical transport and variability were controlled by climatic patterns and soil hydraulic characteristics. Transport to groundwater increased when precipitation and irrigation volumes in the first 30 days after spring fertilization and planting exceeded twice the normal precipitation. If large spring thunderstorms occur soon after chemical application, the likelihood of groundwater contamination by agrichemicals is substantially increased. These data provide the means to relate transport of agrichemicals in and through the vadose zone to geophysical characteristics and irrigation and precipitation inputs.

Keywords. Water quality, Chemical transport, Groundwater, Subsurface flow, Vadose zone, Bromide.

Testing of well water samples collected throughout the world has shown that during agricultural production, the potential exists for agrichemicals to negatively impact drinking water supplies (Goodrich et al., 1991; Hubbard and Sheridan, 1989; Masse et al., 1994). A 1988 and 1989 EPA Survey estimated 10% of the nation’s community drinking water wells and 4% of the rural domestic wells had detectable residues of at least one pesticide (U.S. Environmental Protection Agency, 1990). The survey results also estimated 1.2% of the community wells and 2.4% of the rural wells had concentrations above the 10 mg L\(^{-1}\) nitrate nitrogen (NO\(_3\)– N) maximum contaminant level established to protect human health. Typically, mobile and persistent compounds are found in groundwater. In many cases, these compounds are found in areas where the water table is near the soil surface, infiltration rates are high, and/or recharge rates are high. Of the 16,166 wells sampled in Ohio beginning in 1987, 13% exceeded NO\(_3\)– N concentrations of 3 mg L\(^{-1}\) and 2.9% exceeded 10 mg L\(^{-1}\) (Baker, 1990). The percent of wells with NO\(_3\)– N concentrations greater than 10 mg L\(^{-1}\) was 7.2% for wells less than 15 m deep, 1.7% for wells between 15 and 30 m deep, and 0.9% for wells over 30 m deep. A similar North Carolina study found 1% of wells deeper than 30 m exceeded 10 mg L\(^{-1}\) NO\(_3\)– N; whereas, 9% of wells less than 15 m exceeded this level (Jennings et al., 1991; Sneed et al., 1991).

Losses of agricultural chemicals from the root zone are important relative to both crop production and environmental quality. Agrichemicals percolating out of the root zone are no longer available for crop growth and protection and may negatively impact subsurface water quality. Chemical losses to groundwater may be costly, both from efficiency and remediation standpoints. One-time testing of all private drinking wells vulnerable to NO\(_3\)– N or pesticides could cost up to $2.2 billion, while testing public wells could cost an additional $14 million (Crutchfield, 1991). Transport of agrichemicals depends on rainfall amount, intensity, and duration; chemical solubility and degradation properties; soil properties; biological processes; and management practices. A scientific understanding of these processes requires complex, well-defined research which quantifies each of these factors.
Groundwater contamination by agrichemicals is a potentially severe problem in South Georgia. In a study to evaluate potential groundwater contamination from pesticide use, the Coastal Plain consistently ranked as a high risk area (Nielsen and Lee, 1987). The area’s high proportion of sandy soils require relatively high fertilization and pesticide inputs for successful crop production. Average annual precipitation for the area is 1240 mm, and irrigation is common. As a consequence, the risk of groundwater contamination in the area is high. Groundwater quality in the Fall Line Red Hills agricultural area of Georgia (Clark and Zisa, 1976) is of particular concern because the Upper Floridan and Claiborne aquifers, aquifers which supply several southwest Georgia and northwest Florida municipalities with their drinking water, are recharged there. Data collected from 1989 to 1991 during a south Georgia groundwater survey found that six out of 35 wells contained pesticide concentrations over health advisory levels, with all six of these within the Claiborne aquifer recharge area (personal communication, Leonard, 1996).

In 1988, as a response to this groundwater survey, the U.S. Geological Survey, the Southeast Watershed Research Laboratory (SEWRL), U.S. Department of Agriculture, Agricultural Research Service, the U.S. Environmental Protection Agency (USEPA), and the University of Georgia began a cooperative study of chemical transport on an agricultural field near Plains, Georgia. The site was selected because it was located within the Fall Line Red Hills region of Georgia and was also in the Claiborne aquifer recharge area. A tracer test was designed as part of this research. Conservative tracers have long been used to track the movement of water through the soil (Blume et al., 1987; Bowman, 1984; Bruce et al., 1985; Owens et al., 1985; Owens and Edwards, 1992). Reviews of the use of tracers in soil-water studies are presented in Bowman (1984) and Gerritse and Adeney (1992).

The objectives of this research were to: (1) characterize vadose zone flow paths of water and agrichemicals under normal climatic and management conditions and evaluate their spatial and temporal variability; and (2) relate spatial and temporal transport patterns to geophysical properties of the soil and climatic conditions.

METHODS
SITE DESCRIPTION
The study site was a 0.81-ha rectangular plot (fig. 1) in the recharge area of the Claiborne aquifer system. The soil is a Eustis loamy sand (sandy, silicious thermic Psammentic Paleudult). A soil berm was constructed around the plot perimeter to confine runoff. A H-flume (0.46 m) was installed to measure sediment and chemical transport in surface runoff. The mean sea level elevation of the plot ranges from 141 m on the north side of the plot to 139 m on the south side. The average ground slope is 1.5%. Prior to beginning this study in 1989, this plot was not in agricultural production for many years. The plot was surrounded by forested and non-tilled land, minimizing the likelihood of offsite agrichemical inputs.

HYDROGEOLOGY
Soil cores for physical property characterization were collected in 1989 at each of 12 randomly selected sites within the plot (fig. 1). Samples were collected to a depth of 9.1 m using 61-mm I.D. plastic inserts inside a soil probe contained within a hollow-stem auger. The samples were collected in lengths of 910, 760, and 610 mm and later cut into subsections for determination of particle-size distribution, vertical saturated hydraulic conductivity ($K_{sat}$), soil-water retention, and bulk density. Particle-size distribution measurements were made using the hydrometer method along with sieving of the sand fractions (Gee and Bauder, 1986). A flexible-membrane permeameter (Daniel et al., 1984) was used to determine $K_{sat}$. Soil-water characteristic curves were determined using weighable pressure cells at pressures of 0.4, 6, 30, and 100 KPa (Klute, 1986). Bulk density was determined using the core method (Blake and Hartge, 1986).

FIELD MANAGEMENT AND INSTRUMENTATION
A cropping sequence of summer corn (Zea Maize L.) and winter wheat (Triticum aestivum L.) was followed from 1989 through 1993. The corn was planted in March or April of each year with the exception of 1989, the year the study started, when it was planted in mid June due to difficulty instrumenting the plot. Following corn harvest in August or early September, wheat was planted as a winter crop in late November to early December. Conventional agricultural management practices were used for tillage, fertilization, planting, and harvest. A center-pivot irrigation
system was installed and used to ensure adequate plant soil-water. The plot was tilled and a crop grown in 1994, but without irrigation or fertilization. In 1994, the main emphasis of the study was to track chemicals already present in the groundwater.

The corn was fertilized each spring and early summer, and the wheat was fertilized in the fall (table 1). The broadcast fertilizer applied just prior to planting contained nitrogen, primarily as ammonium sulfate, and chloride (Cl−) as potassium chloride. Ammonium nitrate was applied as a side dressing approximately one month after planting. Rates varied (table 1) each year based on soil test values.

Along with well stations at each site within the plot, two well stations 10 m up-gradient from the plot and three stations 10 m down-gradient were installed (fig. 1). At each of the 17 permanent monitoring stations (fig. 1), sets of three 51-mm ID, PVC wells were installed. In each set of three, one well extended to 10 m from the soil surface and was screened from 9 to 10 m, the second extended to 11 m and was screened from 10 to 11 m, and the third extended to 12 m and was screened from 11 to 12 m. Groundwater samples were collected approximately each month, beginning in 1989, from each well containing water. Weighted tape measurements of water-table elevations were made prior to each sampling. A well into a deeper aquifer, vertically isolated from the monitored Claiborne aquifer, was located 30 m southwest of the plot and provided water to the irrigation system. Precipitation measurements were made using two digital weighing gages with a 2.5-mm resolution. Irrigation volumes were measured using six standard manual rain gages located at the site. The gages recorded 5-min rainfall totals.

VADOSE ZONE TRANSPORT

A Br− tracer, in the form of KBr, was uniformly applied at planting in 1989 and in 1991 (table 1). The Br− was surface applied as a liquid solution using a conventional tractor-mounted sprayer. One-hundred 185-mm D filter papers, placed randomly on the field, were used to monitor application rates. In 1989, forty-two millimeters of irrigation were applied immediately after application to wash the Br− below the surface layer. In 1991, eight millimeters of irrigation water were applied the day before Br− application and 118 mm of rainfall and irrigation were received by the plot the first four days after application.

Vadose zone Br− transport was monitored by collecting soil samples down to the water table. These samples were collected at 45 different times during the five-year period from 1989 to 1994. Samples were collected from multiple sites randomly located within quadrants on the plot. The number of samples per quadrant was normally kept equal. Soil samples were collected in equal length intervals down to various depths, depending upon the expected plume depth. During the growing season, samples were collected with hand bucket augers (50 mm D) down to approximately 2.5 m. In the fall and spring, samples were collected down to the water table using a drill rig equipped with a hollow stem continuous-coring device which collected the soil samples within 50 mm D brass sleeves. Samples were collected in the top 76 mm, every 152 mm from 76 to 1750 mm, and every 305 mm thereafter. For samples below 1750 mm, a 152-mm-long sample was collected from the middle of the interval and thoroughly mixed. For samples collected above 1750 mm, the sample was a composite of the entire interval.

ANALYTICAL TECHNIQUES

The filter papers used to measure Br− application rates were collected immediately after spraying and transported to the laboratory in glass jars for analysis. In the lab, 200 mL of deionized water was added to each jar, swirled until the filter paper was soaked, then allowed to stand for 2 h (swirled every 30 min). A 0.1 mL aliquot was diluted to 10 mL in a centrifuge tube, then filtered through a 0.22 µm Ion Chromatograph Acrodisc into Wisp vials.

Soil samples were air-dried, extracted by shaking 50 gm of sample with 100 mL deionized water for 1 h, and then allowed to settle overnight. An aliquot was centrifuged and then filtered through a 0.22 µm Ion Chromatograph Acrodisc prior to the analysis. Every 35 samples contained six quality assurance samples spiked with either 0, 1, 5 or 10 mg L−1 of Br− stock solution. Soil-water content was determined on the collected soil samples using conventional gravimetric techniques (Gardner, 1986).

All extracted soil samples were analyzed in the laboratory for Br−. Groundwater samples were analyzed for Br−, Cl−, and NO3− N. All samples were analyzed using an Ion Chromatograph with a conductivity detector. The detection limits for these compounds were 0.05 mg L−1 for Br−, 0.01 mg L−1 for Cl−, and 0.01 mg L−1 for NO3− N. The equivalent detection limits for the soil samples were 0.1 mg Br− kg−1 soil.

DATA ANALYSIS TECHNIQUES

The center of mass (COM) for the Br− plume was calculated for each sample date by summing the total Br− in the samples over the entire plot. The center of mass of the Br− plume was determined as the depth at which at least 50% of the Br− mass was contained in samples above that depth. The leading edge of the Br− plume was determined as the maximum depth at which the average Br− concentration was greater than 0.5 mg Br− kg−1 soil. Sample dates where the complete Br− plume was not sampled were not included in this analysis.

Table 1. Chemical application dates and rate of application (kg ha−1)

<table>
<thead>
<tr>
<th>Date</th>
<th>Application Rate kg ha−1</th>
<th>Bromide</th>
<th>Chloride</th>
<th>Nitrogen*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 May 1989</td>
<td>0</td>
<td>118</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>12 June 1989</td>
<td>78</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>23 June 1989</td>
<td>0</td>
<td>0</td>
<td>52†</td>
<td></td>
</tr>
<tr>
<td>14 July 1989</td>
<td>0</td>
<td>0</td>
<td>76†</td>
<td></td>
</tr>
<tr>
<td>15 November 1989</td>
<td>0</td>
<td>70</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>2 March 1990</td>
<td>0</td>
<td>124</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>30 April 1990</td>
<td>0</td>
<td>0</td>
<td>121†</td>
<td></td>
</tr>
<tr>
<td>13 November 1990</td>
<td>0</td>
<td>67</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>21 March 1990</td>
<td>0</td>
<td>166</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>27 March 1991</td>
<td>105</td>
<td>0</td>
<td>0</td>
<td></td>
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<tr>
<td>22 April 1991</td>
<td>0</td>
<td>37</td>
<td>12</td>
<td></td>
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<tr>
<td>23 May 1991</td>
<td>0</td>
<td>0</td>
<td>96†</td>
<td></td>
</tr>
<tr>
<td>9 December 1991</td>
<td>0</td>
<td>57</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>9 March 1992</td>
<td>0</td>
<td>168</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>23 April 1992</td>
<td>0</td>
<td>0</td>
<td>38†</td>
<td></td>
</tr>
<tr>
<td>5 May 1992</td>
<td>0</td>
<td>22</td>
<td>92†</td>
<td></td>
</tr>
<tr>
<td>22 March 1993</td>
<td>0</td>
<td>155</td>
<td>52</td>
<td></td>
</tr>
</tbody>
</table>

* Applications denoted by † were applied as Ammonium Nitrate, all others applied as Ammonium Sulfate.
A mass balance was conducted using the percentage of the total Br⁻ mass accounted for in the soil samples. The average Br⁻ mass across the plot in each sampling interval was calculated and the total mass then determined for the interval based on this average. Mass balance calculations for dates prior to the 1991 application date include only the 1989 application while those after include both. Only the sample dates where there were at least 20 sample sites and the depth of sampling captured the entire plume were used. Sample dates where there were fewer than 20 sample sites yielded highly variable mass recoveries and were judged unreliable.

RESULTS

HYDROGEOLOGY

The geologic units found, in descending order, were (1) the undifferentiated overburden (0-4 m), consisting of a Eustis loamy sand and alternating layers of sand, clayey sand, and clay; (2) the Tallahatta Formation (4-13 m), composed of fine-to-coarse quartz sand; and (3) the Tuscahoma Formation (>13 m), consisting of homogeneous, well sorted, glauconitic, very fine-to-fine argillaceous, quartz sand. The depth to the water table ranges from 6 to 10 m. The saturated zone (Claiborne aquifer) ranges in thickness from 2 to 6 m.

The soil characterization cores showed considerable variability. These cores indicated the vadose zone contained a prominent layer of clay extending from a depth of approximately 1 to 4 m below the land surface (fig. 2). Vertical variability in particle-size distribution was primarily due to changes in percent sand and clay. Laterally, the variability of the vadose zone was primarily related to the percent clay in the 1- to 4-m depth interval and to the thickness of the clay (fig. 2). Bulk density measurements varied from 1.6 gm cm⁻³ at the surface to 1.8 gm cm⁻³ in the subsurface.

Saturated hydraulic conductivity data from sites A, F, G, and L (fig. 1) are representative of the range in properties measured at the plot (fig. 3). As may be expected from examination of the clay content data, there was a considerable decrease in Kₕ from 1 to 4 m depth. While this clay layer was more evident on the east side of the plot, it extends throughout the entire plot (fig. 2).

The soil-water release curves showed considerable variability both with depth and across the plot (fig. 4). Gravimetric water content near saturation (0.4 KPa) was approximately 35 to 40%. Residual water content was approximately 5 to 10%. Soil-water content dropped off rapidly with increasing tension, particularly for the soil layers with higher sand content (figs. 2 and 4). Layers with higher clay content retained more soil-water at higher tension than did sandier layers.

CLIMATIC CONDITIONS AND RESPONSE

During the five years of observation, the plot received an annual average of 1630 mm total water (precipitation + irrigation) (table 2). Irrigation applications were fairly uniform with a coefficient of variation of 10%. No significant runoff was observed. Total water was unusually high in 1989, 1991, and 1994. In 1989, this water was received in June through August, while in 1991 it was received in April through June (fig. 5). In 1994, a single rainfall event supplied 410 mm over a four-day period in early July (fig. 5). From a water quality standpoint, the 1991 occurrence was the most significant because the excess precipitation was received soon after chemical application (table 2). In 1989, planting and chemical application did not occur until mid-June, and a large part of the total water was likely lost to evaporation. However, during 1991 when planting and fertilization occurred at a normal time for the area (late March), much of the total water in the period 30 days after application likely percolated through the root zone.

SOIL-WATER CONTENT

Data determined from vadose zone soil samples indicated a fairly consistent distribution of gravimetric soil-water in the profile over time. Aside from fluctuations in the top 3 m of the profile due to irrigation and precipitation, only small changes in soil-water occurred at any given depth and location over the study. The greatest water contents were consistently observed on the east side of the plot. The surface soil-water content was typically around 5% (by weight), with an increase to approximately 12% in the clay zone from 1 to 4 m. The soil-water content in the unsaturated zone below 4 m was typically around 6 to 7%, with an increase to approximately 10% in the capillary fringe. The standard deviations of the soil-water content of the collected samples ranged from 1% to 10%.

VADOSE ZONE TRANSPORT DATA

Five years of vadose zone transport data, from March 1989 to March 1994, were examined to evaluate transport rates and pathways through the unsaturated zone. Background samples collected on 3 March 1989, prior to Br⁻ application, indicated a maximum Br⁻ background content.
Figure 3–Saturated hydraulic conductivity by depth in the vadose zone for sites A, F, G, and L.

Figure 4–Average and standard deviation of the gravimetric moisture content at 0.4, 16, 30, and 100 KPa of tension, for the sets of samples collected from sites A through L at 0.3, 1.8, 4.8, and 6.9 m depth.
concentration of 0.4 mg kg\(^{-1}\) and mean background concentrations of 0.05 mg kg\(^{-1}\) in the soil above the water table. The coefficient of variations of the Br\(^{-}\) application rates determined from the filter disk data were 2.6% for 1989 and 1.6% for 1991. There were no distinctive spatial patterns to the Br\(^{-}\) applications.

Means and standard deviations of Br\(^{-}\) soil concentrations were examined for several dates representing the first (fig. 6) and second (fig. 7) Br\(^{-}\) applications. The largest mean concentration of Br\(^{-}\) observed was 13 mg kg\(^{-1}\) at approximately 0.6 m on 23 June 1989. Within the first month following the 1989 Br\(^{-}\) application, the plume moved to approximately 1 m depth, coinciding with the 1989 period when the maximum water was received (fig. 5). During the following 21 months, up to 10 March 1991, the plume moved slowly from 1 m to 2 m. This constitutes a rate of approximately 0.6 m yr\(^{-1}\). Peak concentrations in the vadose zone decreased dramatically with time due to dilution and diffusion.

The 1991 Br\(^{-}\) application behaved similar to the 1989 application (fig. 7). There was fairly rapid movement to 1.2 m early in 1991 due to the excess water (fig. 5). Two Br\(^{-}\) peaks were observed on 9 April 1991, and again on 18 June 1991, likely due to the two Br\(^{-}\) applications. The 18 June 1991, plume exhibited considerable mixing. By July 1991, the Br\(^{-}\) plume due to the second application could not be distinguished from the first. It was evident from the 10 November 1991 plume that the greatest potential for transport to the aquifer was in late 1991 (fig. 7).

The Br\(^{-}\) was confined in the 1- to 4-m clay zone. This portion of the vadose zone is influenced by an upward gradient due to evapotranspiration during the growing season and a downward gradient caused by excess precipitation. The slowing of the vertical transport of the Br\(^{-}\) plume during the growing season was observed following both the 1989 and 1991 applications.

There was a dramatic decrease in the mass of Br\(^{-}\) accounted for with time (fig. 8). Samples collected within the first four months after the 1989 Br\(^{-}\) application contained most of the Br\(^{-}\) applied. However, aside from the November 1991 sampling when 100% of the first and second application was collected, the percent recovered was below 50% for the remainder of the study. The variability for the November 1991 sampling was quite high (fig. 7), with very high concentrations observed. This led to a high recovery rate on this date. The mass balance does not include losses to groundwater. The dramatic decrease in the recovered mass in late 1989 and late 1991 could have been due to transport of Br\(^{-}\) to groundwater. However, because the Br\(^{-}\) concentrations observed in the deep vadose zone were quite low, this was unlikely.

Prior to the second Br\(^{-}\) application, the COM of the Br\(^{-}\) samples can be used to track the downward transport of the first plume (fig. 9). After the 1991 Br\(^{-}\) application, the COM is a combination of the two Br\(^{-}\) applications. The COM moved rapidly to 1.2 m after the first Br\(^{-}\) application, corresponding to a period of higher rainfall and irrigation (fig. 5). From August 1989 to the end of that year, the COM was stable. The COM moved to around 2 m in late 1989 or early 1990, where it remained until mid 1991. In mid 1991, the COM moved to 2.4 m, driven again by excess precipitation and irrigation (fig. 5). Following this movement of the COM, larger concentrations were observed deeper in the vadose zone (fig. 7). The upward movement of the COM observed from late 1991 to early 1992 reflected the loss of Br\(^{-}\) to the water table (fig. 7). Precipitation and irrigation in 1990, 1992, and 1993 was lower, which may explain why the COM was stable during those years.

Prior to mid 1991, the leading edge of the Br\(^{-}\) plume remained above 3 m (fig. 9). However, Br\(^{-}\) may have been moving through the vadose zone at levels below detection. The periods in 1991 and 1993 where the leading edge was observed at 9 m were due to an increase in the Br\(^{-}\) concentration just above the water table, in the capillary fringe area. Assuming equivalent Br\(^{-}\) concentrations in the soil solution regardless of the soil-water content, more soil-water would mean a greater Br\(^{-}\) mass in the collected sample.

**Aquifer Observations**

Due to dilution, diffusion, and a low transport rate, the concentrations of Br\(^{-}\) measured in the groundwater were very low. Most samples were below levels of detection, leading to a low average concentration throughout the study. The maximum concentration was 0.65 mg L\(^{-1}\), observed in July 1991. However, this was an isolated observation. Small pulses of Br\(^{-}\) were observed in the groundwater in July 1991, August 1992, May 1993, and June 1994.

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**Table 2. Observed and 39-year average plot water, irrigation and precipitation, for 30, 60, and 90 days after fertilization and planting and for the years from 1989 to 1994.**

<table>
<thead>
<tr>
<th>Days After Chemical Application</th>
<th>Irrigated Water (mm)</th>
<th>Total Water (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>169</td>
<td>520</td>
</tr>
<tr>
<td>60</td>
<td>296</td>
<td>730</td>
</tr>
<tr>
<td>90</td>
<td>296</td>
<td>1769</td>
</tr>
<tr>
<td>Annual</td>
<td>329</td>
<td>306</td>
</tr>
<tr>
<td>30</td>
<td>190</td>
<td>287</td>
</tr>
<tr>
<td>60</td>
<td>287</td>
<td>1240</td>
</tr>
<tr>
<td>90</td>
<td>1769</td>
<td></td>
</tr>
<tr>
<td>1989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>1991</td>
<td>190</td>
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<tr>
<td>1992</td>
<td>287</td>
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</tr>
<tr>
<td>1993</td>
<td>1240</td>
<td></td>
</tr>
<tr>
<td>1994*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39-year average precipitation†</td>
<td>108</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>1240</td>
</tr>
</tbody>
</table>

* No chemical application in 1994.
† Average planting date of 20 March.
Concentrations of NO₃⁻ N in groundwater remained below health advisory levels of 10 mg L⁻¹ throughout the study, with a maximum concentration of 6.9 mg L⁻¹ observed in June 1991. The average concentration of NO₃⁻ N in wells up gradient from the plot was 0.73 mg L⁻¹ while the average Cl⁻ concentration in these wells was 1.44 mg L⁻¹. The impact of fertilization on groundwater was first observed in August 1989 when NO₃⁻ N
concentrations up to 4.1 mg L−1 were observed in plot wells. Elevated Cl− concentrations were observed in plot wells at the same time. Prior to these observations, average concentrations in the plot area were similar to those upgradient (fig. 10). Of the off plot wells, the greatest concentrations were observed in well O (fig. 1). Elevated NO₃− N and Cl− concentrations were observed in the off plot wells from February 1990 to the end of the study. The

Figure 7–Average and standard deviations of Br− concentration in the vadose zone at select dates from 1991 to 1994.
maximum NO₃⁻ N in off plot wells peaked at 6.9 mg L⁻¹ in June 1991, while the maximum Cl⁻ peaked at 4.0 mg L⁻¹ on the same date. The peak average concentrations observed in 1991 and 1994 (fig. 10) corresponded to unusually high precipitation periods (fig. 5).

Groundwater recharge at this site normally occurs from February to June (fig. 11). Recharge occurred late in 1989 and 1991. The greatest recharge occurred in 1991 and 1994 (fig. 11). The 1990 recharge was likely a consequence of the high water input from June through August 1989. Large rainfall in 1991, combined with elevated soil-water conditions from January 1991 precipitation, led to increased recharge to the aquifer (Bosch et al., 1997). There is a rapid response in the water table elevation to periods of high water input (fig. 11). A saturated upper vadose zone provides the driving force for increased percolation to the aquifer. These soils have a low capacity for soil-water storage (fig. 4) and water which percolates below the root zone likely becomes groundwater recharge. From the groundwater data it was difficult to determine if the precipitation in a given year recharged the water table in that same year, or simply re-filled the available water storage in the vadose zone. However, the transport data indicated it took less than one year for agrichemicals to be transported from the surface to the groundwater.

**Spatial Variability of Br⁻**

Spatial Br⁻ distributions throughout the vadose zone on 10 October 1989, and 8 November 1990, were examined graphically (figs. 12 and 13). Although there was considerable variability in the data, Br⁻ appeared to be transported through the vadose zone on the west side of the plot more readily than on the east side, with the greatest transport in the southwest corner. This was evident by deeper transport (1.75 to 2.00 m, fig. 12, and 2.6 to 2.9 m, fig. 13) in this corner. This information is consistent with the particle-size (fig. 2) and conductivity (fig. 3) data. It appeared from this analysis that only in the southwest corner was significant Br⁻ transported to the aquifer. This may explain why the overall average Br⁻ concentrations were quite low in the aquifer below the plot. However, even in this quadrant, the observed Br⁻ concentrations in groundwater samples were very low.
DISCUSSION

The likelihood of transport of NO$_3^-$ N to the water table was increased when total water in the 30 days following spring fertilization and planting was high. Because this data base only consisted of five years of observation, it was difficult to quantify the magnitude of total water necessary for this to occur. Groundwater data indicate higher NO$_3^-$ N levels in 1990, 1991, and 1993. In these years, the total water was 33, 369, and 81% above the 39-year average for the 30-day period following planting and fertilization. The large increase in 1991 was primarily due to excess irrigation used to move Br$^-$ into the rooting zone. While total water during this 30-day period was also high in 1989, fertilization and planting during this year were much later than normal and occurred during a high evapotranspiration period.

In addition to losses to groundwater, preferential transport in localized areas throughout the plot may have also led to the low mass recovery rate. While macropore flow was unlikely because of the sandy texture and lack of soil structure at this site, fingering has been observed in similar soils (Liu et al., 1994). Fingering is a phenomenon

Figure 12–Bromide concentrations (mg kg$^{-1}$ soil) throughout the vadose zone on 10 October 1989.
whereby water and soil chemicals move through vertical channels in the soil profile with little or no flow between the channels.

Because of the detection limits in the analysis, a fairly high percentage of the Br\textsuperscript{–} could have gone undetected in the soil column. If the soil in the entire plot area down to the water table had contained Br\textsuperscript{–} at the minimum detection limit, 16\% of the Br\textsuperscript{–} in the first application could have gone undetected. Soil-water data indicated the average gravimetric soil-water content from 5 to 8 m below the ground surface was approximately 4 to 10\% and varied little throughout the year. With soil-water content at relatively low levels throughout most of the profile, the mass of Br\textsuperscript{–} in the samples was naturally small. Thus, Br\textsuperscript{–} was being transported through a small fraction of the soil pores, leading to a low concentration on a mass basis. In addition, it was likely that some Br\textsuperscript{–} was lost due to plant uptake (Kung, 1990; Owens et al., 1985).

Although not confirmed, there may have been lateral transport in the vadose zone occurring in conjunction with the dense layer in the plot. Hicks et al. (1996) reported an increase in the observed Br\textsuperscript{–} mass in soil cores taken in the southwest corner over time, while cores taken from the northeast corner showed a decrease. Lateral transport off the plot area would explain the observed decrease in total Br\textsuperscript{–} mass. Our spatial analysis indicates Br\textsuperscript{–} was moving at a more rapid rate through the southwest corner of the plot. However, due to the poor mass balance it was impossible to

Figure 13–Bromide concentrations (mg kg\textsuperscript{–1} soil) throughout the vadose zone on 3 November 1990.

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determine if water and chemicals were moving from the northeast corner to the southwest corner above the clay layer. In addition, soil samples collected within the vadose zone outside of the plot boundaries did not contain significant Br\textsuperscript{−} concentrations.

An interesting phenomenon observed on both 10 November 1991 and 10 March 1993, was an apparent increase in the Br\textsuperscript{−} concentration in the capillary fringe area just above the water table (fig. 7). This can most likely be attributed to an increase in water content in these samples which increased the total Br\textsuperscript{−} in that soil sample, increasing the likelihood of detecting the tracer. Thus, our mass balance results appear hampered by low vadose zone soil-water.

At the rates at which Br\textsuperscript{−} was applied, assuming equal distribution throughout the vadose zone, Br\textsuperscript{−} concentrations should have been well above the level of detection. Even with some losses due to flow into the groundwater, plant uptake, and off-plot movement in the vadose zone, it is still difficult to explain the low concentrations observed in the vadose zone.

**CONCLUSIONS**

The transport data collected for this study have several implications for agricultural management in the Coastal Plain. Observed NO\textsubscript{3}\textsuperscript{−} N and Cl\textsuperscript{−} concentrations in the groundwater below the plot were below 7 mg L\textsuperscript{−1} throughout the observation period. Transport throughout the vadose zone was greatly effected by local variations in hydraulic conductivity. Restrictive zones from 1 to 4 m were found to significantly slow Br\textsuperscript{−} transport. Soil-water conditions and total water dramatically influenced the likelihood of transport to groundwater. Transport to groundwater was increased during years where total water in the period 30 days after fertilization exceeded twice the 39-year area average of 108 mm. High saturated hydraulic conductivity zones are more likely to be pathways for groundwater contamination. At this site, NO\textsubscript{3}\textsuperscript{−} N and Cl\textsuperscript{−} were transported to the water table at approximately 9 m in the same year they were applied. Because of the sandy soils and the unusually high total water received at the site, these conditions may be extreme even for this area.

Our results indicate that while Br\textsuperscript{−} was a good tracer for studying transport in the root zone, it was not a good tracer for studying vadose zone transport under our conditions. While concentrations in the root zone were large enough to describe the transport plume well, the concentrations were largely undetectable below 3 m. This appeared to have been heavily influenced by low soil-water conditions. The water-holding capacity of the soil at this site was low. Throughout much of the study the soil-water content throughout the vadose zone was less than 7% by weight. As a consequence of low soil-water and possible preferential flow, the mass balance for Br\textsuperscript{−} was poor. Results may have been improved by increasing application rates or using alternative tracers. Some success has been reported using fluorinated organics as tracers (Bowman, 1984).

The results of this study demonstrate the need for good soil-water and fertilization management. In conjunction with good climatic data, results of this study will be useful for timing fertilization. Saturated profiles, combined with large rainfall soon after chemical application, led to elevated NO\textsubscript{3}\textsuperscript{−} N and Cl\textsuperscript{−} losses from the root zone and elevated groundwater concentrations. Periods of maximum loading coincided with groundwater recharge periods. The risk of groundwater contamination is greatest when the vadose zone soil-water content is high. If large spring thunderstorms occur soon after chemical application with high soil-water conditions, the chance of groundwater contamination by agrichemicals is high on sandy soils in southeast Georgia. By properly timing fertilizer application to avoid these conditions, the risk of groundwater contamination can be reduced.

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