ABSTRACT

ABIT, SERGIO JR. Evaluation of Subsurface Solute Transport and its Contribution to Nutrient Load in the Drainage Ditches Prior to Restoration of a Carolina Bay. (Under the direction of Dr. Aziz Amoozegar and Dr. Michael Vepraskas)

Subsurface solute transport is a major mechanism that contributes to the contaminant load in both surface and ground waters. Among these contaminants are plant nutrients that if transported in excessive amounts to surface waters can cause adverse effects on humans and animals, as well as negative impacts on aquatic life. The general objective of this study was to conduct a field evaluation of subsurface solute transport in the capillary fringe (CF) and shallow ground water (SGW) and their contribution to nutrient load in the ditches prior to restoration of a Carolina Bay. Specifically, this study was aimed at evaluating: a) the horizontal flow of bromide (Br⁻) in the CF and SGW under field conditions, b) the fate of nitrate (NO₃⁻) in the CF and SGW in a sandy field site drained by ditches, and c) the possible contribution of subsurface flow to the increased nutrient load in drainage ditches at a drained Carolina Bay following storm events. The study was conducted in Juniper Bay, a drained Carolina Bay in Robeson County, NC. A solute transport experiment was conducted at a sandy site in the Bay where a solution containing Br⁻ and NO₃⁻ was applied into an auger hole dug to about 10 cm above the CF during the time of application. The transport of Br⁻ and NO₃⁻ in the CF and SGW was monitored by frequently collecting soil water samples using tension lysimeters installed at depths of 45, 60, 75, 90 and 105 cm at lateral distances of 20, 60, 120, 220 and 320 cm from the auger hole along the general direction of the ground water flow. A representative monitoring site from each of the Bay’s mineral and organic soil areas was also chosen for a year-long monitoring of fluctuations in nutrient concentrations in water samples from the Bay’s main ditch exit as well as from the vadose zone, ground water
and lateral ditches. Soil solution from the vadose zone and ground water samples were collected using tension lysimeters installed at 15-cm depth intervals from 15 to 120, and 30 to 180 cm depths at the mineral and organic soil sites, respectively. Ground water samples were collected from three fully perforated wells. Seven piezometers installed at each site also allowed collection of ground water samples from different depth intervals below the water table. The direction and magnitude of the subsurface hydraulic gradient at the monitored sites were also determined using the three-point technique. Lateral transport of Br\(^-\) in the CF was observed in the direction of ground water movement up to 320 cm from the auger hole where solutes were applied. The Br\(^-\) plume from the unsaturated zone that entered into the CF tended to stay and move horizontally in the CF until it was partially moved into the ground water by the fluctuating WT following rain events. The normalized concentrations (concentration in soil solution/concentration in the applied solution) of both NO\(_3^-\) and Br\(^-\) in water samples collected from CF were comparable for all distances from the application spot. However, in the groundwater, the normalized concentration of NO\(_3^-\) was substantially lower than the normalized Br\(^-\) concentrations. We believe the reduction in NO\(_3^-\) concentration in the ground water was due to denitrification. Results from the nutrient monitoring experiment reveal that the sample taken from the main ditch exit following a 5 cm d\(^{-1}\) storm event had higher concentrations of total organic carbon (TOC), phosphates (PO\(_4\)-P), calcium (Ca) and magnesium (Mg) compared to the average of samples collected during baseflow conditions. The same was also observed for samples collected from the vadose zone especially at depths closer to the soil surface where organic carbon and extractable Ca, Mg and PO\(_4\)-P contents were higher. Higher concentrations of these solutes in the ditches and vadose zone coincided with observed increase in the magnitude of the groundwater hydraulic gradient. In addition, it
was observed that following the storm events, the direction of the ground water hydraulic gradient tended to become more perpendicular to the nearby lateral ditch suggesting that the route taken by the water as it moves in the subsurface towards the ditch is shortened. We believe that the increase in concentration of PO$_4$-P, Ca, Mg and TOC in the soil solution at certain depths in the soil profile coupled with their higher rate of movement in the subsurface towards the ditch following the storm event should have contributed to the increase in concentration of such nutrients in the ditches.
EVALUATION OF SUBSURFACE SOLUTE TRANSPORT AND ITS CONTRIBUTION TO NUTRIENT LOAD IN THE DRAINAGE DITCHES PRIOR TO RESTORATION OF A CAROLINA BAY

by:

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SOIL SCIENCE

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To Pam and Andre,

my special reasons to chase a dream.
BIOGRAPHY

Sergio Manacpo Abit Jr. was born on August 28, 1975 in Baybay, Leyte, Philippines. He is the 5th of a brood of five of Sergio E. Abit Sr. and Adelaida Manacpo-Abit. He is married to the former Ms. Pamela Milan Po with whom he has a son, Serge Andre. He completed a Bachelor of Science degree in Agriculture, with a major in Soil Science, from the Visayas State College of Agriculture (now Leyte State University or LSU), in Baybay, Leyte, Philippines. He is connected to the Department of Agronomy and Soil Science at LSU as a junior faculty member. In 2003, he was awarded a full scholarship by the Fulbright-Philippine Agriculture Scholarship Program to pursue graduate studies in Soil Science. In the fall of 2003, he started his Masters of Science program in the Department of Soil Science at North Carolina State University, Raleigh, North Carolina, where he specialized in environmental soil physics under the guidance of Dr. Aziz Amoozegar and Dr. Michael J. Vepraskas. Mr. Abit is a member of the Phi Kappa Phi Honor Society, the Soil Science Society of North Carolina, the Society of Wetland Scientists, the Soil Science Society of America and the American Society of Agronomy.
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CHAPTER I
FIELD EVALUATION OF SOLUTE TRANSPORT IN THE CAPILLARY FRINGE
AND SHALLOW GROUNDWATER

ABSTRACT

Transport of contaminants below the ground surface is generally monitored through collecting and analyzing only groundwater samples. However, laboratory studies in flow cells have shown that subsurface lateral solute transport could occur through the capillary fringe (CF) above the water table (WT). This study was conducted to evaluate the horizontal flow of solutes in the CF and shallow groundwater under field conditions. The study was conducted in a Leon soil (Aeric Alaquod) at Juniper Bay, a Carolina Bay, in Robeson Co., NC. Potassium bromide (KBr) was applied to the bottom of an auger hole dug to within 10 cm above the projected CF at the time of application. Movement of bromide (Br⁻) in the subsurface was monitored by collecting soil water samples at depths of 45, 60, 75, 90 and 105 cm at lateral distances of 20, 60, 120, 220 and 320 cm from the auger hole along the general direction of the groundwater hydraulic gradient. Soil water samples were collected 3, 6, 10, 17, 20, 28, 33, 38, 42, 49 and 59 days after KBr application and analyzed for Br⁻. Lateral transport of Br⁻ in the CF was observed up to 320 cm from the auger hole in the direction of groundwater movement toward the ditches. It was observed that the Br⁻ plume from the unsaturated zone that entered into the CF tended to stay and move horizontally in the CF until it was partially moved into the groundwater by the fluctuating WT following rain events. Fifteen cm of rain and 59 days after tracer solution application, up to 48 percent of the Br⁻ detected 320 cm from the tracer application spot was still in the CF. When monitoring subsurface transport of certain solutes, collecting CF samples should be considered especially in areas where the subsurface horizontal hydraulic gradient is relatively large and the ground water recharge is relatively low.
INTRODUCTION

Land application is commonly used for managing agricultural, municipal and low hazard industrial wastes. Significant removal of some of the dissolved contaminants via plant uptake and biological fixation take place as the water containing the pollutants percolates through the plants’ root zone. In addition, solute attenuation through adsorption by soil as well as chemical and microbial transformations (e.g., volatilization, precipitation) may be significant as this water moves through the profile. Contaminants not removed within the upper layers of the vadose zone continue downward movement until they reach the groundwater. Groundwater moving laterally will eventually transport the contaminants into nearby surface waters or reach a water well.

Presence of dissolved chemicals (e.g., pollutants) and their horizontal movement in the subsurface environment are generally monitored via periodic collection of groundwater samples (i.e., from below the water table) from fully perforated wells or piezometers installed at strategic locations in an area. This is the common method employed in monitoring subsurface pollutant movement near sanitary landfills (Benfenati et al., 2003), chemical-contaminated sites (Lee and Lee, 2003), and even in evaluating the efficacy of certain riparian buffer systems in improving subsurface water quality (Young and Briggs, 2005). This method is founded upon the common concept that horizontal flow of water and dissolved solutes occur only within the saturated zone below the water table (WT). However, results from a limited number of laboratory simulations suggest that horizontal flow and solute transport in the capillary fringe (CF) may be significant.

The CF is the tension-saturated zone above the WT where the pressure head is negative, but the water content is at or very close to saturation (Freeze and Cherry, 1979; Soil Science Society of America, 2005). The thickness of the CF above the water table depends
on many factors, including the nature of the heterogeneous mixture of sediments and encapsulated gases (Ronen, et al., 1997), and presence of surface-active solutes (Henry and Smith, 2002). This thickness can range from a few centimeters in medium fine sand (Jayatilaka and Gillham, 1996) to more than a meter in deep phreatic aquifers (Ronen, et al., 2000). Under equilibrium conditions, the thickness of the CF corresponds to the air-entry value (see Hillel, 1998) of the geologic material in it (Jayatilaka and Gillham, 1996).

Lateral flow in the CF had been demonstrated in as early as 1955 (Luthin and Day, 1955). However, since the height of the CF is often much smaller than the thickness of the underlying saturated zone (i.e., aquifer), “hydrologists often neglect” this zone (Bear, 1979). In fact, with the exception of the quantitative arguments for quasi-horizontal flow in the CF in Bouwer (1978), textbooks on groundwater virtually ignore the role of the CF in fluid flow and transport (Berkowitz, et al., 2004).

The importance of the CF in hydrologic processes had been recognized. Due to the near-saturated nature of the CF, the addition of very small amount of water can fill up the remaining air-filled pores resulting in full saturation. This explains the quick rise of WT across the CF in response to the start of a rain event and the substantial rise in WT level after a minor rain event (Gillham, 1984; Nokarowski and Gillham, 1988). The CF had been reported to affect stream-flow generation in two ways: a) the CF causes a more rapid rise in WT in the watershed relative to the rise in water level in streams causing the rapid generation of hydraulic gradients (Kao, et al., 2001; Abdul and Gillham, 1984) resulting in immediate creation of groundwater discharge to the stream (Abdul and Gillham, 1984; Jayatilaka and Gillham, 1996); and b) the rapidly rising WT may ultimately reach the ground surface and additional rain that falls on it largely becomes part of overland flow into the streams (Abdul and Gillham, 1989). The role of CF in rapid generation of hydraulic gradient near excavation
sites also leads to a rapid generation of drainage water moving into the excavations (Mixon, 1984). Youngs et al. (1996) also reported that when the wetting front of the water infiltrating the soil reaches the CF, infiltration rates decline to a steady-state value approximately equal the saturated hydraulic conductivity ($K_{\text{sat}}$). Particle size distribution was also reported to influence the structure of the CF. In an area with relatively homogenous sediments in the profile, it was observed that there is a sharply-defined boundary between the CF and the unsaturated zone above it (Ronen et al., 1997). Even when the WT rises with recharge, the overall distribution of the CF does not change as it is simply displaced vertically as the WT goes up (Ronen et al., 2000).

Ronen et al. (1997) reported that although there are stagnant regions in the CF, horizontal flow is possible in a portion of CF below a critical height above the WT. Kao et al. (2001) reported that the transport of water above the WT could be as high as 22% of the total flow in sands and up to 7% for sandy clay loam materials. However, simulations using the Hydrus-2D model (Simunek et al., 1999) by Silliman et al. (2002) indicated that lateral flow in the CF may not extend to significant heights above the WT. They reported that 99% of flow only takes place within 0.1 and 1.0 m above the WT in sands and loams, respectively. Results from their simulations also indicate that the CF typically does not contribute significantly to horizontal flow through an aquifer system. They showed that flow through the CF was 6.4 % of total flow for loams when the saturated zone below the WT was 1 m thick and as low as 0.069% of total flow if the saturated zone below the WT was 100 m. Sand-packed flow cell experiments, on the other hand, have shown that solutes in the form of dyes coming from the unsaturated zone can move predominantly (as much as 100%) in the horizontal direction as soon as they reach the CF without intersecting the WT (Silliman et al., 2002, Amoozegar, et al., 2005-unpublished data). Although lateral flow contribution of the
CF to the total groundwater flow may be insignificant, the fact that most if not all of the solutes that reach the CF under certain conditions could be transported horizontally suggests that the CF has a far more vital role in solute transport than what is currently understood.

Demonstration of horizontal solute flow in the CF has so far been studied by evaluating the movement of dye solutions in sand-packed flow cells. In these experiments, water had been forced to move in one direction laterally when the downward gradient was zero. If observations made in the laboratory study prove to hold true under field conditions, they could pose serious doubts about the sufficiency of relying solely on the collection and analysis of groundwater samples for monitoring horizontal subsurface solute movement. The objective of this study was to evaluate the horizontal flow of solutes in the CF and shallow groundwater under field conditions.
METHODOLOGY

The study was conducted at the NE rim of Juniper Bay, a 300-hectare Carolina Bay located 10 km southeast of Lumberton, in Robeson County, North Carolina (34°30’30”N 79°01’30”E) (Fig. 1). The area was mapped to have soils belonging to the Leon series (sandy, siliceous, thermic, Aeric Alaquod) (Vepraskas, et al., 2003). As early as 60 years prior to this study, this bay was drained with a series of lateral ditches connected to a main ditch that traverses the bay in the NE to SW direction.

Soil profile description, soil sample collection and analysis

The soil profile was described in a pit dug 7 m from a lateral ditch and 30 m from the main ditch. At the time of profile description, the water table was at a depth of 105 cm that limited the depth of the sampling pit. Bulk samples were collected from the pit walls at 15 cm depth intervals from the surface down to 105 cm. Intact core samples (7.5 cm diameter and 7.5 cm long) in vertical orientation were also collected in triplicate at 15 cm depth intervals from the surface to 105 cm depth.

Saturated hydraulic conductivity ($K_{sat}$) of the top part of the saturated zone (i.e., aquifer) was measured by slug test (Amoozegar, 2004; Bouwer and Rice, 1976). Saturated hydraulic conductivity computation was done with the Bouwer and Rice Parameter Estimation method using the Super Slug Version 3.1.8 (Starpoint Software Inc., Cincinnati, Ohio). Saturated hydraulic conductivity of the unsaturated zone was measured in situ by the constant-head well permeameter technique (Amoozegar, 2004).

Using the bulk samples, particle size distribution was determined by the hydrometer method (Gee and Or, 2002). For this analysis, soil samples were pre-treated with 30 percent hydrogen peroxide ($H_2O_2$) to oxidize the organic matter prior to the dispersion and sedimentation. Soil water retention of the intact cores between 0 and 1.5 MPa pressure was
measured (Dane and Hopmans, 2002). Bulk density of different depth intervals was determined by the core method (Grossman and Reinsch, 2002) and particle density was determined by the air pycnometer technique (gas displacement) (Flint and Flint, 2002). Total organic carbon was determined through dry combustion with a Perkin-Elmer PE2400 CHN Elemental Analyzer (Culmo, 1988).

**Installation of tension samplers and wells**

Five solution samplers (Fig. 2) were installed in a cluster or nest with their porous cups at depths of 45, 60, 75, 90 and 105 cm depths (Fig. 3). Eight nests were installed on equally spaced spots on the arc of a 120 cm-diameter circle initially laid out on a flat area located 7 m from a side ditch and 20 m from the main exit ditch (Fig. 3). Three fully perforated wells (hereafter referred to as wells) were installed on the vertices of a triangle drawn near the circle of nests. These wells allowed determination of the depth to the water table, thereby giving an indication of the location of the CF. The same set of wells was used to estimate the general direction and magnitude of the subsurface lateral hydraulic gradient via the triangulation or three-point technique (Sanders, 1998). The distance between wells was 3 m.

**Soil water sample collection**

One week after installation of the tension lysimeters, soil water samples were collected and analyzed for background bromide (Br) concentration using the Lachat Quickechem 8000 slow injection auto analyzer (Greenberg et. al., 1992). For this sampling and all subsequent scheduled sampling, water table depths in the three wells were first measured using a dipper (Herron Instruments Dipper T, Ontario, Canada). To collect soil water samples, a vacuum trap was attached to each tension lysimeter (Fig. 2). Using a hand pump, the lysimeter was initially purged by applying vacuum to the trap. After emptying the trap and reattaching it to the sampler, the air from the trap was evacuated to create approximately 800 cm of tension (equivalent to -800 cm of pressure) inside the sampling cup. The vacuum inside the trap was
maintained for 10 to 30 minutes to draw soil solution into the porous cup and then into the sample bottle in the trap. After opening the air vent on the sampler (see Fig. 2), the remaining solution in the porous cup of the lysimeter was drawn into the sample bottle in the trap. Up to 30 mL soil solution were collected by this procedure.

**Location of the capillary fringe**

In a sand-packed flow cell experiment (Amoozegar et al., 2005), the upper boundary of the capillary fringe was observed to be as high as 20 cm above the simulated water table. Based on this, it was conservatively assumed that in the field site, the upper boundary of the capillary fringe was 20 cm above the water table. To verify its location at the study site, a five-segmented Moisture Point time domain reflectometer (TDR) probe (Gable Corp, Victoria, Canada) was installed just outside the circle of nests (Fig. 4). The probe allowed volumetric water content (VWC) measurements at zero (surface) to 15, 15 to 30, 30 to 45, 45 to 60 and 60 to 90 cm depth intervals. Water content measurements were taken every time soil water samples were collected and the results were compared with the computed porosities at the corresponding 15 cm depth intervals in the soil to determine the degree of saturation of each given layer.

**Bromide transport monitoring**

Potassium bromide (KBr) was used as a tracer chemical to evaluate the lateral migration of solutes in the CF. Bromide was used as tracer because no Br had been applied to the site in the past, and as an anion, there is little chance for Br to be attenuated by the sandy soil in the area.

At the center of the circle of nests, an auger hole was dug to a 45 cm depth and 15 L of 50 mM potassium bromide (KBr) solution was applied to the bottom of the hole. A modified Compact Constant Head Permeameter (Amoozegar, 1989) was used to regulate the rate of
application (Fig. 3). At the time of KBr application, the water table was at 75 cm from the surface and the upper boundary of the CF was estimated to be 55 cm from the surface. In effect, the solution containing the Br tracer was applied into an unsaturated region of the soil roughly 10 cm above the capillary fringe (Fig. 5A). The auger hole was backfilled after the KBr solution infiltrated the soil.

Soil water samples were collected from all nests 4, 11 and 24 days after application of the KBr solution. Data from the Br analysis of the water samples collected were used to evaluate the general direction of movement of the plume. Upon determination of the general direction of the ground water movement, additional sets of nests were installed 120 cm, 220 cm and 320 cm from the application spot (Fig. 4), 31, 39 and 49 days after tracer solution application, respectively. Subsequent soil water collections from all nests in the direction of flow were done 31, 39, 49 and 58 days after KBr application to follow the transport of bromides. Data from the initial tracer application and monitoring were used to plan a more detailed monitoring for a second tracer solution application experiment.

Immediately after collecting water samples on day 58, a 30-cm deep auger hole was dug on the spot where the KBr was initially applied. Twenty-five L of distilled water were then applied to the bottom of this auger hole to facilitate flushing of the remaining Br in the monitoring area. The hole was then backfilled. Sixteen days after the application of distilled water, background samples were collected from all the tension lysimeters and analyzed for Br in the laboratory. A week later, a set of 45-, 60-, 75-, 90- and 105-cm lysimeters was installed in a semi-circle 20 cm around the spot where the auger hole was previously dug (nest 0 in Fig. 4) for assessing the initial distribution of Br in the soil after application.

Thirty days from application of distilled water, the water table was at 60 cm depth, and a second pulse of bromide, consisting of 10 L of 76 mM KBr solution, was applied on
the previous application spot. This time, the solution was applied to the bottom of an auger hole (depth of 30 cm) which was approximately 10 cm above the projected upper boundary of the CF (Fig. 5B). After the solution infiltrated the soil, the hole was backfilled and an hour later, soil water samples were collected from the tension samplers immediately next to the auger hole.

Based upon the direction and rate of advance of the plume from the first experiment, soil water samples were collected from specific nests 3, 6, 10, 17, 20, 28, 33, 38, 42, 49 and 59 days after the second tracer solution application. The samples were transported to the laboratory and analyzed for Br as described earlier.
RESULTS AND DISCUSSION

Soil and site characteristics

At the study site, soil textural class from the surface down to 105 cm was either sandy loam or loamy sand with sand contents ranging from 77 to 87% (Table 1). No water-restricting layer was identified. Bulk densities tended to increase with depth while porosities decrease.

Location of the capillary fringe

The time domain reflectometry measurements (TDR) taken immediately after each sampling (during the second Br monitoring study) showed that the minimum thickness of the near-saturated zone above the WT was roughly 20 cm (Fig. 6). This agrees with the data from the earlier-mentioned study of Amoozegar et al. (2005) which demonstrated that in a coarse-textured soil, the capillary fringe could be as thick as 20 cm above the WT. In addition, the moisture release curves of three intact core samples collected from the 45 to 60 cm layer, which were immediately above the WT for most of the second study, indicated that under static conditions, the soil would still be nearly-saturated after application of -20 cm of pressure head (see Fig. 6). This indicate that the CF above the WT (normalized pressure head at WT = 0) would be at least 20 cm thick.

First experiment on subsurface Br transport

Plume movement direction:

Bromide concentrations at 60, 120, 220 and 320 cm from the center of the application spot (auger hole) on 11, 35, 51 and 58 days after KBr application in the first experiment, respectively, for various depth intervals are presented in Figure 7. As shown in Figure 7A at 11 days after the initial application, Br distribution was limited to nests 2 and 3 with no Br detected by the other nests located on the circumference of the 60 cm radius circle. The Br
concentration in nest 2 on day 11 was substantially higher than in nest 3. After 35 days, the plume was detected at 120 cm from the application spot around nests 6 and 7 only (Fig 7B). The plume expanded as it reached 220 cm from the application spot with highest concentrations detected at nest 11 after 51 days (Fig 7C). Subsequent collection and analysis of soil water samples showed that high Br concentrations were detected at nests 15 and 16 as the plume moved through the layer of nests installed at 320 cm from the application spot (Fig 7D). Based on these observations, we estimated that the Br plume in the CF and shallow groundwater (SGW) was moved within the area inscribed by the broken line in Figure 4.

From the above results, and with reference to the nest locations in Figure 4, it could be deduced that the plume moved in a rather straight line through nests 2, 6, 11 and 16, which was in agreement with the general direction of subsurface water flow (see Fig 4) as determined by the three-point technique.

**Plume movement relative to the WT:**

 Eleven days after Br was applied 30 cm above the WT (initial WT at 75 cm), the bulk of the Br plume was in the CF zone at 45 and 60 cm depths (Fig 7A) (see Fig. 8 for WT data). The concentration of Br in SGW was an order of magnitude less than the Br concentration in the CF. The data also indicated that the 0.24 cm rain event on day 4 (Fig. 8) was not significant enough to effectively push the plume below the WT. The 1.1 cm rain on day 20, however, seems to have pushed a part of the plume below the WT based on the relatively higher Br concentrations at the 75 and 90 cm depths in nest 6 on day 35 (Fig 7B). The detection of Br at the 105 cm depth also indicated that the plume had moved downward.

 Additional indication of downward movement of the plume resulting from rain events was observed on day 51 at 220 cm from the application spot. The 1.0 cm rain that fell on day 39 resulted in a temporary rise of the WT. As the WT receded, the Br was carried to greater
than 105 cm depths below the land surface. In fact, Br concentration at 90 and 105 cm depths were higher than those at 45 and 60 cm (which were above the WT) (Fig. 7C). At a distance of 320 cm from the application spot the Br concentrations at the 90 and 105 cm depths in nest 15, 16 and 17 were higher than above the WT (45 and 60 cm - Fig 7D). However, it is interesting to note that despite the rain events, Br was still present in the top layer of the CF at 320 cm away from the application spot.

This experiment showed that solutes applied to the unsaturated zone tended to stay above the WT and move horizontally in the CF until they were carried below the WT by sufficient percolation arising from rain (or irrigation) events.

**Second experiment on bromide transport**

On the day of KBr solution application at 30 cm above the WT (WT at 60 cm), Br was only detected at the 45 cm depth at nest 0. This indicated that initially, the Br plume stayed in the CF (Fig. 9). The peak of the plume was detected at nest 0 three days after KBr application with much of the Br remaining at 45 cm and 60 cm which were above the WT. It was only after the rain event (0.9 cm) in day 4 that Br was detected in the SGW at the 75 cm depth (see Fig. 9 for rain data). We believe water percolation following the rain event in this case pushed some of the Br downward. Figure 9 also indicates that the Br plume at nest 0 did not go deeper than 75 cm (or more than 15 cm below the initial water table) despite the numerous rain events totaling 8.43 cm that took place during the first 28 days when Br was detected at nest 0.

Six days after Br application, the WT was below 60 cm depth and Br was detected at 45 and 60 cm depths in nest 2 and 3 (see Fig. 4 for nest locations) at a distance of 60 cm from the application spot (Fig. 10). On day 10, Br concentrations were higher than 100 mg L$^{-1}$ at the 45, 60 and 75 cm depths at nest 2 whereas no Br was detected at 75 cm at nest 3. It
appears that the core of the plume was near nest 2 and that the rain events that occurred on
days 10, 12 and 13 pushed some of the Br downward into the SGW around nest 2. This is
based on the fact that after day 10, there was a marked decrease in concentrations at the 45
and 60 cm depths that were coupled by an increase in concentrations at 75 and 90 cm (both in
the SGW). Although Br was only detected at 45 and 60 cm depths (which were above the
WT for most of the study) at nest 3, there were indications that these rain events were able to
push part of the plume downward as evidenced by a marked decrease in Br concentration at
45 cm and an increase at the 60 cm depth after day 10. We believe that the lack of direct
agreement between the Br concentrations at nests 2 and 3 is due to the shape of the Br plume
in the CF and SGW.

Bromide was detected in the CF and the upper part of the aquifer at 120 cm from the
KBr application spot on day 17 (Fig. 11). The highest Br concentration at each of 45, 60 and
75 cm depths was observed in nest 7. Unlike nests 2 and 3 where the highest Br
conscentration was first detected at the 45 cm depth, higher Br concentrations were initially
detected at the 60 cm depth at nests 6 and 7. In addition, relatively high levels of Br were
detected at 75 cm depth and a small amount of Br was detected at 90 cm depth. These
suggest that the plume had indeed moved downward within the CF and into the SGW. Also,
only a small amount of Br was at the 105 cm depth in nest 6 after 49 days.

Among the nests located 220 and 320 cm from the application spot, the highest Br
concentrations were detected at nests 12 and 17, respectively. Bromide was observed at 45
and 60 cm depth (within the CF) 17 days after the initiation of the experiment at 220 cm from
the source (Fig. 12). At nest 12, higher concentrations were detected at 45, 60 and 75 cm
depths than at 90 and 105 cm depths until day 38. Figure 12 also shows that parts of the
plume had been pushed further down as soon as it reached nest 17. In fact, highest
concentration of Br was detected at 105 cm on day 49. It could also be noted that after 59 days of being exposed to field conditions, significant amounts of Br were still detected in the CF in nests 12 and 17.

**Bromides in the CF and SGW**

A linear transect of nests along the direction of plume movement was chosen to assess how the relative amount of Br detected in the CF and the SGW at different distances from the source changed with time. Included in the transect were nests 0, 3, 7, 12 and 17 to represent the nests of tension samplers installed at 20, 60, 120, 220 and 320 cm from the application spot, respectively (see Fig. 4 for nest locations). The relative proportions of Br detected in the CF and SGW (mg Br detected in CF or SGW/total mg of Br detected in a nest location) at the nests in the transect on days 3, 10, 17, 28, 38 and 59 are shown in Figure 13.

Figure 13A shows that after 3 rainless days following KBr application (see rain data in Fig. 9) the plume had traveled at least 20 cm horizontally in the CF and remained above the WT. Ten days after KBr application the plume had traveled at least 60 cm horizontally in the CF (Fig. 13B). It could also be noted that 3% of the amount of Br which was still detected at 20 cm from the source was in the SGW. This suggests that the 0.9 cm rain event on day 4 was able to partially push the plume into the groundwater.

The rain events that followed after day 10, including the 2.7 cm rain on day 12, raised the WT to at least 45 cm below the land surface (see Fig. 9 for rain data). We should note that this rise in the WT is the result of water entering the remaining unsaturated pores in the CF from above causing complete saturation and instantly raising the level of the WT (Gillham, 1984). This suggests that a rise in WT would not necessarily cause the plume to move up. As soon as the CF becomes fully saturated, additional percolation then fills a larger volume of air filled pores above the former CF and causes a more deliberate rise in WT.
When the percolation stops, the receding WT should have resulted in effective leaching of the plume below the WT. This is evidenced by the fact that on day 17, as high as 96% of the Br detected 20 cm from the source was already in the SGW (Fig. 13C). It should be noted, however, that despite the rain events, Br still could be detected in the CF up to a distance of 220 cm from the source 17 days after KBr application. The lack of uniformity of the distribution of Br in the CF and SGW as the plume moved through the monitored area could be attributed to the combined effect of the irregularity of the shape of the plume below and above the WT, the fluctuation in WT depth, and the non-uniformity of the soil properties at different distances from the source.

On day 28, the plume had already moved passed nest 0 (20 cm from application spot) and had reached as far as 320 cm from the application spot (Fig 13D). By this date, the WT was at less than 60 cm depth and almost all of the Br was below the WT. As mentioned earlier, the rain events after day 12 should have generated enough percolation to raise the WT effectively lowering the plume and then transporting Br to below the WT as the groundwater receded.

The plume passed the 60 cm nest by day 40 (see Fig 10), and by day 59 part of the plume moved beyond the monitoring area (Fig 13F). Precipitation was very limited between days 38 and 59 (only 3.2 cm of rain in 21 days). This could have resulted in a relatively reduced downward movement of the plume during such period. Hence, when the WT was as deep as 79 cm on day 59, much of Br (as high as 55% at nest 7) was detected above the WT (Fig. 13F).
CONCLUSIONS

This study evaluated the horizontal flow of bromide (Br), a non-reactive solute, in the capillary fringe (CF) and shallow groundwater in a sandy soil. In two experiments conducted at the study site, Br was transported laterally within the CF and the top portion of the shallow groundwater to a distance of 320 cm from the Br application spot in 59 days. Although mass flow and diffusion are the two possible mechanisms responsible for the movement of solutes in the subsurface environment (Hillel, 1998), our results showed that mass flow (i.e., convective transport) was the major mechanism responsible for the subsurface transport of Br in this study. This is based on the fact that Br did not move in all directions and that it was only detected in the lysimeter nests along the direction of the subsurface horizontal hydraulic gradient.

The results indicate that the laboratory findings of Silliman et al. (2002) and Amoozegar, et al. (2005) demonstrating that solutes could be transported horizontally in the CF can hold true under field conditions. The result also suggest that a large portion of the mass of solutes that enter into the CF from a point or non-point source could be laterally transported a relatively long distance before entering the water table (WT). This finding is important because the contribution of the CF to the subsurface transport of solutes is generally ignored when monitoring waste disposal sites through ground water sampling. We believe that the solutes that move vertically down in the unsaturated zone would stay and move horizontally in the CF until they are moved by the fluctuating WT following rain events.

Our concept of how a fluctuating water table affects solute flow in the CF is shown in Figure 14. Prior to a rainfall event, the solutes that come into the CF would tend to remain
in it (Fig 14A). A portion of the water percolating through the soil enters the original CF and results in the rise of the WT without causing a significant vertical water movement within the original saturated zone (originally below the WT) (Fig 14B). Conversely, solutes that originally resided at the original CF prior to the rain event remained at such depth despite the WT rise. When water percolation ceases, a new CF is established and the former CF now becomes the top of the saturated zone (below the WT) (Fig. 14B). Continued absence of percolation causes the WT to drop and a limited volume of water moves vertically downward through the newly formed CF and top of the saturated zone. Continued drainage causes the top portion of the saturated zone to become the CF again without moving an appreciable amount of solute from that zone (Fig. 14C).

Based on the findings of this study, we believe that collection of CF samples should be considered when monitoring the subsurface transport of contaminants. This is particularly true for areas where the subsurface horizontal hydraulic gradient is relatively large and the ground water recharge is relatively low.
LITERATURE CITED


Table 1. Selected soil properties of the soil in the experimental area.

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<th>Depth Interval (cm)</th>
<th>Sand</th>
<th>Clay</th>
<th>Soil Texture</th>
<th>$K_{sat}$</th>
<th>Bulk Density</th>
<th>Particle Density</th>
<th>Porosity</th>
<th>Organic carbon</th>
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<td>86.55</td>
<td>12.77</td>
<td>LS</td>
<td>ND</td>
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<td>2.51</td>
<td>0.53</td>
<td>3.70</td>
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<td>12.76</td>
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<td>2.41</td>
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<td>LS</td>
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<td>1.61</td>
<td>2.58</td>
<td>0.37</td>
<td>1.16</td>
</tr>
</tbody>
</table>

ND- Not Determined
Figure 1. Aerial photograph of Juniper Bay with marked location of the sandy mineral soil site, and the main and lateral ditches. In the inset, the location of Juniper Bay in the southeastern part of North Carolina is shown by the star.
Figure 2. Schematic illustration of a tension sampler with its associated vacuum trap.
Figure 3. Photograph showing the first set or “circle of nests” and the constant head permeameter used to apply the tracer solution into an auger hole dug at the center of the circle. In the inset is a photograph of a “nest” composed of tension samplers with porous cups at 45 cm (18 in), 60 cm (24 in), 75 cm (30 in), 90 cm (36 in) and 105 cm (42 in) below the soil surface.
Figure 4. Schematic illustration of the monitoring set-up for the bromide tracer study showing the location of the nests, wells, time domain reflectometry (TDR) probes and the area covered by the plume for the first and second Br monitoring studies.
Figure 5. Schematic diagrams for the first (A) and second (B) tracer solution application.
Figure 6. Depth to water table and the upper boundary of the near-saturated zone (measured using TDR) through the duration of the second Br monitoring study (A) and the moisture release curves of the soil at the 45 to 60 cm layer which is location of the CF for most of the study (B).
Figure 7. Bromide concentrations detected along the plume movement direction at different distances from the KBr application spot for the initial bromide experiment. Nest locations are shown in Figure 4.
Figure 8. Rainfall data and measured water table depths for the duration of the initial bromide experiment.
Figure 9. Rainfall and water table data, and the bromide concentrations detected at various depths at nest 0 throughout the duration of the second Br monitoring study. Nest 0 was 20 cm from the tracer solution application spot.
Figure 10. Bromide concentrations detected at various depths at nests 2 and 3 for the duration of the second Br monitoring study. Nests 2 and 3 were 60 cm from the tracer solution application spot.
Figure 11. Bromide concentrations detected at various depths at nests 6, 7 and 8 for the duration of the second Br monitoring study. Nests 6, 7 and 8 were 120 cm from the tracer solution application spot.
Figure 12. Bromide concentrations detected at various depths at nests 12 and 17 for the duration of the second Br monitoring study. Nests 12 and 17 were located 220 cm and 320 cm from the tracer solution application spot, respectively.
Figure 13. Relative proportions of bromide detected in the capillary fringe (CF) and the shallow ground water (SGW) at nest 0, 3, 7, 12 and 17 located 20, 60, 120, 220 and 320 cm from the application spot, respectively, along the plume flow transect at various days after KBr application.
Figure 14. Schematic illustration showing the location of the plume before and after the rain event, and after drainage following the rain event.
CHAPTER II

FATES OF NITRATE IN THE CAPILLARY FRINGE AND SHALLOW GROUNDWATER IN A SANDY SOIL DRAINED BY DITCHES

ABSTRACT

Nitrate (NO$_3^-$) is a potential contaminant in soil and water bodies that could trigger health and environmental problems. Monitoring of its accumulation and transport in soils and groundwater are generally accomplished by collecting groundwater samples using fully perforated wells or piezometers. Laboratory simulation using flow cells have shown that lateral transport of solutes in the capillary fringe (CF) above the water table (WT) is significant. This study was aimed at evaluating the fate of NO$_3^-$ in the capillary fringe (CF) and shallow groundwater (SGW) in a sandy field site drained by ditches. It was conducted at a site with sandy soil and a shallow water table at Juniper Bay, a drained Carolina Bay in Robeson County, NC. Ten L of a solution containing 1,113 mg L$^{-1}$ nitrate (equivalent to approximately 18 mmol L$^{-1}$ nitrate) and 6,123 mg L$^{-1}$ bromide (equivalent to approximately 77 mmol L$^{-1}$ bromide) was applied to the bottom of an auger hole dug to within 10 cm above the CF at the time of solute application. Movement of each of NO$_3^-$ and Br$^-$, a relatively stable reference anion, in the subsurface was monitored by frequently collecting soil water (including ground water) samples using tension lysimeters installed at depths of 45, 60, 75, 90 and 105 cm at radial distances of 20, 60, 120, 220 and 320 cm from the auger hole along the general direction of the ground water flow. Soil water samples were collected 3, 6, 10, 17, 20, 28, 33, 38, 42, 49, 59 and 84 days after tracer solution application and were analyzed for NO$_3^-$ and Br$^-$ content. Nitrate and Br$^-$ plumes that entered into the CF from the unsaturated zone stayed and moved horizontally in the CF until they were partially carried into the groundwater by the fluctuating WT following rain events. Both NO$_3^-$ and Br$^-$ were
detected in relatively high concentrations after 84 days at a distance of 320 cm from the application spot. The normalized concentrations (concentration in soil solution/concentration in the applied solution) of both NO$_3^-$ and Br in water samples collected from CF were comparable for all distances from the application spot. However, in the groundwater, the normalized concentration of NO$_3^-$ was substantially lower than the normalized Br concentrations. We believe the reduction in NO$_3^-$ concentration in the ground water was due to denitrification. We also attribute the relatively extended persistence of NO$_3^-$ in the CF to the partially saturated nature of the CF that may have inhibited the development of anoxic conditions that consequently minimizes NO$_3^-$ loss through denitrification. This allowed more NO$_3^-$ to travel longer and to relatively greater distances in the CF than it would in the SGW. When monitoring subsurface NO$_3^-$, solely relying on collection of groundwater samples may lead to an underestimation of the extent of NO$_3^-$ accumulation and transport in the subsurface. This is particularly true in areas with limited precipitation.
INTRODUCTION

The U.S. Environmental Protection Agency (USEPA, 2002) reported that 104 million people, or 37% of the U.S. population, rely on groundwater as a source of drinking water. Groundwater contamination by nitrate (NO$_3^-$) leached from the soil is a major health and environmental problem that must be addressed. Rising concentrations of NO$_3^-$ in groundwater have been of concern due to its links with infantile methemoglobinemia or “blue baby syndrome”, an abnormality of the blood that impairs its ability to convey oxygen. Although blue baby syndrome is relatively rare in industrialized nations, it is still a risk in developing countries, especially where drinking water is from shallow wells in heavily fertilized farming areas (WHO, 2005a). In addition, NO$_3^-$ from drinking water could be converted by stomach enzymes in the gastrointestinal tract into carcinogenic compounds like nitrosamines (Cogger, 1988; Gerba, 1996). As a standard, the USEPA had set 10 mg L$^{-1}$ NO$_3^-$-N as the safe level of NO$_3^-$ in drinking water in the U.S. (USEPA, 2005a). The World Health Organization (WHO), on the other hand, has set 50 mg L$^{-1}$ NO$_3^-$ (11.3 mg L$^{-1}$ NO$_3^-$-N) as the safe limit (WHO, 2005b). Nitrate concentrations above 100 mg L$^{-1}$ are also considered unfit for livestock (Freitas and Burr, 1996). Excessively high NO$_3^-$ concentrations in groundwater that are subsequently discharged to surface water bodies can also cause eutrophication (increased aquatic plant growth) that leads to a decrease in dissolved O$_2$, ultimately impacting aquatic animal life negatively (Brady and Weil, 2002).

Nitrogen is an essential element to plant growth and development. Nitrogen is also a highly versatile element that can be found in different forms. Plants can take up nitrogen as ammonium (NH$_4^+$) and nitrate (NO$_3^-$). Nitrate salts are generally highly soluble in water and dissociate to NO$_3^-$ and the corresponding cations. To assure that sufficient nitrogen is
available to crops, $\text{NO}_3^-$ is often applied to soils in the form of nitrogen-containing fertilizers. Hallberg (1989) reported that the application of these fertilizers to irrigated crops has been the most extensive human cause of $\text{NO}_3^-$ pollution in ground water systems. In the U.S. alone, the amount of inorganic $\text{NO}_3^-$ that had been released to land and water bodies from 1991 through 1993 was approximately 112 million pounds, of which about 50.2 million pounds were from nitrogenous fertilizer inputs (USEPA, 2005b). Worldwide, industrial production of nitrogen-fertilizer is estimated to be $9.04 \times 10^7 \text{ Mg yr}^{-1}$ (Food and Agriculture Organization Database, 1996). This high level of fertilizer production speaks about the possible water quality impact it may bring about when used improperly. In addition, significant $\text{NO}_3^-$ contributions to soil are derived from animal manure (Griffin and C.W. Honeycutt, 2000; Eghball, 2000) and surface-applied wastewater (Reddy and Dunn, 1984). Other sources of $\text{NO}_3^-$ in the soil are atmospheric deposition (Rubio et. al, 2002; Cerón et. al., 2002) and in situ decomposition of organic matter in well-aerated soils (Brady and Weil, 2002).

As indicated earlier, nitrate salts are generally highly soluble, and because $\text{NO}_3^-$ is negatively charged, it is not strongly adsorbed to soil colloids and is considered highly mobile within the soil liquid phase (Jenkinson and Smith, 1998; Artiola, et al., 1996). In areas of low rainfall, unutilized $\text{NO}_3^-$ can accumulate in soils. Since most cultivated fields are in a pseudo-equilibrium with regards to N transformations (i.e., that the annual mineralization is approximately equal to annual immobilization), excess $\text{NO}_3^-$ in areas with abundant rainfall is subject to loss (Gilliam, 1988). Because of its solubility and negative charge, $\text{NO}_3^-$ generally moves with moving water at about the same rate (Fuller and Warrick, 1984). The rate of nitrate transport depends on a number of factors including precipitation.
and infiltration rates, soil texture and structure, and even conservation tillage (Brady and Weil, 2002). However, despite its high solubility and mobility, excess NO$_3^-$ entering the soil may not immediately pollute the groundwater. In fact, the full extent of the effect of NO$_3^-$ migration on groundwater quality may not be felt for years, especially in areas where the water table is relatively deep (Hillel, 1998). For instance, under irrigated citrus plantations in California, Pratt et al. (1970) discovered plumes of NO$_3^-$ that had moved below the root zone but had not yet reached the water table.

The primary mechanisms that can reduce NO$_3^-$ concentrations in soil are uptake by plants and microbial denitrification, (van der Ploeg et al, 1997). It should be noted that plants are only effective seasonally and the effective depth of treatment is determined by the degree of root penetration. When NO$_3^-$ leaches below the rhizosphere, there are other possible fates besides continued leaching that could be significant. These include soil retention, assimilatory nitrate reduction into microbial biomass, dissimilatory nitrate reduction to ammonium, and biological denitrification. All of these fates apart from denitrification can only temporarily immobilize nitrates (Korom, 1992). Essential conditions favoring denitrification include: (1) the presence of denitrifying bacteria, (2) presence of organic materials as electron donors, (3) anaerobic conditions or restricted oxygen availability, and (4) the presence of NO$_3^-$ as a terminal electron acceptor. (Firestone, 1982; Vepraskas and Richardson, 2000).

Fully perforated wells or piezometers are generally used in monitoring subsurface movement of NO$_3^-$ at agricultural watersheds (Tomer and Burkart, 2003; Thurnburn et al., 2003), high density animal farming operations (Rodvang et al., 2004), septic systems (Kampbell et al., 2003), and even in evaluating the efficacy of certain riparian buffer systems.
for improving subsurface water quality (Bedard-Haughn et al., 2004; Young and Briggs, 2005). Despite being limited to collecting ground water samples (i.e., below the WT) wells and piezometers are widely used because of the common concept that horizontal flow of water and solutes occur only within the saturated zone below the water table. On this basis, it is assumed that NO$_3^-$ is not transported horizontally through the area’s subsurface if it is not detected below the WT. Results from a limited number of laboratory simulations, however, have posed a question on this concept by demonstrating that horizontal water flow and solute transport in the capillary fringe (CF), the tension-saturated zone above the water table where the water content is close to saturation (Freeze and Cherry, 1979; Soil Science Society of America, 2005), is possible. Up to 100% of solutes coming from the surface have moved laterally as they enter the CF as shown in flow-cell experiments (Silliman et al., 2002; Amoozegar et al., 2005). The fact that the CF can be more than a meter thick above the WT (Ronen et al., 2000) even increases the likelihood that wells and piezometers may not detect a moving plume.

Nitrate is considered a redox-positive ion and if conditions below the water table meet the requirements for denitrification, the GW moving horizontally in the aquifer may be devoid of NO$_3^-$. The CF, on the other hand, due to its “partially saturated” nature, will have pores that remain aerated. Therefore, anaerobic conditions may not be achieved in the CF and denitrification may not occur. Thus, it is likely that NO$_3^-$ that enters into the CF would retain its chemical integrity, and like other highly soluble pollutants, could be transported horizontally into water wells or nearby drainage systems. If the retention of NO$_3^-$ in the CF is proven to hold true under field conditions, it could pose a serious doubt about the sufficiency of relying solely on the collection and analysis of groundwater samples for monitoring
horizontal subsurface NO$_3$\textsuperscript{-} movement. The objective of this study was to evaluate the fate of NO$_3$\textsuperscript{-} in the capillary fringe and shallow groundwater in a sandy field site drained by ditches.
METHODOLOGY

A field solute transport experiment was conducted in a flat area at the northeastern end of Juniper Bay, a 300-hectare Carolina Bay located 10 km southeast of Lumberton, in Robeson County, North Carolina (34°30′30″N 79°01′30″E) (Fig. 1). At the time of the study, this bay had been drained by a series of lateral ditches connected to a main ditch that traversed the bay in the NE to SW direction. The soils in the general area of the study were mapped as Leon series (sandy, siliceous, thermic, Aeric Alaquod) (Vepraskas, et al., 2003). Experiments were conducted 7 m from a lateral ditch and 20 m from the main ditch. A pit was dug to 105 cm depth to describe the soil profile and collect soil samples. The pit was dug 10 m from the experiment area, and 7 m from the lateral ditch. Bulk soil samples were collected at every 15 cm depth intervals to a depth of 105 cm. Intact core samples (7.5 cm diameter and 7.5 cm long) in vertical orientation were collected in triplicate from the same depth intervals.

Below-WT saturated hydraulic conductivity ($K_{sat}$) was measured by a slug test (Amoozegar, 2004; Bouwer and Rice, 1976) with computations done with the Bouwer and Rice Parameter Estimation method using the Super Slug Version 3.1.8 (Starpoint Software Inc., Cincinnati, Ohio). Saturated hydraulic conductivity of the unsaturated zone was measured in situ by the constant-head well permeameter technique (Amoozegar, 2004). Soil water retention of the intact cores between 0 and 1.5 MPa pressure was measured (Dane and Hopmans, 2002). Bulk density of different depth intervals was determined by the core method (Grossman and Reinsch, 2002) and particle density was determined by the air pycnometer (gas displacement) technique (Flint and Flint, 2002). Particle size distribution was determined by the hydrometer method (Gee and Or, 2002). Soil bulk samples were pre-
treated with 30 percent hydrogen peroxide (H$_2$O$_2$) to oxidize the organic matter prior to the dispersion and sedimentation. Total organic carbon was determined through dry combustion with a Perkin-Elmer PE2400 CHN Elemental Analyzer (Culmo, 1988).

**Installation of tension samplers and wells**

Soil solution samplers, also referred to as tension lysimeters, were used to collect samples of soil solution (above the WT) and shallow ground water (below the WT). Each tension lysimeter was made up of a ceramic porous cup (air-entry pressure = 1 atm) attached to a section of ¾-inch (outside diameter) schedule 80 polyvinyl chloride (PVC) pipe. The length of the PVC pipe connected to each porous cup was based on the desired depth to which the porous cup was installed. The other end of the pipe was plugged by a rubber stopper with tight access holes for two plastic tubes: one extending to the bottom of the inside chamber of the lysimeter while the other serving as a vent. Each tension lysimeter was attached to a dedicated trap for collecting sample (see Figure 2).

One spot of the experiment site was selected for application of a solution containing potassium bromide (KBr) and magnesium nitrate Mg(NO$_3$)$_2$. Five tension lysimeters were installed in a cluster or nest with their porous cups at depths of 45, 60, 75, 90 and 105 cm depths (Fig. 3- inset) at various radial distances around this spot. A total of 23 nests were installed in an arrangement shown in Figure 4. The first set of nests was installed on equally spaced spots on the arc of a circle (radius of 60 cm) centered on the chosen application spot (see Figures 3 and 4). Three other sets, each containing five nests, were installed at 120, 220 and 320 cm from the center (referred to as 2$^{nd}$, 3$^{rd}$ and 4$^{th}$ set of nests in Fig. 4, respectively) along the general direction of the ground water flow based on subsurface hydraulic gradient. Finally, a set of 45-, 60-, 75-, 90- and 105-cm long samplers was installed in a semi-circle 20
cm around the application spot (nest 0 in Fig. 4) for assessing the initial distribution of the tracer ions in the soil after application.

The tension lysimeters were used to collect soil water samples from different depths in both saturated and unsaturated zones. To extract soil solution or a ground water sample, a vacuum trap was attached to each tension lysimeter. The lysimeter was initially emptied by applying vacuum to the trap using a hand pump. After emptying the trap and placing the sample bottle in it, the air in the trap was removed to create approximately 800 cm of tension (equivalent to -800 cm of pressure) inside the sampling cup. After maintaining vacuum inside the trap for 10 to 30 minutes, the air vent cover on the tension lysimeter (see Fig. 2) was removed, thereby drawing the remaining solution in the lysimeter cup into the sample bottle in the trap. Up to 30 mL sample of soil solution or groundwater was collected each time by this procedure.

Three fully perforated wells (hereafter referred to as wells) were installed at the vertices of a triangle near the nests for determination of the depth to the water table. The distance between wells was 3 m. The location of the CF was based on the depth of the WT. The same set of wells was used to estimate the general direction and magnitude of the subsurface horizontal hydraulic gradient via the triangulation or three-point technique (Sanders, 1998). Water table depths in the three wells were measured using a dipper (Herron Instruments Dipper T, Ontario, Canada) every time water samples were collected.

A five-segmented Moisture Point time domain reflectometer (TDR) probe (Gable Corp, Victoria, Canada) was installed outside the first set of lysimeters (circle of nests-Fig. 4). The probe measured volumetric water content (VWC) at depths of 0 to 15, 15 to 30, 30 to 45, 45
to 60 and 60 to 90 cm. Water content was taken every time soil water samples were collected from the lysimeters.

**Monitoring of solute transport**

Prior to the application of the tracer solution, background soil solution and ground water samples were collected from all the tension lysimeters and analyzed for bromide (Br\(^-\)) and NO\(_3^-\) concentration using a Lachat Quickchech 8000 slow injection auto analyzer (Greenberg et. al., 1992).

Fourteen days after the collection of background soil solution and ground water samples, an auger hole was dug a to 30 cm depth at the center of the 1\(^{st}\) layer of nests (i.e. circle of nests) and 10 L of solution containing 6,123 mg L\(^{-1}\) Br\(^-\) (equivalent to approximately 77 mmol L\(^{-1}\) Br\(^-\)) and 1,113 mg L\(^{-1}\) NO\(_3^-\) (equivalent to approximately 18 mmol L\(^{-1}\) NO\(_3^-\)) were applied to the bottom of the hole (see Fig. 4 for location of application spot). A modified Compact Constant Head Permeameter (Amoozegar, 1989) was used to apply the solution to the bottom of the hole (Fig. 3). At the time of tracer solution application, the water table was at 60 cm from the surface and the upper boundary of the CF was projected to be at 40 cm depth. In effect, the solution containing the Br\(^-\) and NO\(_3^-\) tracers was applied into an unsaturated region of the soil roughly 10 cm above the CF (Fig. 5). The auger hole was back filled after the solution infiltrated the soil.

An hour after the solution had completely infiltrated, water samples were collected from the lysimeters at nest 0 (20 cm from application spot) to determine the initial depth reached by Br\(^-\) and NO\(_3^-\). Soil water samples were then collected from nest 0 and all nests in the 1\(^{st}\) and 2\(^{nd}\) set of lysimeters 3 and 6 days after solution application. In addition to samples from nest 0 and the 1\(^{st}\) and 2\(^{nd}\) sets, samples were also collected from the 3\(^{rd}\) set on days 10 and 17. Judging upon the rate of advance of the plume, the nests at the 4\(^{th}\) set were included
among the nests sampled on days 20 and 28. On day 28, both solutes were already below the detection limit at nest 0 and were only detected at nests 1 and 2 in the 1st set. Based on our analysis of samples, on days 30 and 38 samples were only collected from nest 1 and 2 (in 1st set) and all nests in the 2nd, 3rd and 4th sets. Concentration of each of the two solutes at the 1st set was already below the detection limit on day 38 so for days 42, 49, 59 and 84, samples were only collected from nests in the 2nd, 3rd and 4th sets.

Detected concentrations of Br\(^{-}\) and NO\(_3\)\(^{-}\) (in mg L\(^{-1}\)) were converted to normalized concentrations by dividing the detected solute concentration in each soil water sample by the concentration of the corresponding solute in the applied solution. This allowed the comparison of the relative degree of persistence of the applied Br\(^{-}\) and NO\(_3\)\(^{-}\) as they moved through the CF and shallow groundwater.
RESULTS AND DISCUSSION

Soil and site characteristics

The slope of the land in the bay is generally less than 2% and the soil at the location where the solute transport study was conducted had textural classes of either loamy sand or sandy loam with sand content ranging from 78 to 87% from the surface down to a depth of 105 cm (Table 1). Saturated hydraulic conductivity ranged from 0.41 to 1.97 m d\(^{-1}\) without any indication of a restricting layer. Bulk density increased from 1.17 g cm\(^{-3}\) at the surface layer to 1.61 g cm\(^{-3}\) at 105 cm. Porosity was observed to decrease from 0.53 at the surface layer to only 0.37 at the 105 cm depth.

Results from the analysis of background samples reveal that detectable NO\(_3^-\) concentrations were only observed at the 45 and/or 60 cm depths in most nests. The highest background NO\(_3^-\) concentration detected at the site was 1.6 mg L\(^{-1}\) at the 45-cm depth at nest 3. No background sample yielded Br\(^-\) above the detection limit.

Soil water characteristic curves of samples collected from the 45 to 60 cm layer, which was immediately above the water table for most of the study period, indicated that the soil at the depth remained nearly-saturated after application of 20 cm of tension (Fig. 6). This indicates that the CF above the water table would be at least 20 cm thick. Because of the relatively uniform soil texture at depths where the WT fluctuated, it was expected that the thickness of the CF would remain to be close to 20 cm. The time domain reflectometry (TDR) measurements taken after each sampling showed that the minimum thickness of the near-saturated zone above the water table was roughly 20 cm (Fig. 6). These results agree with the data from a laboratory study by Amoozegar et al. (2005) which demonstrated that in a coarse-textured soil, the capillary fringe could be as thick as 20 cm above the water table.
Based on these, it was conservatively assumed that soil solution samples collected within 20 cm above the water table were from the CF.

Subsurface transport of Br\(^-\) and NO\(_3^-\) relative to the water table

On the day that the tracer solution was applied 30 cm above the water table (initial depth of water table = 60 cm), both Br\(^-\) and NO\(_3^-\) were detected only at 45 cm depth at a distance of 20 cm from the application spot (Fig. 7). On day 3, the peak concentrations at a distance of 20 cm from the center (nest 0) were achieved and all of the Br\(^-\) and NO\(_3^-\) at nest 0 were still detected at the 45 and 60 cm depths in the CF above the water table. The 0.9 cm rain on day 4 (Fig. 7) must have resulted in a partial leaching of the plume because on day 6, both solutes were also detected below the water table at the 75 cm depth. In addition, between days 3 and 6, there was a marked decrease in Br\(^-\) and NO\(_3^-\) concentrations at the 45 cm depth that was coupled by an increase in concentration of both solutes at 60 cm from the surface. Solute concentration at all three depths were decreasing on day 10 suggesting that the bulk of plume had moved further to the direction of nests 1 and 2 (see Fig. 4 for nest locations). It is interesting to note that the distribution of normalized concentration (concentration in soil solution/concentration in applied solution) with depth and time at nest 0 is similar for both Br\(^-\) and NO\(_3^-\), suggesting that initially they moved together in the CF and top of shallow ground water.

Both solutes were initially detected on day 6 (water table at 63 cm depth) at the 45 and 60 cm depths in nest 1 (60 cm from the application spot) (Fig 8). When the peak of the plume arrived at nest 1 on day 10 (Br\(^-\) and NO\(_3^-\) concentrations of 1,564 and 338 mg L\(^{-1}\), respectively), there was evidence of partial leaching of Br\(^-\) and NO\(_3^-\) below the water table as both solutes were also detected at 75 cm depth. After a major rain event (2.7 cm) on day 12,
the water table rose to as shallow as 45 cm on day 17 (Fig. 7). We should note that this rise in
the water table is the result of water entering from above into the limited number of
unsaturated pores in the CF causing complete saturation and rapidly raising the level of the
WT (Gillham, 1984). This suggests that a rise in water table would not necessarily cause the
plume to move upward. As soon as the CF becomes fully saturated, additional percolation
then inundate the air-filled pores above the former CF causing more rise in water table.
When the percolation stops, a temporary CF forms above the new water table. As the water
table drops due to lateral drainage into the ditches or deep percolation through the underlying
slowly permeable layer below the shallow aquifer, a limited volume of water moves
vertically through newly formed CF and top of the saturated zone (former CF). The drop in
water table is accompanied by relocation of the CF. The fluctuation of the shallow water
table within a relatively short depth interval at this site results in limited vertical leaching
below the level of the water table. As a result, it appears that a major portion of solutes
entering the CF tend to stay and move laterally as water moves in the CF. This is evidenced
by the fact that on day 10 (water table at 68 cm depth) concentration of both Br⁻ and NO₃⁻
were below the detection limit at the 90 cm depth in nest 1. But on day 17 (after the major
rain on day 12), solute concentrations decreased at 45 and 60 cm depths which were coupled
by the detection of relatively low amounts of Br⁻ and NO₃⁻ at 90 cm depth (concentrations of
2.1 and 13.2 mg L⁻¹, respectively). However, no Br⁻ or NO₃⁻ was detected at the 105 cm
depth. The decrease in concentration of both solutes at the 45 cm depth coupled by a marked
increase at 60 cm on day 17 in nest 2 is additional evidence of limited leaching brought about
by the receding WT following the major rain event on day 12. We believe that the lack of
direct agreement in Br⁻ and NO₃⁻ concentrations between the nests 1 and 2 is due to the
irregularity in the shape of the plume as it moved in the subsurface. It appears that the center of the plume was closer to nest 1 than nest 2.

Bromide and NO$_3^-$ were detected in the CF at 120 cm from the tracer application spot on day 17 (nests 3, 4 and 5) (Fig. 9). Among the samples collected from these nests, the highest Br$^-$ and NO$_3^-$ concentrations (694 and 139 mg L$^{-1}$, respectively) were detected on day 17 at the 60 cm depth in nest 4. Unlike nests 0, 1 and 2 where Br$^-$ and NO$_3^-$ concentrations were higher at the 45 cm depth when initially detected, higher solute concentrations were initially detected at the 60 cm depth at nests 3 and 4. However, appreciable amounts of both solutes (peak concentrations of 144.7 and 15.6 mg L$^{-1}$ for Br$^-$ and NO$_3^-$, respectively) were present at the 45 cm depth. In addition, both Br$^-$ and NO$_3^-$ were detected at 75 cm depths in all nests (including nest 5). These suggest that the plume had indeed moved downward within the CF and partially below the water table, perhaps as a result of major rain event that occurred on day 12.

Among the nests installed 220 cm from the application spot, the highest Br$^-$ and NO$_3^-$ concentrations were detected at nest 7 (Fig. 10). At this nest, both solutes were first detected on day 17 at the 45 cm depth (in the CF). This suggests that Br$^-$ and NO$_3^-$ had at least traveled 220 cm horizontally in the CF in 17 days. It is also noted that neither of the two solutes was at the 90 cm depth until day 28 (WT at 58 cm depth) when 29.9 and 1.72 mg L$^{-1}$ of Br$^-$ and NO$_3^-$, respectively, were detected. This means that from the time that the plume was detected at nest 7 (day 17) it took roughly 4.0 cm of rain before a part of the plume was leached to 90 cm from the surface on day 28. At nest 8, both solutes were detected on day 20 (water table at 47 cm depth) with highest concentrations at the 90 cm depth (76.8 and 20.8 mg L$^{-1}$ for Br$^-$ and NO$_3^-$, respectively). We believe that the difference in the initial depth in
which Br\(^{-}\) and NO\(_3\)^{-} were detected at nest 7 and 8, is due to the irregularity in the shape of the moving plume.

Among the nests located 320 cm from the application spot, nest 12 had the highest concentrations of both solutes indicating that this nest should have been in the way of the center of the moving plume (Fig. 11). As high as 115 and 17 mg L\(^{-1}\) of Br\(^{-}\) and NO\(_3\)^{-}, respectively, were still detected at the 45 cm depth at nest 12. This indicates that some Br\(^{-}\) and NO\(_3\)^{-} had traveled in the CF through a horizontal distance of at least 320 cm. The observation is supported by the detection of considerable amounts of Br\(^{-}\) and NO\(_3\)^{-} at the 45 cm depth at nests 10, 11 and 13. Nest 14 appears to be at the edge of the plume as indicated by the relatively lower amounts of solutes detected in its location.

**Fates of nitrates in the CF and SGW**

Unlike NO\(_3\)^{-}, Br\(^{-}\) is a stable anion that is not preferentially taken-up by plants nor utilized by microorganisms in the soil. Because of these properties, we used it as a reference tracer to evaluate the degree of persistence of biologically essential and redox positive nitrate, as they were jointly applied to the unsaturated soil above the CF to be observed as they moved horizontally in the subsurface.

The plotted normalized concentrations of Br\(^{-}\) and NO\(_3\)^{-} at 20 cm from the application spot (nest 0) provide initial indication that nitrates tend to persist longer in the CF than it would below the water table (Figure 7). Between days 6 and 10, the normalized concentration of Br\(^{-}\) at 75 cm depth (below the water table for the entire duration that Br\(^{-}\) and NO\(_3\)^{-} were detected at nest 0) only had a slight decrease but the NO\(_3\)^{-} had a more significant reduction. In contrast, at the 45 cm depth, which was always in the CF for the duration of the study, NO\(_3\)^{-} was detected on all days that Br\(^{-}\) was detected. In fact the normalized
concentrations of NO$_3^-$ were comparable to that of Br$^-$ for all the days that they were detected at the 45 cm depth at nest 0.

Nitrate was detected in all depths where Br$^-$ was present at nests 1 (60 cm from application spot) (Fig. 8). Peak normalized concentrations of Br$^-$ and NO$_3^-$ were similar although their actual concentrations differed (1,564 and 338 mg L$^{-1}$ for Br$^-$ and NO$_3^-$, respectively). A slight tailing in normalized Br concentration at the 75 and 90 cm depths (always below the water table for the duration that both solutes were detected at nest 1) was observed as compared to the relatively accelerated decrease in nitrate concentrations at such depths. In contrast, the distribution of normalized concentrations at the 45 cm depth (in the CF) was similar for both solutes. Nest 2 also showed indications of tailing in bromide and a relatively accelerated decrease in normalized nitrate concentrations. Although not very significant, these are added indications that NO$_3^-$ could persist longer in the CF than it would below the water table.

Comparison of the Br$^-$ and NO$_3^-$ plots for nests 3, 4 and 5 (120 cm from the application spot) (Fig. 9) show the same trend observed in nests 0, 1 and 2 where normalized Br$^-$ concentrations tended to have a tailing compared to a more accelerated NO$_3^-$ loss, specially at depths that are sometimes or always below the WT. The detection and persistence of Br$^-$ at 90 cm depth, and the virtual absence of NO$_3^-$ at such depth in nest 3 support the earlier observation that when below the water table, NO$_3^-$ may be transformed.

More obvious evidence of NO$_3^-$ persisting longer in the CF than below the water table is shown in Figure 10 (220 cm from applications spot). Nest 7 detected the highest concentrations of Br$^-$ and NO$_3^-$ (570 and 133 mg L$^{-1}$, respectively, at 60 cm depth). At this nest, the distribution of normalized concentration of Br$^-$ and NO$_3^-$ at the 45 cm depth (always
in the CF) was similar from start of detection on day 20 until day 59 suggesting that in the CF, loss of NO$_3^-$, which we believe is largely due to denitrification, is relatively minimal. In contrast, Br$^-$ and NO$_3^-$ started to be detected on day 28 at the 90 cm depth (always below the water table except on day 84) and while 5.76 mg L$^{-1}$ of Br$^-$ was still detected on day 84, NO$_3^-$ was only detected at such depth until day 49. In addition, Br$^-$ was also detected from day 28 through 84 at the 105 cm depth (always below water table) while NO$_3^-$ was only present at such depth for a rather shorter period from day 38 until 49. At nest 8, highest Br$^-$ and NO$_3^-$ normalized concentrations at 45 cm depth were detected on day 42 and similar normalized concentrations of both solutes were observed on day 59. In contrast, both solutes were already detected at 90 cm on day 20 but on day 59, normalized Br$^-$ concentration was more than an order of magnitude higher than that of NO$_3^-$. At nest 6, Br$^-$ was detected at 105 cm depth from day 20 through 84 while NO$_3^-$ was undetected. Although we cannot separate the contribution of the applied and mineralized NO$_3^-$ at the 45 cm depth at nest 6, the fact that NO$_3^-$ persisted at such depth until day 59 while was never detected at 105 cm depth tells us that NO$_3^-$ is more likely to persist in the CF than below the water table. Nest 9 seems to be at the boundary of the plume as bromide and nitrate concentrations were lower than those of nest 6, 7 and 8. Nonetheless, comparison of Br$^-$ and NO$_3^-$ normalized concentrations detected at such nest also indicate loss of nitrates at deeper depths.

Results from nests located 320 cm from the application spot (Fig. 11) also support the results discussed earlier for nests located 20, 60, 120 and 220 cm from the application spot. Taking nest 12 as a representative for nests located 320 cm from the application spot, normalized concentrations of NO$_3^-$ at the 45 cm depth were consistently comparable to those of Br. However, while Br$^-$ was detected at 90 and 105 cm depths, NO$_3^-$ was virtually absent
at such depths for the entire duration of the study. Evidence of extended NO₃⁻ existence at 45 cm depth and its absence or accelerated loss at depths that were always or frequently below the water table could also be observed in the other nests located 320 cm from the application spot.

The four requirements for denitrification; which includes presence of organic matter, active microorganisms, anoxic environment, and stagnant conditions (Vepraskas and Richardson, 2000) may have been met below the water table causing nitrates to be converted to N₂. The CF, because of its “partially saturated” property, still has some unsaturated pores that allow regular re-supply of oxygen. This may have inhibited the development of anoxic conditions, thus preventing denitrification of the nitrates contained in it.
CONCLUSIONS

This study evaluated the fate of nitrate (NO$_3^-$) in the capillary fringe (CF) and shallow groundwater (SGW) in a sandy field site drained by ditches. Results showed that NO$_3^-$ could be transported horizontally in the CF in the same manner as bromide (Br$^-$) under field conditions.

The results also showed that the nitrate plume that entered into the CF from the unsaturated zone stayed and moved horizontally in it until it was partially carried below the WT by the rain events. It also appeared that NO$_3^-$ persisted longer in the CF than in the SGW. We believe that conditions favoring denitrification are not totally met in the CF largely due to its “nearly saturated” nature which still allows room for re-supply of oxygen and inhibiting development of anoxic conditions.

Although this study monitored the horizontal transport of NO$_3^-$ through a distance of only 320 cm from an application spot, we believe we have generated enough evidence to suggest that monitoring of subsurface horizontal flow of NO$_3^-$ should include efforts to collect samples in the CF. Solely relying on groundwater samples may result in an underestimation of the amount of nitrates that can travel horizontally through the subsurface from a source.

We recommend that further study be conducted to examine the development (or non-development) of a reduced state in the CF under various field conditions as this may have implications on the extent and duration of nitrate transport in the subsurface.
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Table 1. Soil physical properties of the soil in the experimental area.

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<th>Clay</th>
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ND - Not Determined
SL - Sandy Loam
LS - Loamy sand
Figure 1. Aerial photograph of Juniper Bay with marked location of the sandy mineral soil site, and the main and lateral ditches. In the inset, the location of Juniper Bay in the southeastern part of North Carolina is shown by the star.
Figure 2. Schematic illustration of a tension sampler with its associated vacuum trap.
Figure 3. Photograph showing the first set (circle of nests) and the constant head permeameter used to apply the tracer solution into an auger hole dug at the center of the circle. In the inset is a photograph of a “nest” composed of tension samplers with porous cups at 45 cm (18 in), 60 cm (24 in), 75 cm (30 in), 90 cm (36 in) and 105 cm (42 in) below the soil surface.
Figure 4. Schematic illustration of the monitoring set-up for the tracer study showing the location of the nests, wells, time domain reflectometry (TDR) probes and the area covered by the plume for the duration of the study.
Figure 5. Schematic diagram for the tracer solution application.
Figure 6. Moisture retention curves of the soil at the 45 to 60 cm layer which is the location of the CF for most of the study (A), and the depth to water table and the upper boundary of the near-saturated zone (measured using TDR) through the duration of the study (B).
Figure 7. Rainfall and water table data, and plots comparing the normalized concentrations of the bromide and nitrate detected 20 cm from the tracer application area throughout the duration of the study.
Figure 8. Comparison of normalized concentrations of bromide and nitrate detected at nests located 60 cm from the tracer application area throughout the duration of the study.
Figure 9. Comparison of normalized concentrations of bromide and nitrate detected at nests located 120 cm from the tracer application area throughout the duration of the study.
Figure 10. Comparison of normalized concentrations of bromide and nitrate detected at nests located 220 cm from the tracer application spot throughout the duration of the study.

Note: Hollow point marker means that it is from a CF sample.
Figure 11. Comparison of normalized concentrations of bromides and nitrates detected at nests located 320 cm from the tracer application area throughout the duration of the study.
CHAPTER III

STORM EFFECTS ON NUTRIENT CONCENTRATIONS IN THE VADOSE ZONE, SHALLOW GROUNDWATER, AND DITCHES PRIOR TO WETLAND RESTORATION OF A CAROLINA BAY

ABSTRACT

Rain events have been known to cause significant increase in nutrient discharge into surface waters from drainage basins, wetlands and agricultural watersheds. Much of the added nutrients in surface waters following storm events is attributed to surface runoff that carries dissolved nutrients and particles with sorbed nutrients into water bodies. This study was designed to evaluate possible contributions of subsurface flow as a mechanism responsible for the increased nutrient load in ditches at a Carolina Bay following a storm event. The study was conducted in Juniper Bay, a drained Carolina Bay in Robeson County, NC. A representative monitoring site from each of the Bay’s mineral and organic soil areas was chosen. Soil water samples from both saturated and unsaturated zones, as well as samples from the side and main drainage ditches were collected from both sites at least monthly for a year, with more frequent sampling during the summer. Soil solution from the vadose zone and groundwater samples below the water table were collected using tension lysimeters installed at 15-cm depth intervals from 15 to 120, and 30 to 180 cm depths at the mineral and organic soil sites, respectively. Groundwater samples were collected from three fully perforated wells. Seven piezometers installed at each site also allowed collection of ground water samples from different depth intervals below the water table. Water samples from the lateral ditch directly across each monitoring location and from the main ditch immediately below and above the point of discharge of the lateral ditch into the main ditch at both organic and mineral soil sites were collected every time soil solution and ground water
samples were collected. In addition, a sample from the main ditch exit was collected for analysis. The direction and magnitude of the subsurface hydraulic gradient at the monitored sites were determined using the three-point technique. Soil water samples were classified as either collected during baseflow conditions, following a regular rain, and following a storm event (rain exceeded 5 cm d\textsuperscript{-1}). Sample taken from the main ditch exit following a storm event had higher concentrations of total organic carbon (TOC), phosphate (PO\textsubscript{4}-P), calcium (Ca) and magnesium (Mg) compared to the average of those gathered during baseflow conditions. A general increase in concentrations of the same solutes was also observed in the lateral ditches. Concentrations of TOC, PO\textsubscript{4}-P, Ca and Mg in soil solution samples were also observed to be higher after a storm event compared to baseflow samples. This was especially true at depths closer to the soil surface where there was higher organic carbon and extractable Ca, Mg and PO\textsubscript{4}-P contents. The increase in concentration of TOC, PO\textsubscript{4}-P, Ca and Mg in the ditches and upper layers of the soil profile coincided with observed increase in the magnitude of the subsurface hydraulic gradient. In addition, it was observed that immediately following a storm event, the direction of the subsurface lateral hydraulic gradient tended to become more perpendicular to the nearby lateral ditch suggesting that the route taken by the water as it moved in the subsurface towards the ditch was shortened. Although we cannot separate the contributions of surface runoff and subsurface flow to the increased concentration of PO\textsubscript{4}-P, Ca, Mg and TOC in the ditches, we believe the increase in concentration of these chemicals in the soil solution at certain depths in the soil profile coupled by its higher rate of movement in the subsurface towards the ditch is one reason for the increase in concentration of such solutes in the ditches following the storm event.
INTRODUCTION

Plant nutrients, mainly phosphorus and nitrogen, are principal stressors that may adversely affect surface water quality. Of the 700,000 miles of rivers and streams assessed for water quality status in the U.S. in 2000, 8% or 55,398 miles of rivers and streams were impaired by excess nutrients (USEPA, 2000). In addition, excessively high nutrient load is the primary reason for the impairment of 22% of the 6.9 million hectares (equal to 1.52 M ha) of lakes that had been assessed (USEPA, 2000). Concerns related to excess nutrients include adverse effects on humans and domestic animals, as well as aesthetic impairments and negative impacts on aquatic life (Dodds and Welch 2000). Excess nitrogen and phosphorus are also known chemicals that lead to eutrophication that can cause proliferation of algal masses leading to degradation of water quality (Brady and Weil, 2002; Correll, 1998).

On a watershed scale, dissolved nutrients are transported with water as water moves towards the streams via overland flow, subsurface stormflow (or interflow) and ground water flow (Freeze and Cherry, 1979). Overland flow or runoff takes place when rainfall rates exceed infiltration capacity of the soil at certain portions of the watershed. In runoff, rainwater that cannot infiltrate the soil will dissolve nutrients near or at the soil surface and also transport the suspended soil particles (including the sorbed nutrients ions) as it moves laterally according to the land surface gradient. Subsurface stormflow resulting from storm events is comprised of the lateral inflow to streams that takes place in a shallow horizon with high permeability underlain by a slowly permeable soil layer (Freeze, 1972). Groundwater flow, is characterized by the movement of water below the water table along streamlines in a flow net in response to the subsurface hydraulic gradient. In addition to the water moving
into withdrawal wells, this process is responsible for the regular supply of water to streams and other surface bodies of water (Hillel, 1998). The same processes could also be assumed to contribute to the transport of dissolved nutrients to drainage ditches at a field scale.

Significant changes in nutrient discharges from an area (e.g., drainage basin and wetlands) had been reported following storm events. In a karst terrain in northwest Arkansas, it is reported that as much as 26% of the nitrate-nitrogen that exits the drainage basin in a year are a result of rapid recharge associated with a few storm pulses (Peterson et al., 2002). Davis et al. (2000) also reported that elevated nitrate nitrogen (NO$_3$-N) concentration (16.7 mg L$^{-1}$) in selected springs in northwest Arkansas was observed during storm events as compared to baseflow (13.0 mg L$^{-1}$). A wetland treating water from an agricultural and forest watershed was also found to export significantly higher soluble reactive phosphorus and total phosphorus during precipitation events as compared to dry-weather conditions (Fink and Mitsch, 2004). The increased rainfall intensity in storm events causes an increase in the extent of transfer of ions into runoff water due to the increased degree of turbulent mixing and dispersion of the soil resulting from a greater raindrop impact (Ahuja, 1986).

In a study related to variations in nutrient loads in surface water that takes place within a storm event, Langlois and Mehuys (2003) reported a delay in the release of nutrients to surface water when the soil was initially dry prior to a rain event. In contrast, when the soil was initially pre-wetted, surface water had higher nutrient loads early into the storm event. While studying the release of soil phosphorus to runoff within a rain event, Sharpley et al. (1981) found that concentration of soluble reactive phosphorus (SRP) in the drainage water decreased with time. The movement of the pre-storm soil solution, which had higher SRP concentration, into the overland water flow was believed to contribute to the relatively higher
SRP in surface water early in the storm event. Thereafter, the SRP concentration in surface water became relatively lower as it was controlled by the relatively slow desorption of ions from the surfaces of soil particles. Increasing the interval of simulated rain events from 1 to 6 days increased the mean soluble phosphorus concentration in runoff (Sharpley, 1980). The increased event interval allowed more time for mineralization of organic phosphorus in between simulated rain events. Hence, more phosphorus was leached following an extended wet period.

On a field scale, rainfall intensity has been reported to influence significant changes in nutrient levels in drainage ditches. In a year-long monitoring of nutrient concentration at the main ditch exit in Juniper Bay, a Carolina Bay in Robeson County, North Carolina, two rain events which exceeded 5 cm d\textsuperscript{-1} accounted for 74\% of the phosphates and almost all of the nitrates exported out of the bay (Kreiser, 2003). It also accounted for 62, 66 and 61 percent of the total organic carbon, calcium and magnesium exported out of the bay in the drainage water for the year, respectively. This increase in nutrient load in the drainage water was attributed to surface runoff contributions to the ditch which may have occurred when the heavy rain during storm events exceeded the infiltration rate.

In addition to inducing surface runoff, we hypothesized that these major storm events (e.g., 5 cm d\textsuperscript{-1}) cause significant changes in the nutrient concentrations in the soil solution in the subsurface and that subsurface flow of soil water and dissolved nutrients contribute to the elevated nutrient load in the ditches. The objective of this study was to evaluate the impact of storm events on the soil solution nutrient concentrations in the vadose zone, groundwater and ditch water in Juniper Bay.
METHODOLOGY

The study was conducted at Juniper Bay, a 300-hectare Carolina Bay located 10 km southeast of Lumberton, in Robeson County, North Carolina (34°30’30”N 79°01’30”E). The site was drained by a number of lateral ditches connected to a main ditch that traversed the entire width of the Bay. Two relatively small areas, one containing a mineral soil located at the NE end and the other with an organic soil near the center of the Bay, were chosen for nutrient monitoring (Fig. 1). These locations were chosen because they were typical of mineral and organic soils in Juniper Bay and for their close proximity to lateral ditches that drained into the main ditch.

Soil profile characterization, soil sampling and soil analysis

The soil profile at the mineral soil site was described in a pit dug 7 m from a lateral ditch and 30 m from the main ditch. Soil profile was described for the top 105 cm as the water table was at 105 cm when profile description was performed. Bulk samples intended for soil analysis were collected from the pit walls at 15 cm depth intervals from the surface down to 105 cm. An additional sample was collected from the 105 to 120 cm section using a bucket auger. Intact core samples (7.5 cm diameter and 7.5 cm long - collected vertically), for assessment of a number of soil physical properties, were also collected in triplicate at 15 cm depth intervals from the surface to a depth 105 cm.

In the organic soil site, the soil profile was described to 135 cm in a pit 7 m from a lateral ditch and 50 m from the main ditch. Soil profile characterization was only done for the top 135 cm as the water table was at 135 cm when profile description was done. This also limited the collection of intact soil cores at 15-cm depth intervals to 135 cm from the surface. Soil samples for chemical analysis were collected at 15 cm depth interval from the surface up to a depth of 180 cm. Soil samples above the water table were collected from the pit walls.
Samples from below the water table were collected using a bucket auger. The bulk soil samples from both mineral and organic sites were air-dried and passed through a 2-mm sieve before analysis.

Extractable P, K, Ca, Na and Mg were determined by running Mehlich III extracts (Mehlich, 1984) through an inductively coupled plasma (ICP) emission spectrograph. Cation exchange capacity (CEC) was the summation of exchangeable basic cations determined using Mehlich III extracts (Mehlich, 1984) in addition to the exchangeable acidity (Mehlich et al., 1976). The pH was determined using a 1:1 soil to water ratio. Organic carbon and total nitrogen were determined through dry combustion with a Perkin-Elmer PE2400 CHN Elemental Analyzer (Culmo, 1988).

Using bulk samples, particle size distribution was determined by hydrometer method (Gee and Or, 2002) where soil samples were pre-treated with 30 percent hydrogen peroxide ($\text{H}_2\text{O}_2$) to oxidize the organic matter prior to the dispersion and sedimentation. Saturated hydraulic conductivity ($K_{\text{sat}}$) of the intact core samples was measured by the constant head procedure (Amoozegar and Wilson, 1999). Soil water retention of the intact cores between 0 and 1.5 MPa pressure was measured (Dane and Hopmans, 2002). Bulk density at different depth intervals was determined by the core method (Grossman and Reinsch, 2002) and particle density was determined by the air pycnometer (gas displacement) technique (Flint and Flint, 2002).

**Installation of tension lysimeters, piezometers and wells**

At the mineral site, eight tension lysimeters (soil solution samplers) with their porous cups at 15, 30, 45, 60, 75, 90, 105 and 120 cm depths were installed on equally spaced spots on the arc of a 60 cm diameter circle at a distance of five meters from the side of the soil
profile characterization pit (also seven meters from the side ditch). Seven observation/sampling wells (hereafter referred to as piezometers), each with 15-cm long perforation at the bottom, were installed at equally spaced spots on the arc of a 120 cm diameter circle inscribing the tension lysimeters. The perforated sections of these wells were located at 38 to 53, 53 to 68, 68 to 83, 83 to 98, 98 to 113, 113 to 128 and 128 to 143 cm depths. Three fully perforated wells (hereafter referred to as wells) were also installed on the vertices of a triangle enclosing the two concentric circles. The distance between wells was 3.6 m. Figure 2 presents a photograph of the monitoring set-up showing the locations of the lysimeters, piezometers and wells.

Tension lysimeters, piezometers and wells were also installed at a distance of five meters to the side of the soil profile characterization pit at the organic soil site using the same pattern as in the mineral soil site. The only difference was that the depth of the tension lysimeters ranged between 30 to 180 cm.

The depth at which tension lysimeters, piezometers and wells were installed were based on three years of water fluctuation data that were collected prior to the initiation of this study (Vepraskas, et. al., 2003). These depths were selected to assure that both soil solution samples from the vadose zone and ground water samples from different depth intervals below the water table could be collected during the course of the study. Subsurface hydraulic gradient at both sites was determined using the three-point technique (Sanders, 1998) using the water table depths determined from the three wells arranged in a triangle at each site.

**Monitoring instrumentation**

A tipping bucket rain gauge was set up halfway between the mineral and organic soil sites (roughly 300 m from either site). A system, modified after Liken et al. (1967), was devised to collect rain samples (Fig. 3). Volumetric water content (VWC) at different depths
in the monitoring sites were measured by Time Domain Reflectometer (TDR) using two five-
segmented Moisture Point TDR probes (Gable Corp, Victoria, Canada) installed just outside
the circle of piezometers (see Figure 2 for location of probes). One probe measured VWC at
zero (surface) to 15, 15 to 30, 30 to 45, 45 to 60 and 60 to 90 cm depth intervals. The other
probe measured VWC at zero to 15, 15 to 30, 30 to 60, 60 to 90 and 90 to 120 cm depth
intervals. Time domain reflectometry measurements were taken every time soil water
samples were collected from the monitoring sites. These were then compared to the
computed porosities at the corresponding 15 cm depth intervals in the soil to determine the
degree of saturation of each given layer. Tensiometers were also installed at 15 cm depth
intervals from 30 to 150 cm depths to measure matric potential at different depths (see Figure
2 for location of tensiometers). To monitor redox potential at the mineral soil site, five
platinum (Pt) redox electrodes were installed at each of 25 and 60 cm depths from the surface
(see Fig. 2). At the organic soil site, five Pt electrodes were installed at each of the 25, 60 and
90 cm depths.

Water sample collection and on-site measurements

Soil water samples were collected from both mineral and organic sites at least
monthly, with more frequent sampling during the summer months. Samples were also
collected within 36 hours after a major rain event. During a scheduled sampling date, water
table depths in the three wells and the depth to the water level in the piezometers were first
measured using a dipper (Herron Instruments Dipper T).

To collect soil water samples, a vacuum trap was attached to each tension lysimeter
(Fig. 4) in both saturated and unsaturated zones. Using a hand pump, each sampler was
initially purged (i.e., emptied) by applying vacuum to the trap. After emptying the trap and
reattaching it to the sampler, the air from the trap was evacuated to create approximately 800
cm of tension (equivalent to –800 cm of pressure) inside the sampling cup. The vacuum inside the trap was maintained for thirty minutes to two hours to draw soil solution into the porous cup and then into the sample bottle in the trap. After opening the air vent on the sampler (see Fig. 4), the remaining solution in the porous cup of the sampler was drawn into the sample bottle in the trap. Up to 60 mL of soil solution samples was collected by this procedure.

Using plastic hand bailers, the wells were bailed slowly for up to three times. Then each well was allowed to fill with ground water to the static level before 60 mL of groundwater sample was collected. The same procedure was used with the piezometers to collect ground water samples from different depth intervals below the water table.

Water samples from the lateral ditch directly across each monitoring location and from the main ditch immediately below and above the point of discharge of the lateral ditch into the main ditch at both organic and mineral soil sites were collected every time soil solution and ground water samples were collected. In addition, one sample from the main ditch exit (where all the water in the ditches exits the Bay) was collected for analysis. For relative locations of surface water sampling points see Figure 1.

After collecting ground water samples, matric potential and VWC at various depths were measured using a digital tensimeter (Soil Moisture Measurement System, Arizona) and the Moisture Point TDR System, respectively.

**Chemical analysis of water samples**

Prior to chemical analysis, soil water samples were filtered using a Whatman #40 filter paper (Whatman Int. Ltd, Maidstone, England). Two drops of concentrated sulfuric acid (H₂SO₄) were then added to 60 mL of filtered sample to reduce the pH to around 1 to
eliminate microbial activity in the sample. Nutrient analyses were performed on bulk precipitation, ditch water, soil solution and ground water samples. Water samples were tested for NH$_4^+$-N, NO$_3^-$-N, PO$_4^{3-}$, total organic carbon (TOC), Ca$^{2+}$, K$^+$, Mg$^{2+}$, Cl$^-$ and Na$^+$. Phosphate, TOC, NH$_4^+$-N, and NO$_3^-$-N were measured using Lachat Quickechem 8000 slow injection auto analyzer. Calcium, K$^+$, Mg$^{2+}$ and Na$^+$ were measured using ICP. Chloride concentration was analyzed using ion chromatography. Methods used in the analysis are outlined in Greenberg et al. (1992).
RESULTS AND DISCUSSION

Soil and site characteristics

As described earlier, one site was chosen to represent each of the mineral soil area (at the peripheries) and the organic soil area (towards the center) of Juniper Bay. The mineral soil site had textural classes of either loamy sand or sandy loam with sand content ranging from 78 to 87% from the surface down to a depth of 120 cm (Table 1). Saturated hydraulic conductivity ranged from 0.92 to 5.65 m d\(^{-1}\) without any indication of a restricting layer. Bulk density increased and porosity decreased from the surface down to 105 cm depth. Selected soil chemical properties are outlined in Table 2. Potassium, Ca and Mg contents were observed to be considerably higher in the upper 45 cm with highest concentrations of 31, 698, and 97 mg L\(^{-1}\), respectively. Concentrations of these cations in layers below 45 cm were considerably lower. Total nitrogen and percent organic carbon (OC) were also observed to be considerably higher in the upper 45 cm. Organic carbon ranged from 3.4 to 3.7% while total N ranged from 1,053 to 2,360 mg L\(^{-1}\). High levels of Mehlich-extractable Phosphorus (P) were also observed closer to the surface with concentrations of 96 to 142 mg L\(^{-1}\) in the upper 30 cm while those below had less than 17 mg L\(^{-1}\). Soil pH was acidic with values ranging from 4.0 to 4.8 from the surface down to 120 cm.

The organic site had organic soil in the upper 60 cm. Mineral soils were observed below 60 cm with clay contents ranging from 23 to 45%. A slowly permeable layer was observed beginning at the 90 to 120 cm depth (Table 3). The surface layer (top 15 cm) had an OC content of 12% and the mucky layers (15 to 60 cm depth) had OC content ranging from 40 to 45%. As in the mineral soil site, higher concentrations of K, Ca, Mg, total N and P were observed closer to the surface. Potassium, Ca, Mg and N were observed to be higher
at the organic site than the mineral site (Table 4). This could be attributed to the fact that the organic site had been in agriculture 10 years longer (Ewing, 2003), hence was limed and fertilized longer than the mineral site. Redox potential (Eh) data for both sites are summarized in Appendix Table 1. Do obvious effect of the storm event on the Eh at various depths monitored was observed.

**Hydrologic observations**

Rain data are presented in Figure 5. Through the monitoring period, a total of 94 cm of rain was recorded wherein two major rain events took place. Rain events that exceeded 5 cm d\(^{-1}\) were considered major rain events. Major rain events were recorded on August 29-30 and November 23, 2004. Water table data at both mineral and organic sites taken during days when water samples were collected are also presented in Figure 5. For both sites, deepest WT measurements were observed on July 16 and November 3. High demand for water by shrubs and weeds growing on site should have contributed to the deep WT in July when weed growth was observed to be very extensive. The absence of rain in the days prior to November 3 may have caused the deep WT. Shallow water tables were observed during days with rain events or during days immediately following days with significant rain events. For example, the water table that was relatively shallow on August 31 was largely due to the increased recharge resulting from the 6.7 cm-rain event that took place on August 29 and 30.

Figure 6 shows that in the organic site, during the days that the WT was observed to be shallow (Aug. 31 and Sept. 14), the general direction of the subsurface gradient tended to be more perpendicular to the ditch. In contrast, when the WT was deep (July 16 and Nov. 2), the flow was going away from the ditch. The same trend was observed at the mineral site (Fig. 7).
Water table depths also had an effect on the magnitude of the subsurface hydraulic gradient. Shown in Figure 8 are the WT data together with the computed magnitude of the subsurface hydraulic gradient along an axis perpendicular to the lateral ditch. By convention, a positive value indicates that the flow is towards the ditch and away from the ditch if it is negative. The plot shows that the magnitude of the gradient increases when the WT is closer to the surface. Conversely, it is also observed to decrease when the WT goes deeper.

Due to their influence on the water table and the water level in the ditch, rain and evapotranspiration should largely affect the changes in hydraulic gradient in the area. Assuming no subsurface recharge to the ditches, we expect the increase in water level in the ditches to be equivalent to the amount of rain. For example a 2 cm-rain would lead to a 2 cm rise in water level in the ditch. Due to the fact that water that enters the soil can only fill the air-filled pore volume, 2 cm of rain percolating in the soil at the monitored site would translate into a rise in WT far in excess of 2 cm. In addition, the capillary fringe above the WT, being already close to saturation, could lead to an immediate rise in WT even with minimal percolation (Gilliam, 1984). These factors make the WT significantly higher relative to the surface of the water in the ditch leading to an increase in hydraulic gradient towards the ditch (i.e. recharging the ditches). During dry days, continuous evapotranspiration by plants growing near the monitored site and lateral drainage into the ditch may result in accelerated removal of groundwater. When this happens the water table could recede at a much higher rate than the decrease in water level at the ditch. This could result in a decrease in the magnitude of the hydraulic gradient towards the ditch or in some cases, would lead in the shift of the gradient to a direction away from the ditch causing water discharge from the ditches back into the groundwater.
**Solute concentration in the water samples from ditch and wells**

Soil water samples collected were classified as one of the following:

- storm samples are those collected following the rain event that exceeded 5 cm d\(^{-1}\) on August 31, 2004.
- baseflow samples are those collected at least 2 days since the last rain event (not a storm event)
- regular rain samples are those collected within two days after a rain event not classified as a storm event.

Average concentration of phosphate (PO\(_4\)-P), TOC, Ca and Mg in the water that exits the bay through the main exit were observed to be higher in storm samples as compared to baseflow and regular rain samples (Fig. 9). This was consistent with the results of the nutrient budget experiment of Kreiser et al. (2003) in Juniper Bay. The same trend was observed at the lateral ditches except for Mg at the mineral site which was higher in baseflow samples.

Well water samples were collected to evaluate the impact of the rain events on the concentrations of solutes in the groundwater. Figure 10 shows that at the mineral site, no significant spikes in the solute concentration plots were observed on the August 31 sampling date (storm sample). The same was also observed with the organic site well samples except for the significantly higher TOC concentration on August 16 and August 31. This could indicate that the immediate relative increase in concentration of the said nutrients in the ditches following a major rain event of August 29 and 30 did not largely result from the contributions of the shallow ground water to the ditches.
**Solute concentration in the profile**

**Total organic carbon (TOC)**

At the mineral site, TOC concentration of soil solution samples collected on August 31 were considerably higher than the TOC concentrations determined in samples collected prior to the storm event (Fig. 11). At the 15 cm depth, TOC in soil solution increased from 112 mg L\(^{-1}\) on August 12, 2004 (baseflow condition) to 186 mg L\(^{-1}\) on August 31. The same was observed for the TOC concentrations at the 30, 45, 60 and 75 cm depths. It could be noted, however, that the degree of increase at the 75 cm depth was relatively minimal.

As in the mineral site, increased TOC concentrations at depths closer to the surface were also observed in soil solution samples collected after the storm at the organic site (Fig. 11). At the 60 cm depth for instance, concentration of TOC was only 163 mg L\(^{-1}\) on August 12 but was increased to 242 mg L\(^{-1}\) on August 31. Increase in TOC resulting from the storm event was observed until a depth of 90 cm where the concentration increased from 107 to 156 mg L\(^{-1}\) for August 12 and 31, respectively.

It should be noted that while the effect of the storm event on TOC concentration was only observed until the 60 cm depth at the mineral site, an increase in TOC concentration was observed until the 90 cm depth at the organic site. This could be due to the fact that the organic site had higher organic carbon content and such high OC content extended to deeper depths in the organic site. Soil organic carbon contents below 90 cm from the surface were actually substantial (Table 4). However, no obvious effect of the storm event on soil solution TOC concentration was observed below 90 cm. This could be due to the presence of a restricting layer at around 90 cm (see Table 3) that may have limited the amount of water percolating to such depth.
Relatively high amounts of organic carbon were limited to layers close to the surface (Tables 2 & 4). It was then expected that during rain events, organic carbon near the surface could be dissolved and an increased TOC concentration in the soil solution would be most obvious closer to the surface.

**Calcium, Magnesium and Phosphate**

Elevated levels of calcium in the soil solution samples collected at the mineral site on August 31 were also observed. However, while significantly higher TOC concentrations were only observed up to the 60 cm depth, significant increase in soil solution Ca were observed up to the 90 cm depth (Fig. 12). This could be attributed to the fact that extractable soil Ca contents remain relatively high until the 90 cm depth while much of the organic carbon could only be found at the upper 45 cm (see Table 2). Slight increase in calcium concentration was also observed on August 31 at the organic site from 60 cm through a depth of 120 cm from the surface (Figures 12).

Considerably higher Mg concentrations were also detected in the soil solution samples collected from the mineral site at the 60, 75 and 90 cm depths on August 31 (Fig. 13). As with Ca, this could be attributed to the relatively higher amount of extractable Mg up to the 90 cm depth. No significant response (to the storm event) in soil solution Mg concentration was observed at the organic site (Fig. 13).

The soil in the upper 15 cm had a relatively higher Mehlich extractable P content than the rest of the depths (see Table 2). It was also at such depth where a considerable increase in soil solution P was observed at the mineral site on August 31 (Fig. 14). Considerable changes in PO₄-P concentration was observed in the upper 60 cm in the organic site beginning on August 3 (Fig. 14). Although the trend points towards an increase in PO₄-P concentration,
not enough data were collected on August 31 to illustrate the effect of the storm event on P concentration in solution (Fig 15).

Extractable levels of Ca, Mg and PO$_4$-P were relatively higher at certain depths close to the soil surface (Tables 2 and 4). During a major storm event, significant amounts of rainwater, which had very minimal Ca, Mg and PO$_4$-P content (Table 5), may have immediately percolated to deeper depths. To achieve equilibrium conditions, some of the Ca, Mg and PO$_4$-P sorbed in the soil could have come into solution, thereby increasing the soil solution concentration of Ca, Mg and PO$_4$-P at depths where relatively higher extractable quantities of these soil nutrients are found.

**Chloride**

We evaluated the fluctuation in chloride (Cl) concentration as a representative ion for those that were observed to have lower concentrations at the main ditch exit in storm compared to baseflow (see Figure 9). It is interesting to note that on August 31, a marked decrease in Cl concentrations were observed in samples from all depths in the upper 90 cm at the mineral site (Fig. 15). It could also be noted that after August 31, the detected Cl concentration at most depths never increased back to the maximum pre-storm levels. Chloride concentration at sampled depths above 120 cm at the organic site significantly decreased during the month of August with frequent rain event that culminated with a major storm event towards the end of the month (Fig. 15).

Chloride ions, being negatively charged, could not be sorbed in large quantities at the predominantly negatively charged exchange sites. Hence, in the event that rainwater (that is low in Cl) enters the pores, very limited amount of Cl could go into solution and the native concentration of the Cl in the soil is further diluted.
**Solute changes with depth (rain effect)**

To evaluate the effect of the rain event on the changes in solute concentration in the soil solution in the profile, the samples collected on August 3, 12 and 31 were chosen to represent regular rain, baseflow and storm samples, respectively. Figure 16 shows that at the mineral site, there was a marked increase in TOC and phosphate concentrations at depths closer to the surface following a storm event. It should be noted that higher organic carbon and extractable P contents were also determined to be limited to soil layers closer to the surface. Calcium and magnesium concentrations in soil solution, on the other hand, were observed to be highest in storm samples in most depths until 105 cm from the surface. Also observed is the generally lower concentration (relative to the baseflow concentrations) of all four solutes following a regular rain event.

At the organic site, a general increase in TOC concentration in the soil solution was observed at depths closer to the surface (Fig. 17). This is particularly true from 60 to 105 cm depth. An increase in Ca concentrations following a major storm event was also observed at 60, 75 and 105 cm depths. Changes in Mg and PO₄-P concentrations following storm events were observed to be relatively minimal.

Chloride concentrations in sample collected following a regular rain were observed to be generally lower than baseflow values for most depths sampled at both organic and mineral sites (Fig. 18). Even lower are the chloride concentrations in the storm sample collected from all depths at both sites.
SUMMARY AND CONCLUSION

Juniper bay is a 300-hectare Carolina Bay in Robeson, County, North Carolina. It is originally a pocosin (wetland in inter-stream divides that are poorly or very poorly drained with nearly impenetrable thickets of shrubs and vines with pools of water beneath them) that had been drained and devoted to agricultural production. Results from a year-long nutrient budget experiment conducted at the site by Kreiser (2003) revealed that storm events (with rain that exceeds 5 cm d$^{-1}$) caused a significant increase in nutrient load of the water leaving the bay through its main ditch exit. Such increases in nutrient load in ditch water were attributed to the surface runoff contributions to the ditch that may have occurred when heavy rain during storm events exceeds the infiltration rate.

This study was designed to evaluate possible contributions of subsurface flow as a mechanism responsible for the increased nutrient load in the ditches following a storm event by evaluating the changes in nutrient concentrations in the ditch, groundwater and vadose zone at representative mineral and organic sites. Possible relationships between variation in nutrient loads (in ditch water, groundwater and soil solution) and changes in subsurface hydrology were also evaluated.

Our results show that the sample taken from the main ditch exit following a storm event had higher concentrations of total organic carbon (TOC), phosphates (PO$_4$-P), calcium (Ca) and magnesium (Mg) compared to the average of those gathered during baseflow conditions. The same was observed at the lateral ditch near the organic soil site. At the lateral ditch near the mineral site, the same was observed except for Mg which was observed to be lower following the storm event as compared to the concentrations in baseflow samples.
Except for TOC at the organic site, analysis of well water samples revealed no immediate response in nutrient concentration to the storm event indicating that the increase in nutrient concentration in the ditches was not due to groundwater flow. On the other hand, changes in nutrient concentrations in the soil solution at specific depths in the vadose zone and immediately below the water table were observed following the storm event. At the mineral site, TOC, PO$_4$-P, Ca and Mg concentrations in soil solution following the storm event were higher at depths closer to the surface especially where there was higher TOC as well as extractable P, Ca and Mg concentrations in the soil, respectively. At the organic site, increases in TOC and Ca in soil solution were observed closer to the surface but no considerable increase in PO$_4$-P and Mg were observed following major rain events. Chloride concentration was observed to decrease in the ditches following a storm event. Its concentration at various depths in the profile was also observed to be diluted following the storm.

Percent organic carbon as well as extractable P, Ca and Mg were higher at depths closer to the surface. During major storm events, more organic carbon near the surface could be dissolved and an increased TOC concentration in the soil solution would be most obvious closer to the surface. Significant amounts of rainwater, which had very minimal Ca, Mg and PO$_4$-P content, may have percolated to deeper depths during and immediately after the storm event. In response, some of the Ca, Mg and PO$_4$-P sorbed in the soil could have come into solution, thereby increasing the soil solution concentration of Ca, Mg and PO$_4$-P at depths where relatively higher extractable quantities of these soil nutrients are found. In contrast, chloride ion, being negatively charged, could not be sorbed in large quantities at the predominantly negatively charged exchange sites. Hence, in the event that rainwater (that is
low in Cl) enters the pores, very limited amount of Cl could go into solution and the native concentration of the Cl in the soil solution could be further diluted.

The increase in concentration of some nutrients in the ditches and upper layers of the soil profile coincided with observed increase in the magnitude of the subsurface hydraulic gradient. In addition, it was observed that immediately following the storm event, the direction of the subsurface lateral hydraulic gradient tended to become more perpendicular to the nearby lateral ditch suggesting that the route taken by the water as it moves in the subsurface towards the ditch is shortened. We believe that the increase in concentration of \( \text{PO}_4^- \text{-P}, \text{Ca}, \text{Mg} \) and \( \text{TOC} \) in the soil solution at certain depths in the soil profile coupled by its more effective movement in the subsurface towards the ditch following the storm event should have contributed to the increase in concentration of such nutrients in the ditches.

Although we cannot separate the contributions of surface runoff and subsurface flow to the increased concentration of \( \text{PO}_4^- \text{-P}, \text{Ca}, \text{Mg} \) and \( \text{TOC} \) in the ditches, we believe that we have generated data to suggest that contributions of subsurface flow may be significant.
LITERATURE CITED


Table 1. Selected physical properties of the soil in the mineral soil site.

<table>
<thead>
<tr>
<th>Depth Interval (cm)</th>
<th>Sand</th>
<th>Clay</th>
<th>Soil Texture</th>
<th>K&lt;sub&gt;sat&lt;/sub&gt; (m day&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Bulk Density (g cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>Particle Density (g cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
<th>Porosity (cm&lt;sup&gt;3&lt;/sup&gt; cm&lt;sup&gt;-3&lt;/sup&gt;)</th>
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<td>LS</td>
<td>1.59</td>
<td>1.40</td>
<td>2.45</td>
<td>0.44</td>
</tr>
<tr>
<td>45 to 60</td>
<td>87</td>
<td>13</td>
<td>LS</td>
<td>1.60</td>
<td>1.52</td>
<td>2.61</td>
<td>0.42</td>
</tr>
<tr>
<td>60 to 75</td>
<td>79</td>
<td>19</td>
<td>SL</td>
<td>0.92</td>
<td>1.52</td>
<td>2.55</td>
<td>0.41</td>
</tr>
<tr>
<td>75 to 90</td>
<td>85</td>
<td>114</td>
<td>LS</td>
<td>2.35</td>
<td>1.51</td>
<td>2.60</td>
<td>0.42</td>
</tr>
<tr>
<td>90 to 105</td>
<td>78</td>
<td>20</td>
<td>SL</td>
<td>2.55</td>
<td>1.61</td>
<td>2.58</td>
<td>0.37</td>
</tr>
<tr>
<td>105 to 120</td>
<td>80</td>
<td>15</td>
<td>SL</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND-Not Determined
Table 2. Selected chemical properties of the soil in the mineral soil site.

<table>
<thead>
<tr>
<th>Depth Interval (cm)</th>
<th>CEC cmol c kg⁻¹</th>
<th>OC %</th>
<th>BS</th>
<th>pH</th>
<th>P mg L⁻¹</th>
<th>K mg L⁻¹</th>
<th>Ca mg L⁻¹</th>
<th>Mg mg L⁻¹</th>
<th>Total N mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 15</td>
<td>7.4</td>
<td>3.7</td>
<td>49.0</td>
<td>4.8</td>
<td>141.6</td>
<td>31.4</td>
<td>698.6</td>
<td>84.9</td>
<td>2,360</td>
</tr>
<tr>
<td>15 to 30</td>
<td>6.9</td>
<td>3.4</td>
<td>39.0</td>
<td>4.8</td>
<td>96.0</td>
<td>17.6</td>
<td>534.3</td>
<td>60.9</td>
<td>1,936</td>
</tr>
<tr>
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<td>7.6</td>
<td>3.7</td>
<td>34.0</td>
<td>4.3</td>
<td>8.4</td>
<td>11.8</td>
<td>444.6</td>
<td>97.3</td>
<td>1,053</td>
</tr>
<tr>
<td>45 to 60</td>
<td>1.2</td>
<td>0.2</td>
<td>25.0</td>
<td>4.6</td>
<td>3.6</td>
<td>3.9</td>
<td>62.0</td>
<td>11.1</td>
<td>304</td>
</tr>
<tr>
<td>60 to 75</td>
<td>5.1</td>
<td>1.0</td>
<td>25.0</td>
<td>4.5</td>
<td>6.0</td>
<td>7.8</td>
<td>237.6</td>
<td>68.0</td>
<td>274</td>
</tr>
<tr>
<td>75 to 90</td>
<td>3.1</td>
<td>0.6</td>
<td>23.0</td>
<td>4.5</td>
<td>5.9</td>
<td>10.8</td>
<td>125.9</td>
<td>38.3</td>
<td>290</td>
</tr>
<tr>
<td>90 to 105</td>
<td>3.7</td>
<td>1.2</td>
<td>16.0</td>
<td>4.4</td>
<td>13.2</td>
<td>9.8</td>
<td>115.6</td>
<td>38.3</td>
<td>426</td>
</tr>
<tr>
<td>105 to 120</td>
<td>3.2</td>
<td>0.4</td>
<td>34.0</td>
<td>4.0</td>
<td>16.8</td>
<td>13.7</td>
<td>221.2</td>
<td>44.8</td>
<td>288</td>
</tr>
</tbody>
</table>

mg L⁻¹ – liters refers to bulk volume of soil
Table 3. Selected physical properties of the soil in the organic soil site.

<table>
<thead>
<tr>
<th>Depth Interval (cm)</th>
<th>Sand</th>
<th>Clay</th>
<th>Soil Texture</th>
<th>$K_{sat}$ (m day$^{-1}$)</th>
<th>Bulk Density (g cm$^{-3}$)</th>
<th>Particle Density (g cm$^{-3}$)</th>
<th>Porosity (cm$^{3}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 15</td>
<td>33</td>
<td>30</td>
<td>CL</td>
<td>7.32</td>
<td>0.76</td>
<td>2.03</td>
<td>0.63</td>
</tr>
<tr>
<td>15 to 30</td>
<td>42*</td>
<td>58*</td>
<td>muck</td>
<td>7.46</td>
<td>0.32</td>
<td>1.38</td>
<td>0.77</td>
</tr>
<tr>
<td>30 to 45</td>
<td>49*</td>
<td>57*</td>
<td>muck</td>
<td>2.91</td>
<td>0.31</td>
<td>1.31</td>
<td>0.76</td>
</tr>
<tr>
<td>45 to 60</td>
<td>11*</td>
<td>67*</td>
<td>muck</td>
<td>2.8</td>
<td>0.39</td>
<td>1.32</td>
<td>0.70</td>
</tr>
<tr>
<td>60 to 75</td>
<td>5</td>
<td>28</td>
<td>SiCL</td>
<td>2.94</td>
<td>0.69</td>
<td>2.19</td>
<td>0.69</td>
</tr>
<tr>
<td>75 to 90</td>
<td>2</td>
<td>37</td>
<td>SiCL</td>
<td>1.25</td>
<td>0.75</td>
<td>2.28</td>
<td>0.67</td>
</tr>
<tr>
<td>90 to 105</td>
<td>1</td>
<td>42</td>
<td>SiC</td>
<td>0.02</td>
<td>1.05</td>
<td>2.58</td>
<td>0.59</td>
</tr>
<tr>
<td>105 to 120</td>
<td>7</td>
<td>45</td>
<td>SiC</td>
<td>0.04</td>
<td>0.99</td>
<td>2.02</td>
<td>0.50</td>
</tr>
<tr>
<td>120 to 135</td>
<td>29</td>
<td>33</td>
<td>CL</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>135 to 150</td>
<td>10</td>
<td>39</td>
<td>CL</td>
<td>ND</td>
<td>0.99</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>150 to 165</td>
<td>42</td>
<td>28</td>
<td>CL</td>
<td>ND</td>
<td>1.15</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>165 to 180</td>
<td>59</td>
<td>23</td>
<td>SCL</td>
<td>ND</td>
<td>1.26</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

*- percent of mineral matter left after oxidation of organic material
ND- Not Determined
Table 4. Selected chemical properties of the soil in the organic soil site.

<table>
<thead>
<tr>
<th>Depth Interval (cm)</th>
<th>CEC cmol$_{c}$ kg$^{-1}$</th>
<th>OC %</th>
<th>BS %</th>
<th>pH</th>
<th>P mg L$^{-1}$</th>
<th>K mg L$^{-1}$</th>
<th>Ca mg L$^{-1}$</th>
<th>Mg mg L$^{-1}$</th>
<th>Total N mg L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 15</td>
<td>15.70</td>
<td>12.12</td>
<td>67.0</td>
<td>4.8</td>
<td>54.0</td>
<td>147.0</td>
<td>1,313.5</td>
<td>305.8</td>
<td>4,183</td>
</tr>
<tr>
<td>15 to 30</td>
<td>19.40</td>
<td>40.24</td>
<td>37.0</td>
<td>3.6</td>
<td>9.6</td>
<td>129.4</td>
<td>553.3</td>
<td>175.5</td>
<td>6,324</td>
</tr>
<tr>
<td>30 to 45</td>
<td>16.80</td>
<td>41.76</td>
<td>27.0</td>
<td>3.6</td>
<td>2.4</td>
<td>121.5</td>
<td>252.0</td>
<td>102.1</td>
<td>4,650</td>
</tr>
<tr>
<td>45 to 60</td>
<td>14.70</td>
<td>45.01</td>
<td>25.0</td>
<td>3.5</td>
<td>3.6</td>
<td>105.8</td>
<td>201.7</td>
<td>78.8</td>
<td>4,851</td>
</tr>
<tr>
<td>60 to 75</td>
<td>11.70</td>
<td>7.01</td>
<td>11.0</td>
<td>3.5</td>
<td>57.6</td>
<td>45.1</td>
<td>122.1</td>
<td>37.1</td>
<td>1,740</td>
</tr>
<tr>
<td>75 to 90</td>
<td>11.10</td>
<td>8.32</td>
<td>10.0</td>
<td>3.7</td>
<td>36.0</td>
<td>35.3</td>
<td>117.2</td>
<td>35.6</td>
<td>2,024</td>
</tr>
<tr>
<td>90 to 105</td>
<td>8.60</td>
<td>4.37</td>
<td>10.0</td>
<td>3.8</td>
<td>8.4</td>
<td>39.2</td>
<td>99.1</td>
<td>40.2</td>
<td>1,248</td>
</tr>
<tr>
<td>105 to 120</td>
<td>8.20</td>
<td>3.01</td>
<td>12.0</td>
<td>4.0</td>
<td>ND</td>
<td>49.0</td>
<td>97.4</td>
<td>39.5</td>
<td>990</td>
</tr>
<tr>
<td>120 to 135</td>
<td>4.70</td>
<td>1.05</td>
<td>6.0</td>
<td>3.9</td>
<td>ND</td>
<td>23.5</td>
<td>30.5</td>
<td>12.3</td>
<td>432</td>
</tr>
<tr>
<td>135 to 150</td>
<td>5.60</td>
<td>2.32</td>
<td>7.0</td>
<td>3.9</td>
<td>ND</td>
<td>33.3</td>
<td>44.4</td>
<td>13.5</td>
<td>891</td>
</tr>
<tr>
<td>150 to 165</td>
<td>4.30</td>
<td>0.82</td>
<td>7.0</td>
<td>3.9</td>
<td>ND</td>
<td>21.6</td>
<td>29.7</td>
<td>12.0</td>
<td>460</td>
</tr>
<tr>
<td>165 to 180</td>
<td>4.20</td>
<td>1.47</td>
<td>10.0</td>
<td>3.6</td>
<td>ND</td>
<td>15.7</td>
<td>63.5</td>
<td>12.9</td>
<td>630</td>
</tr>
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</table>

ND-Not Determined
mg L$^{-1}$ – liters refers to bulk volume of soil
Table 5. Concentration of selected nutrients in rainfall samples collected.

<table>
<thead>
<tr>
<th>Date</th>
<th>pH</th>
<th>PO₄-P</th>
<th>NH₄-N</th>
<th>NO₃-N</th>
<th>Cl</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/4 to 6/8</td>
<td>5.73</td>
<td>BDL</td>
<td>0.21</td>
<td>BDL</td>
<td>0.72</td>
<td>0.13</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>6/11 to 6/18</td>
<td>6.88</td>
<td>0.28</td>
<td>2.50</td>
<td>BDL</td>
<td>1.40</td>
<td>0.25</td>
<td>0.68</td>
<td>BDL</td>
<td>0.50</td>
</tr>
<tr>
<td>6/18 to 6/25</td>
<td>6.55</td>
<td>0.34</td>
<td>1.30</td>
<td>0.12</td>
<td>4.80</td>
<td>BDL</td>
<td>0.35</td>
<td>BDL</td>
<td>0.48</td>
</tr>
<tr>
<td>6/25 to 7/16</td>
<td>6.27</td>
<td>0.47</td>
<td>2.10</td>
<td>0.29</td>
<td>6.00</td>
<td>0.32</td>
<td>0.76</td>
<td>BDL</td>
<td>0.42</td>
</tr>
<tr>
<td>7/16 to 7/29</td>
<td>6.32</td>
<td>0.40</td>
<td>1.60</td>
<td>BDL</td>
<td>4.40</td>
<td>0.16</td>
<td>0.20</td>
<td>BDL</td>
<td>0.25</td>
</tr>
<tr>
<td>7/29</td>
<td>5.77</td>
<td>0.01</td>
<td>0.18</td>
<td>BDL</td>
<td>7.90</td>
<td>0.27</td>
<td>0.39</td>
<td>BDL</td>
<td>1.54</td>
</tr>
<tr>
<td>7/29 to 8/3</td>
<td>4.77</td>
<td>BDL</td>
<td>0.11</td>
<td>BDL</td>
<td>4.60</td>
<td>BDL</td>
<td>1.00</td>
<td>BDL</td>
<td>0.28</td>
</tr>
<tr>
<td>8/16</td>
<td>5.82</td>
<td>0.43</td>
<td>1.00</td>
<td>BDL</td>
<td>4.80</td>
<td>0.27</td>
<td>0.47</td>
<td>0.54</td>
<td>0.20</td>
</tr>
<tr>
<td>1/29 to 2/4</td>
<td>4.96</td>
<td>BDL</td>
<td>1.20</td>
<td>0.18</td>
<td>2.50</td>
<td>0.34</td>
<td>BDL</td>
<td>0.10</td>
<td>1.00</td>
</tr>
<tr>
<td>2/24</td>
<td>4.60</td>
<td>BDL</td>
<td>0.24</td>
<td>0.33</td>
<td>3.10</td>
<td>0.82</td>
<td>0.38</td>
<td>0.17</td>
<td>0.74</td>
</tr>
<tr>
<td>3/14</td>
<td>5.13</td>
<td>BDL</td>
<td>BDL</td>
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<td>2.00</td>
<td>0.31</td>
<td>0.19</td>
<td>0.07</td>
<td>0.83</td>
</tr>
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<td>3/16 to 3/17</td>
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<td>0.02</td>
<td>BDL</td>
<td>0.32</td>
<td>1.50</td>
<td>0.27</td>
<td>0.15</td>
<td>BDL</td>
<td>0.48</td>
</tr>
<tr>
<td>3/27 to 3/28</td>
<td>4.30</td>
<td>0.02</td>
<td>0.16</td>
<td>0.33</td>
<td>2.40</td>
<td>0.22</td>
<td>0.16</td>
<td>0.05</td>
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</tr>
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<td>4/7 to 4/8</td>
<td>4.25</td>
<td>0.01</td>
<td>0.13</td>
<td>0.44</td>
<td>2.60</td>
<td>0.30</td>
<td>0.24</td>
<td>0.09</td>
<td>1.00</td>
</tr>
<tr>
<td>4/9</td>
<td>4.58</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>1.80</td>
<td>0.11</td>
<td>0.16</td>
<td>BDL</td>
<td>0.53</td>
</tr>
<tr>
<td>4/13 to 4/15</td>
<td>4.38</td>
<td>BDL</td>
<td>BDL</td>
<td>0.16</td>
<td>1.00</td>
<td>0.15</td>
<td>0.06</td>
<td>0.06</td>
<td>0.42</td>
</tr>
</tbody>
</table>

BDL – Below Detection Limit
Figure 1. Aerial photograph of Juniper Bay with marked location of the organic and mineral soil sites, the main and side ditches, the main ditch exit and the ditch sample collection spots. In the inset, the location of Juniper Bay in the southeastern part of North Carolina is shown by the star.
Figure 2. Photograph of the monitoring set-up
Figure 3. Photograph of the tipping-bucket rain gauge connected to a rain sample collector.
Figure 4. Illustration of the tension sampler connected to a vacuum trap.
Figure 5. Rainfall and water table data at the mineral and organic soil sites for the duration of the experiment.
Figure 6. Relative direction of the subsurface lateral hydraulic gradient at the organic soil site determined using the three-point technique.
Figure 7. Relative direction of the subsurface lateral hydraulic gradient at the mineral soil site determined using the three-point technique.
Figure 8. Effect of water table depth on the magnitude of the subsurface lateral hydraulic gradient computed for the axis that is perpendicular to the ditch. By convention, a positive value means that gradient is towards the ditch and going away from the ditch if the value is negative.
Figure 9. Average concentrations of different solutes monitored at the main ditch exit, side ditch at the mineral site and side ditch at the organic site for baseflow condition, days following a regular rain event and days following a major storm event.
Figure 10. Average concentration of total organic carbon (TOC), calcium, magnesium and phosphate in well water samples in the mineral and organic soil sites for the duration of the study. Solid point markers refer to the storm sample.
Figure 11. Total organic carbon (TOC) at various depths in the mineral and organic soil sites for the entire duration of the study. Depths that are not reflected in the plot have either concentration that were very low and fairly uniform throughout the study, or depths that weren’t sampled. The gray arrow shows the storm sample collection date.
Figure 12. Concentration of calcium detected at various depths in the mineral and organic soil site for the entire duration of the study. Depths that are not reflected in the plot have either concentrations that are very low and fairly uniform throughout the study, or depths that weren’t sampled. The gray arrow shows the storm sample collection date.
Figure 13. Concentration of magnesium detected at various depths in the mineral and organic soil site for the entire duration of the study. Depths that are not reflected in the plot have either concentration that were very low and fairly uniform throughout the study, or depths that weren’t sampled. The gray arrow shows the storm sample collection date.
Figure 14. Concentration of phosphate detected at various depths in the mineral and organic soil site for the entire duration of the study. Depths that are not reflected in the plot have either concentrations that are very low and fairly uniform throughout the study, or depths that weren’t sampled. The gray arrow shows the storm sample collection date.
Figure 15. Concentration of chloride detected at various depths in the mineral and organic soil site for the entire duration of the study. Depths that are not reflected in the plot have concentrations that are very low and fairly uniform throughout the study. The gray arrow shows the storm sample collection date.
Figure 16. Soil solution nutrient profile for sampling dates that represented baseflow conditions, days following a regular rain and the day following the storm event at the mineral soil site.
Figure 17. Soil solution nutrient profile for sampling dates that represented baseflow conditions, days following a regular rain and the day following the storm event at the organic soil site.
Figure 18. Soil solution chloride profile for sampling dates that represented baseflow conditions, days following a regular rain and the day following the storm event at the organic and mineral soil sites.
APPENDICES
Appendix Table 1. Redox data collected from the mineral and organic soil sites for the duration of the study.

<table>
<thead>
<tr>
<th>Location</th>
<th>Depth</th>
<th>Date</th>
<th>Rep</th>
<th>8/12</th>
<th>8/16</th>
<th>8/31</th>
<th>9/14</th>
<th>10/2</th>
<th>10/5</th>
<th>11/2</th>
<th>11/3</th>
<th>12/3</th>
<th>1/6</th>
<th>2/4</th>
<th>3/7</th>
<th>4/11</th>
<th>5/6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mineral</td>
<td>25</td>
<td>1</td>
<td>942</td>
<td>772</td>
<td>192</td>
<td>277</td>
<td>-62</td>
<td>188</td>
<td>-74</td>
<td>-75</td>
<td>157</td>
<td>93</td>
<td>142</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site</td>
<td>2</td>
<td>949</td>
<td>718</td>
<td>165</td>
<td>260</td>
<td>-141</td>
<td>243</td>
<td>-75</td>
<td>-62</td>
<td>129</td>
<td>94</td>
<td>99</td>
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