Soil nitrate-nitrogen in forested versus non-forested ecosystems in a mixed-use watershed

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A B S T R A C T

In tracking nutrients that enter the Gulf of Mexico via the Suwannee Basin, a disproportionate amount of the nitrate-nitrogen (NO₃-N) has been shown to originate in the Santa Fe River Watershed (SFRW). This study investigated soil NO₃-N distributions across the range of land-use and soil order combinations that exist in the SFRW with a focus on comparing NO₃-N levels in forested versus non-forested land-uses. The SFRW consists of 52% forested land-uses (i.e. pine plantations, forest regeneration, upland forest, and forested wetland), 47% non-forested land-uses (i.e. agriculture, rangeland, and urban), and 1% water. Soil samples were collected from four depth intervals (0–30, 30–60, 60–120, 120–180 cm) at 101 to 141 sites with a stratified-random design in six sampling events (Sept. 2003, Jan. 2004, May 2004, Jan. 2005, May 2005, and Sept. 2005). No samples were collected in Sept. 2004 due to flooding associated with two hurricanes. Nitrate-nitrogen was significantly lower in forested versus non-forested land-uses across all sampling events, depth intervals, and for profile average data. Within the non-forested land-use category, NO₃-N levels were highest in row crop agriculture and improved pasture sites. In terms of soil order, NO₃-N values were generally higher in Ultisols and Spodosols, but soil order explained less of the variation in the NO₃-N data than did land-use or sampling date. Nitrate-N concentrations were considerably altered by Hurricanes Frances and Jeanne which passed over the SFRW in late summer of 2004. In the post-hurricane sampling events, NO₃-N concentrations were lower in both forested and non-forested sites. A year later, however, NO₃-N concentrations in forested sites remained quite low, while concentrations in non-forested sites had begun to increase. © 2008 Elsevier B.V. All rights reserved.

1. Introduction

Human activity has dramatically increased the flux of nitrogen (N) and phosphorus (P) to coastal zones (Rabalais et al., 2002). For example, the change in N flux from pre-industrial times to the present has been estimated as fourfold for the Mississippi River, eightfold in rivers of the northeastern United States, and tenfold in rivers draining to the North Sea (Howarth et al., 1996). This increased nutrient loading to coastal zones tracks increases in population, agricultural expansion in river basins, and increasing food and energy consumption (Nixon 1995; Howarth et al., 1996; Vitousek et al., 1997; Bennett et al., 2001). Globally, nitrate-nitrogen (NO₃-N) is the main contributor to increased N loading in larger rivers (Turner et al., 2003). Since the 1950s, increased marine productivity and hypoxic conditions in the Gulf of Mexico parallel the increases in NO₃-N loads to the Gulf (Rabalais et al., 2002; Turner et al., 2006). In the summer of 2002, the hypoxic zone in the Gulf of Mexico extended over an area of 22,000 km² (Turner et al., 2006).

Hypoxia is just one of many nutrient enrichment symptoms in coastal zones. Other symptoms include reduced light penetration, increased abundance of nuisance macro algae, loss of aquatic habitat such as seagrass beds, noxious and toxic algal blooms, and shifts in trophic interactions and food webs (Schramm 1999; Anderson et al., 2002; Rabalais et al., 2002). With the growing world population, more fertilizer will be needed for greater crop production; as a result, watershed disturbances and nutrient pollution will likely intensify (Carpenter et al., 1998). Thus, there is a current need to identify terrestrial sources of nutrients such as NO₃-N at the watershed scale, and assess their contribution to the degradation of downstream aquatic and coastal ecosystems.

The Suwannee River Basin has experienced population growth, increases in agricultural production, and subsequent increases in nutrient loading to surface waters, groundwater, and coastal zones (Pittman et al., 1997; Hornsby and Ceryak, 1999; Katz et al., 2001; Katz et al., 2004). The basin covers an area of 25,900 km² that spans parts of southern Georgia and north-central Florida (Fig. 1). Water quality monitoring data from the major rivers in the Suwannee Basin have shown a significant increasing trend in NO₃-N concentrations over a period of two decades (Ham and Hatzell, 1996). More recently, the Suwannee Basin was shown to have the largest area of elevated NO₃-N
concentrations in the Floridian Aquifer system (SRWMD, 2002). According to a groundwater monitoring program, NO$_3$-N was elevated in the Santa Fe River Watershed (SFRW), a subwatershed within the larger Suwannee River Basin (SRWMD, 2002). Although the SFRW (3,585 km$^2$) comprises only 13.8% of the greater Suwannee Basin, it accounted for 22.2% (2,676 t NO$_3$-N) of the total N load in 2000 and 19.7% (2,971 t NO$_3$-N) of the total N load in 2003 (SRWMD, 2000; SRWMD, 2003). Thus, based on its areal extent, the SFRW has contributed a disproportionate amount of NO$_3$-N from the Suwannee Basin to the Gulf of Mexico. Recent studies in the Suwannee Basin have indicated that the dominant NO$_3$-N sources include inorganic fertilizers and organic animal wastes (Katz et al., 1999).

The SFRW also contains a number of groundwater springs that support threatened aquatic ecosystems. These springs are biodiversity
hotspots in the north-central region of Florida that support various reptile, amphibian, fish, and bird species, as well as threatened and endangered species such as the Gulf Sturgeon *Acipenser oxyrhynchus desotoi* and the West Indian Manatee (*Trichechus manatus*). The springs in the Middle Suwannee Watershed have surface water NO$_3$-N concentrations ranging from 1.2 to 17.0 mg L$^{-1}$ (SRWMD, 2002). Such high NO$_3$-N concentrations can lead to nuisance levels of algae and macrophytes in many of the spring-fed rivers of this region (Jones et al., 1996; Hornsbyte and Mattson, 1998). Thus, NO$_3$-N loading not only causes remote effects beyond terrestrial watershed boundaries, it also causes local changes in the freshwater ecosystems within the watershed.

The increases in nutrient loading within and from the SFRW can be linked to land-use changes within the watershed. Recently there has been an increasing trend of converting less intensively-managed to more intensively-managed land-uses (Katz, 2004; Sabesan, 2004). For example, in the SFRW from 1990 to 2003 the areal extent of pine plantations increased from 23.5 to 37.3% (Sabesan, 2004). These shifts in land-use have major implications for export of NO$_3$-N from the watershed if the tight nutrient cycles of forested ecosystems such as pine plantations, upland forests, and wetlands retain inorganic nutrients such as NO$_3$-N and serve as N sinks at the watershed scale (Band et al., 2001; Groffman et al., 2004). Other non-forested ecosystems such as agriculture, improved pasture, and urban areas can become saturated with NO$_3$-N and serve as NO$_3$-N sources at the watershed scale (Freifelder et al., 1998). Soils along with land-use play a critical role in the transport, cycling, and retention of nitrogen within a watershed. Thus, the overall goal of this project was to investigate spatial and temporal variability of soil NO$_3$-N across the range of land-use and soil order combinations that exist in the SFRW. The specific objectives of this study are as follows: 1) to compare soil NO$_3$-N levels in forested versus non-forested land-uses since there is a local concern that forested land uses which dominate the area are important contributors to N increases in the Santa Fe and Suwannee Rivers; 2) to compare NO$_3$-N levels in the SFRW before and after the 2004 hurricanes Frances and Jeanne; and 3) to compare NO$_3$-N levels across the different soil orders that are found in the SFRW.

### 2. Materials and methods

#### 2.1. Study Area

The SFRW spans across eight counties in north-central Florida (Fig. 1a) and comprises the southeastern section of the greater Suwannee Basin. In 1990, the dominant land-uses in the SFRW included pine plantation (29.5%), agriculture (including row crops and improved pasture, 25.3%), rangeland (15.1%), wetland (13.7%), upland forest (8.9%), and urban (5.5%). The remaining 2.0% was classified as water or could not be classified due to cloud cover (Sabesan, 2004). By 2003, the land-use distribution had shifted as follows: pine plantation (23.3%), agriculture (37.3%), rangeland (4.3%), wetland (17.9%), upland forest (10.5%), and urban (5.6%). The remaining 1.1% was classified as water or could not be classified due to cloud cover (Sabesan, 2004). The soils of the SFRW are predominantly sandy in texture although there are areas with loamy to clayey deposits, organic soils, and karst terrain (Lamsal et al., 2006). The dominant soil orders in the watershed include Ultisols (36.7%), Spodosols (25.8%), and Entisols (14.7%) with smaller areas of Histisols (2.0%), Inceptisols (1.1%), and Alfisols (1.0%) (Lamsal et al., 2006).

Elevation in the SFRW ranges from 3 to 91 m above mean sea level (Grunwald et al., 2006). Generally, the land is level (0–2% slopes) or gently sloping and undulating (2–5% slopes) with the major exception to this pattern being the moderately and strongly sloping land (5–12% slopes) along the Cody Scarp. The two main physiographic regions in the watershed are the Gulf Coastal Lowlands and the Northern Highlands, which are separated from one another by the Cody Scarp (Schmidt, 1997). Underlying geologic units in the SFRW include Eocene limestone, which occurs near the ground surface in the high-recharge, strongly karst-influenced Gulf Coastal Lowlands. The Eocene limestone is capped by Miocene sediments, which tend to be clayey and phosphatic (occurring at or near the surface along the Cody Scarp). The Miocene sediments are capped by Pleiocence and Pleistocene-Holocene sediments, which tend to be sandy at the surface but have loamy subsoils at varying depths (Brown et al., 1990; Randazzo and Jones, 1997).

The stream network reflects the underlying geology as it shows a much higher density in the eastern part of the watershed (Fig. 1b). The presence of the karst terrain and sinkholes has prevented the establishment of such a stream network in the western part of the watershed (Grunwald et al., 2006). The Santa Fe River actually flows underground for approximately 3 km as it passes through the Cody Scarp. Based on the National Oceanic and Atmospheric Administration (NOAA) records at seven monitoring stations located within or nearby the watershed, the mean annual precipitation calculated for the period from 1971 to 2000 was 1,334 mm and the mean annual temperature was 20.4 °C (NCDC, 2006).

#### 2.2. Land-use reclassification

For the purposes of this study, upland forest, regenerating pine forest, and forested wetland were reclassified into the broader category of forested ecosystems. In the SFRW, these forested ecosystems experience little to no managed ungluate activity, and except for periods of harvest, are not subject to mechanical manipulations such as tillage or mowing. Typically the pine plantations are, at most, fertilized twice during a 20 year rotation period with a cumulative input of less than 300 kg N ha$^{-1}$, but often they are not fertilized at all. It is also important to point out that the majority of the wetlands in the SFRW are forested systems as opposed to emergent freshwater marshes. In contrast, non-forested sites in this watershed are more intensively managed than the forested sites. For example, both the frequency (i.e. seasonal fertilization, mowing, and tillage) and the intensity of inputs to the site (i.e. application of inorganic fertilizers, concentrated unglulate activity, and heavy-machinery operation) are distinctly different. Thus, we reclassified the agriculture (including row crops and improved pasture), rangeland, and urban systems into the broader category of non-forested ecosystems. Fig. 1c shows the distribution of forested versus non-forested lands across the SFRW.

#### 2.3. Field data collection

We selected 141 sampling locations using a stratified-random sampling design. Strata were derived from land-use soil order combinations in ArcGIS 9.1 (Environmental Systems Research Institute, Redlands, CA). This design targeted sampling locations that were representative of the range of soil-landscape conditions that existed in the SFRW. As such, multiple sites within each of the land-uses, soil orders, within the same land-use but different soil orders, and within the same soil order but different land uses were sampled to ensure adequate representation of the land-use soil order combinations that existed in the SFRW. See Lamsal et al. (2006) for further information about the stratified-random design. Soil samples were collected during Sept. 2003, Jan. 2004, May 2004, Jan. 2005, May 2005, and Sept. 2005. These dates represented typical seasonal patterns with “wet/end of cropping season” (Sept.), “dry winter season” (Jan.), and “dry spring season” (May). Samples could not be collected in Sept. 2004 due to the flooding of sites and access roads caused by Hurricanes Frances (Sept. 4–8, 2004) and Jeanne (Sept. 26–30, 2004). A representative plot was selected at each site, and the center point of the plot was mapped with global positioning unit so that the plot could be located in future sampling events. Soil cores were collected within a 1 m distance from the center point with a 6.5-cm diameter
auger. Four soil cores were collected from the 0 to 30 cm depth, three soil cores were collected from the 30 to 60 cm depth and 60 to 120 cm depths, and two soil cores were collected from the 120 to 180 cm depth. The cores were composited for each respective depth and a subsample was collected for analysis. This sampling protocol ensured constant sample support in the different depth layers.

Not all sampling depths could be sampled in each event due to field conditions (e.g. high water table during rainy season). Likewise, not all sites could be sampled during each event as land owner permission was not granted for every sampling event. Therefore, the number of samples collected varied slightly by season and depth (Table 1).

2.4. Laboratory analyses

The soil samples were stored in a cooler on ice until being returned to the laboratory. In the laboratory, samples were placed in a refrigerator and extracted within 24 h of collection. The extractions were conducted with 2M potassium chloride (KCl) (Keeney and Nelson, 1982). Extracts were then analysed for NO$_3$-N content with an autoanalyser. Soil moisture content of the samples was determined by drying a subsample for 24 h at 105 °C. Final NO$_3$-N concentrations were expressed as µg NO$_3$-N g$^{-1}$ dry soil. Detection limits ranged from 0.02–0.05 ppm NO$_3$-N (1.4–3.6 µM NO$_3$-N). Samples below the detection limit were assigned the mean value (derived from averaging the lowest observed value in the respective sampling event and Null).

Profile average NO$_3$-N values ($z^a$) were derived according to Eq. (1).

$$z^a = \frac{\sum_{i=1}^{n} (z_i x_i) + d_i}{\sum_{i=1}^{n} d_i}$$

where $z_i x_i$ is the measured NO$_3$-N in µg g$^{-1}$ soil at sampling sites ($z_i$) for the ith layer ($i = 1, 2, 3$ and 4) and $d_i$ is the thickness in cm of the ith layer.

2.5. Statistical analyses

Our objective was to investigate the effects of land-use, sampling date (climatic component), soil order, and their combinations on soil NO$_3$-N. The NO$_3$-N data from the individual layers (i.e. 0–30, 30–60, 60–120, 120–180 cm) as well as the profile average NO$_3$-N data were log transformed and analyzed with a series of mixed models (Proc Mixed) (SAS Institute, Raleigh, NC). These mixed models included fixed effects (land-use and soil order), random effects (site), and sampling date as a type one autoregressive repeated measure effect. Proc Mixed also allowed us to use separate variance components for the forested versus the non-forested sites as we expected greater variability in the NO$_3$-N values from the non-forested sites than from the forested sites.

This model used a Restricted Maximum Likelihood (REML) method to estimate the mixed model parameters. The Akaike Information Criteria (AIC) was used to select among possible mixed models. Mean values were compared across the different sample groupings with the least squared (LSMeans) procedure in SAS. The NO$_3$-N data was log transformed so that it would better conform to the assumptions of the mixed model. We added a constant (+1) to the NO$_3$-N values before the log transformation to keep the log values > 1. While the statistical analyses were conducted with the transformed data, the figures show the raw data for ease of interpretation (i.e. raw numbers instead of log-scale).

3. Results and discussion

3.1. Forested versus non-forested sites across all dates

There were distinct trends in the NO$_3$-N data in forested versus non-forested sites, across the six sampling events, and with depth in the soil profile. All events showed positively-skewed NO$_3$-N distributions for both forested and non-forested sites. Skewness was higher for the forested sites across all sampling events as many of the NO$_3$-N measurements were below the detection limit for the forested land-uses (Table 1). It is a common phenomenon that environmental datasets show many more low than high values (Saito and Goovaerts, 2000).

Prior to the hurricanes, the majority of forested and non-forested sites had NO$_3$-N levels above the detection limit. After the hurricanes there was a dramatic shift, with none of the forested sites having NO$_3$-N levels above the detection limit in the Jan. 2005 event, and less than half of the forested sites having values above the detection limit in the May and Sept. 2005 events. The decreases in NO$_3$-N were most likely due to the intense precipitation from Hurricanes Frances (Sept. 4–8, 2004) and Jeanne (Sept. 16–18, 2004), which caused significant rainfall and runoff events.
2004) and Jeanne (Sept. 26–30, 2004), which passed directly over the SFRW. These storms caused a decrease in soil NO$_3$-N concentration by both direct and indirect processes. First, the inputs of precipitation leached NO$_3$-N from all four layers of the soil profile and caused it to be lost in surface water runoff and groundwater flow. Second, and more indirectly, the precipitation inputs raised local water tables and were assumed to stimulate high rates of denitrification of the remaining NO$_3$-N in surface soil horizons.

According to the mixed model, forested versus non-forested status accounted for a greater proportion of the variance than did sampling date across each of the four individual depths as well as for the profile average data (Table 2). The effect of forested versus non-forested status was greatest in the upper 0–30 cm and tended to decrease with depth (Table 2). Other studies have shown that the effects of agriculture are greatest at the surface and decrease with depth in the soil profile (Braekke, 1999; Compton and Boone, 2000; Bruland et al., 2003). While sampling date had less explanatory power than forested versus non-forested status, sampling date did account for a significant proportion of the variance in the NO$_3$-N data across each of the depth categories as well as with the profile average data (Table 2).

The forest versus non-forest by sampling date interaction term was also significant across each layer and for the profile averaged data (Table 2) indicating that differences in NO$_3$-N between forested and non-forested sites were not consistent across all sampling dates. For

Fig. 2. Mean concentrations of nitrate-nitrogen in the forested and non-forested sites in the upper 0–30, 30–60, 60–120, 120–180 cm, and the profile average during the six sampling events. Error bars represent one standard error.
example, while mean NO$_3$-N was lower in forested than non-forested sites for each sampling event and across all depths and the profile average data (Table 1, Fig. 2), the magnitude of these differences varied considerably from approximately 1 μg g$^{-1}$ in the 2005 events to 15 μg g$^{-1}$ in the January 2004 event (Fig. 2). The highest NO$_3$-N values were observed in January 2004 followed by May 2004, and this was consistent across all four depths.

Mean NO$_3$-N was also significantly higher in the forested sites across all depths and in the profile average data in the May 2004 event when compared to the three 2005 events that followed Hurricanes Frances and Jeanne. Mean NO$_3$-N values in the non-forested sites were significantly higher in the pre-hurricane (2003–2004) events than they were in the post-hurricane (2005) events (Fig. 2) and this was most pronounced in the 0–30 cm soil layer. It also appeared that NO$_3$-N was not being retained in the 30–60 cm soil layer. In this zone, a combination of root uptake, denitrification, and leaching may have been responsible for the low observed NO$_3$-N concentrations. The lower organic matter content in this zone may have also resulted in less NO$_3$-N retention and lower in-situ mineralization rates. Interestingly, in Jan. 2004, NO$_3$-N values increased in the 60–120 and 120–180 cm layers indicating that NO$_3$-N may have accumulated in these horizons due to changes in soil properties with depth or the presence of deeper spodic horizons. While mean NO$_3$-N values in the non-forested sites showed considerable variability prior to the hurricanes, ranging between 1–14 μg g$^{-1}$, across the four soil depth categories, mean NO$_3$-N values across all depths were much less variable after the hurricanes, ranging from 0.25–2.0 μg g$^{-1}$ (Fig. 2).

The profile average median NO$_3$-N values (often considered more robust than mean values when dealing with somewhat skewed datasets) were also lower in the forested than in the non-forested sites across the sampling dates (Table 1). Median NO$_3$-N values were actually highest for both forested and non-forested sites in the May 2004 event, while mean values were highest in the Jan. 2004 event. This was largely due to a few very high (50–110 μg g$^{-1}$) NO$_3$-N values measured during the Jan. 2004 event. These high values observed in Jan. 2004 may have been caused by a number of factors including recent fertilization of the non-forested crops and pastures, low plant uptake and microbial immobilization during the winter period, and low precipitation that stimulated high rates of nitrification.

The lower mean NO$_3$-N content during Sept. 2003 and in all three 2005 sampling events could be attributed to the influence of substantial precipitation from tropical storms and hurricanes (Table 3). High rainfall during the fall of 2003, and especially high rainfall associated with Hurricanes Frances and Jeanne in late summer of 2004 flushed NO$_3$-N from soils in the SFRW. Large storm events have been shown to lead to redistribution and export of N in other watersheds (Welter et al., 2005). In the case of the SFRW in fall 2004, NO$_3$-N was most likely lost from the soils by some combination of surface runoff, shallow groundwater flow, and deep groundwater movement into the underlying aquifer. However, this increased export of soil NO$_3$-N was most likely diluted by the large volumes of surface water flow that were generated from the hurricane rainfall. Thus, despite the large pulse of NO$_3$-N from soils, concentrations of NO$_3$-N in surface and groundwater following the hurricanes may have actually been less than during baseflow due to the effect of dilution.

Interestingly, as water tables remained near the soil surface in much of the watershed for several weeks following the hurricanes, we assume the subsequent anaerobic conditions that most likely developed in both upland and wetland areas stimulated denitrification and resulted in further transformation of NO$_3$-N to N$_2$ gas and loss from the soil. Similar results were found in another study that documented NO$_3$-N leaching due to rainfall-runoff events (Guo et al., 2001).

Another study of water quality in the Neuse River Watershed in North Carolina reported that three hurricanes in September 1999 flushed nutrients out of the soil profile (Dukes and Evans, 2006). These three events resulted in 584 mm of precipitation over a 21 day period (Dukes and Evans, 2006). By comparison, in Sept. 2004 the SFRW received an average of 368 mm of precipitation (based on 7 weather stations) over a 26 day period. These results indicated that extreme weather events in the south-eastern United States have the potential to alter soil NO$_3$-N status at the watershed scale. While the N cycle is quite complex and involves numerous interactive mechanisms, it appears that extreme climatic events in this watershed, which occur at low frequency, override other process that control soil NO$_3$-N, such as fertilization, mineralization, microbial immobilization, and nitrification. For example, years with heavy rainfall (often from hurricanes) have been shown to cause NO$_3$-N to be flushed/denitrified from the soil, while years with low rainfall cause NO$_3$-N to accumulate in the soil (Katz et al., 2001). Thus, climatic variability may play an important role in NO$_3$-N export from the SFRW. For example, rainfall at the Live Oak Station just north of the SFRW was 1,890 mm in 1991 and 840 in 1995, a difference of ~1000 mm (Katz et al., 2001); NO$_3$-N biogeochemical cycling and export in these 2 years were most likely very different.

### 3.2. Specific land-uses across all dates

According to the mixed model, both specific land-use (i.e., agriculture, improved pasture, rangeland, urban, upland forest, pine plantation, forest regeneration, and wetland) and sampling date accounted for a significant proportion of the variance in the NO$_3$-N data across each soil depth category and the profile average data (Table 4). The specific land-use by sampling date interaction was

<table>
<thead>
<tr>
<th>Layer</th>
<th>Source of Variation</th>
<th>Degrees of freedom$^a$</th>
<th>F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–30 cm</td>
<td>LU</td>
<td>7, 135</td>
<td>23.2</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 573</td>
<td>13.5</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>30–60 cm</td>
<td>LU</td>
<td>7, 135</td>
<td>15.8</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 564</td>
<td>25.9</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>60–120 cm</td>
<td>LU</td>
<td>7, 132</td>
<td>12.5</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 514</td>
<td>15.9</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>120–180 cm</td>
<td>LU</td>
<td>7, 129</td>
<td>12.2</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 417</td>
<td>10.0</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>Profile Average</td>
<td>LU</td>
<td>7, 135</td>
<td>25.7</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 572</td>
<td>22.3</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td></td>
<td>LU$^b$Date</td>
<td>35, 352</td>
<td>2.7</td>
<td>0.0001</td>
</tr>
</tbody>
</table>

$^a$ Reported as numerator degrees of freedom, denominator degrees of freedom.

$^b$ Significantly higher in the pre-hurricane (2003–2004) events than they were in the post-hurricane (2005) events (Fig. 2).

### Table 3

Average precipitation data for different time periods during the 2003–2005 period based on data from seven climatic stations in or near the Santa Fe River Watershed (NCDC 2006).

<table>
<thead>
<tr>
<th>Month and year</th>
<th>Monthly average (mm)</th>
<th>Previous 3-month average (mm)</th>
<th>Annual average (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sept. 2003</td>
<td>93.9</td>
<td>656.8</td>
<td>2003: 1,403.5</td>
</tr>
<tr>
<td>Jan. 2004</td>
<td>52.4</td>
<td>153.2</td>
<td></td>
</tr>
<tr>
<td>May 2004</td>
<td>52.8</td>
<td>191.1</td>
<td></td>
</tr>
<tr>
<td>Sept. 2004$^c$</td>
<td>387.1</td>
<td>645.6</td>
<td>2004: 1,523.2</td>
</tr>
<tr>
<td>Jan. 2005</td>
<td>442.2</td>
<td>194.1</td>
<td></td>
</tr>
<tr>
<td>May 2005</td>
<td>139.5</td>
<td>389.9</td>
<td></td>
</tr>
<tr>
<td>Sept. 2005</td>
<td>76.1</td>
<td>511.7</td>
<td>2005: 1,424.8</td>
</tr>
</tbody>
</table>

$^c$ High monthly average due to rainfall from Hurricanes Frances and Jeanne.
significant for the upper three depths and the profile average data but not for the 120–180 cm layer (Table 4). Overall, when specific land-uses were considered rather than the more general forested versus non-forested classification, the F values for the effects of specific land-use were less than the F values for forested versus non-forested status. Despite the decrease in the F statistic, the effect of specific land-use continued to have more explanatory power than sampling date for the 0–30 cm (F=23.2), 120–180 cm (F=12.2), and the profile average data (F=25.7). Interestingly, sampling date had more explanatory power for the 30–60 cm (F=25.9) and 60–120 cm depths (F=15.9) suggesting that different N transformation, retention, and loss mechanisms were occurring at each of the different depths or that the rates of these different mechanisms varied with depth.

The effect of specific land-use decreased consistently with depth while the effect of sampling date did not (Table 4). This may be related to a number of factors including a decrease in sample size with the specific

Fig. 3. Mean concentrations of nitrate-nitrogen across the specific land-uses in the upper 0–30, 30–60, 60–120, 120–180 cm, and the profile average during the six sampling events. Error bars represent one standard error.
land-uses and higher within class variability among the specific land-use classes. Despite the drop in the F value with the inclusion of the specific land-uses, there were striking and consistent differences across the land-use categories over time. For example, across all depths and all six sampling events, the highest mean NO3-N values were generally for the Jan. 2004 and May 2004 events, improved pasture sites had higher mean NO3-N values than row crop agricultural sites in the 0–30 (Jan.=26 µg g−1, May=10 µg g−1) and 30–60 cm (Jan.=5 µg g−1, May=3 µg g−1) depths. This suggested that in certain seasons and in surface soil depths, N inputs from a combination of fertilizer and animal wastes in improved pastures may exceed those of N inputs of fertilizer to row crop agriculture. After row crops and improved pastures, rangelands had the next highest mean NO3-N values.

Profile average mean NO3-N values in row crop agricultural sites were higher in the three events prior to Hurricanes Frances and Jeanne (Sept. 2003=1.90 µg g−1, Jan. 2004=17.6 µg g−1, May 2004=3.86 µg g−1) than in the three events that followed (Jan. 2005=2.25 µg g−1, May 2005=2.10 µg g−1, Sept. 2005=2.56 µg g−1). Following the hurricanes, mean NO3-N values were highest in the agricultural and improved pasture sites, many of which would have been fertilized and received N inputs from animal waste (urine or fecal material). Rangelands, urban areas, and all forested sites showed low, if not undetectable, NO3-N values. The fact that NO3-N concentrations had not increased in the rangelands after the hurricanes suggests that grazing and natural fertilization in these sites was less intense than in improved pastures. Woodard et al. (2002) compared NO3-N in soil water below the rooting zone and forage N removal for two forage systems on thermic, uncoated Typic Quartzipsamments comparable to soils and forage systems in the SFRW. They found that perennial bermudagrass (Cynodon spp.) was superior at preventing NO3-N from leaching below the rooting zone than a rotation of corn (Zea mays L.), forage sorghum (Sorghum bicolor L.), and rye (Secale cereale L.). Thus, the process of crop rotation results in greater NO3-N leaching, as the plant species are being established, in contrast to a system like a rangeland in which vegetative cover and plant uptake of NO3-N occur on a more continuous basis.

Throughout all sampling events and soil depths, pine plantations, forest regeneration, and upland forest sites showed consistently low mean NO3-N values. Typical fertilization regimes for pine plantations in this region provide (if utilized) 45–50 kg N ha−1 once during the first 5 years (forest regeneration phase) and as much as 200–300 kg N ha−1 applied once or in two applications of about 150 kg N ha−1 during the following 15 years (Pritchett and Comerford, 1982; Pritchett and Comerford, 1983; Jokela, 2004). The low NO3-N values in the majority of the forested sites were representative of upland forested ecosystems in Florida that are characterized by their tight cycling of N and low fertilizer input. Forest fertilization, while an increasingly common management option, currently involves the application of no more than 300 kg N ha−1 during a 20 to 25 year period with as much as 30 to 50% of the fertilizer being removed from solution by plant uptake (Johnson, 1992; Blazier et al., 2006). That is in contrast to agricultural operations that will add that much N in a single year to 2 years. Furthermore, pine forests continue to absorb nutrients such as NO3-N from the soil during the winter (Comerford et al., 1987) unlike deciduous, hardwood forests. The upland forests sampled most likely received no fertilizer during the study or for long periods prior to the study.

Although wetlands are positioned in the landscape to receive nutrient inputs from up slope areas (Bruland and Richardson, 2004; Bruland and Richardson, 2006; Grunwald et al., 2007), the wetlands in the SFRW did not show high NO3-N concentrations. For example, low mean NO3-N values were observed in each of the depth categories. This lead to the observation of low profile average NO3-N values across the six sampling events. The low NO3-N concentrations in wetlands were assumed to be due to receiving water from low NO3-N pine plantation surrounding the wetlands, denitrification of NO3-N, and mixing of water from the river and groundwater by water level fluctuations. McMahon and Böhlke (1996) showed that the median NO3-N concentration in groundwater from adjacent floodplain deposits (461 µmol L−1) and riverbed sediments (461 µmol L−1) were lower than the median concentration in the terrace deposits (1,857 µmol L−1). The authors estimated that 15–30% of the difference between floodplain/riverbed and terrace deposits was accounted for by denitrification and the rest by mixing of river and floodplain water.

A chronological assessment of nutrient loading using age dating techniques showed that the NO3-N concentrations of springs of the Suwannee River Basin have responded to increased N loads from various sources in the basin for decades (Katz et al., 2001). Long-term trends of NO3-N in the basin showed that the increasing NO3-N concentrations in spring waters followed the steady increase in fertilizer use over time (Katz et al., 1999). Katz (2004) found that inorganic fertilizers were the dominant source of N in spring waters in the Suwannee River Basin based on 15N isotope tracers. This study confirmed that land-use is closely related to soil NO3-N and that non-forested land-uses were probably contributing to the majority of the NO3-N export from the watershed.

3.3. Soil orders across all dates

According to the mixed model, both soil order and sampling date accounted for a significant proportion of the variance in the NO3-N data across each soil depth category and the profile average data (Table 5). The mixed models indicated that sampling date had more explanatory power than soil order across the four depths and the profile average data. This indicated that climatic factors associated with different seasons such as droughts, wet periods, and hurricanes may have a greater effect on soil NO3-N than soil type in this watershed. The soil order by sampling date interaction was not significant at any depth nor for the profile average data (Table 5). The non-significant interaction term indicated that the differences in mean values across the soil orders were generally consistent across the sampling dates. Mean NO3-N values were generally higher in Ultisols across all depths and sampling dates (Fig. 4). The one exception to this pattern was that mean NO3-N in the 120–180 cm layer was highest in Spodosols in the January 2004 event. This was most likely due to retention of NO3-N in the spodic horizon. For the profile average data, the highest mean value for any order was for Ultisols in the Jan. 2004 event (7.5 µg g−1). Entisols had the next

<table>
<thead>
<tr>
<th>Layer</th>
<th>Source of Variation</th>
<th>Degrees of freedom</th>
<th>F</th>
<th>p-value</th>
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<tr>
<td>0–30 cm</td>
<td>Order</td>
<td>4, 137</td>
<td>4.2</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 589</td>
<td>6.2</td>
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<td></td>
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<td>1.6</td>
<td>0.05</td>
</tr>
<tr>
<td>30–60 cm</td>
<td>Order</td>
<td>4, 137</td>
<td>2.9</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 580</td>
<td>9.8</td>
<td>&lt;0.0001</td>
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<td></td>
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<td>0.77</td>
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<tr>
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<td>2.8</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Date</td>
<td>5, 530</td>
<td>3.2</td>
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<td>120–180 cm</td>
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<td>0.05</td>
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<tr>
<td>Profile Average</td>
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<td>&lt;0.0001</td>
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<td>Order×Date</td>
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<td>0.51</td>
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</table>

a Reported as numerator degrees of freedom, denominator degrees of freedom.
highest mean NO$_3$-N values followed by Spodosols and then by Alfisols, although these differences were not significant according to the post hoc LSD test. Again, the highest values were observed in the 0–30 cm layer, followed by the 60–120 cm layer, and the 120–180 cm layer. The 30–60 cm layer appeared to be a zone of NO$_3$-N transport and leaching rather than a zone of retention across all soil orders. The final category, titled “Other” in Fig. 4, included soils from the Inceptisol and Mollisol soil orders. Soils in this category had high mean NO$_3$-N values in the Sept. 2003 and May 2004 events, but low values in all other sampling events (Fig. 4). Previous studies have shown that agricultural practices increase NO$_3$-N concentrations in shallow groundwater particularly in areas with sandy soils (Dukes and Evans, 2006). The profile average mean values in the Ultisols, Spodosols, and Entisols were also significantly higher in May 2004 prior to the hurricanes than they were in Jan. 2005.

We compared the mean profile average NO$_3$-N values in the forested and non-forested sites stratified by soil order in the two events that occurred before and after Hurricanes Frances and Jeanne.
In the non-forested sites mean NO$_3$-N was significantly lower after the hurricanes for the Ultisol and Entisol soil orders, while the Spodosols did not show much change, and Alfisols showed little change or even a slight increase. In the forested sites, NO$_3$-N was considerably lower in all four of the major soil orders following the hurricanes. We did not have any non-forested sites that were classified as Mollisols or Inceptisols, therefore this comparison could not be made for the final category (Other). In Jan. 2005, mean NO$_3$-N values in the non-forested sites for the four soil orders were almost identical, all having mean NO$_3$-N values around 1 $\mu$g g$^{-1}$. For the Ultisols and Entisols, this represented a drop in average soil NO$_3$-N concentrations by about 2 $\mu$g g$^{-1}$. By comparison, the NO$_3$-N values in the forested sites had mean NO$_3$-N values of essentially zero. This suggests that extreme weather events and land-use control soil NO$_3$-N concentrations in the SFRW to a greater degree than soil order. The majority of the non-forested sites would have experienced some sort of external NO$_3$-N inputs from sources such as fertilization (in the agriculture and improved pasture) or animal wastes (from urination and fecal deposits in the improved pasture and rangeland sites). It has been argued that unlike cows and humans, the other biota in a watershed function largely by recycling nutrients (Freifelder et al., 1998). Thus, non-forested ecosystems dominated by humans, cows, or both, would be expected to show higher N concentrations and export, while forested ecosystems would be expected to have lower N concentrations and export; this pattern existed in the SFRW.

Entisols in this part of Florida are characterized by sandy soil profiles with low organic matter content (Grunwald et al., 2006). Using ArcGIS, we mapped areas of agricultural land-use that were located on Entisols (Fig. 6). Entisols would have the greatest potential for NO$_3$-N export as most of these soils in the SFRW are excessively drained, and water movement through these sandy soil profiles would be much faster than in the more clay-rich Ultisols or the Spodosols with their spodic horizons of illuvial organic material and sesquioxides. By slowing the movement of water through the soil profile, ponding water above the soil surface, or perching water above confining subsurface layers, soil orders with fine-textured soils (i.e. Ultisols, Spodosols) would allow microbes a greater opportunity to denitrify porewater NO$_3$ and prevent it from reaching the Gulf of Mexico through groundwater transport. The shaded sections in Fig. 6 show the areas in the SFRW of agricultural land-use located on Entisols and represent areas that land managers and policy makers could target for the implementation of best management practices to prevent loss of NO$_3$-N to surface and groundwater in the western part of the watershed. Across the SFRW as a whole, land-use is a more important determinant of soil NO$_3$-N concentration than soil order and best management practices should be implemented for row crop agricultural and improved pasture sites regardless of the soil order on which they occur. It has been shown that 90% of the NO$_3$-N inputs to

![Fig. 5. Mean concentrations of nitrate-nitrogen in the different land-use soil order combinations before (May 2004) and after (Jan. 2005) Hurricanes Frances and Jeanne](image_url)
the Mississippi Basin are from nonpoint sources, of which 74% are agricultural in origin (Rabalais et al., 2002). The SFRW appears to mirror this pattern of nonpoint source NO$_3$-N export from agricultural areas. If the majority of NO$_3$-N exports within the SFRW watershed are derived from agricultural areas, and particularly those located on Entisols, this suggests that these are the areas that need to be targeted for BMP development. Identifying these areas and working with landowners may enable us to significantly reduce the amount of NO$_3$-N exported to coastal zones (Fig. 6).

4. Conclusions

In each of six sampling events spanning a period from 2003–2005, soil NO$_3$-N was significantly lower in forested than non-forested land-uses across all four depths and in the profile average data. When hurricanes in Sept. 2004 passed over the SFRW, NO$_3$-N was flushed/denitrified from the soil, resulting in some of the lowest NO$_3$-N concentrations observed in the forested and non-forested sites. However, in sampling events following the hurricanes (2005), NO$_3$-N concentrations in forested and non-forested sites followed different trajectories. Non-forested sites, especially those in agricultural and improved pasture land-uses, showed significantly higher NO$_3$-N concentrations both in the upper 0–30 cm of the profile but also at depths up to 180 cm, indicating that inputs from subsequent fertilization and animals were elevating soil NO$_3$-N in the SFRW. Across the SFRW, land-use is a more important contributor to soil NO$_3$-N concentration than soil order and best management practices should be implemented for agricultural sites regardless of the soil order on which they occur. In particular, certain intensive land-uses (i.e., row crop agriculture and improved pasture) on certain soil types (i.e., Entisols) may result in the export of NO$_3$-N from the soils and eventually into the Gulf of Mexico. This type of information can help land managers and policy makers identify critical source areas and guide the establishment of best management practices or the development of incentive programs to change land-use practices in the identified high-risk areas in the SFRW.

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