SPECIAL PUBLICATION SJ2007-SP10

SOURCES, TRANSPORT AND TRANSFORMATIONS OF NITRATE-N IN THE FLORIDA ENVIRONMENT

Final Report
May 7, 2007

Sources, Transport and Transformations of Nitrate-N in the Florida Environment

by

Matthew J.Cohen, Ph.D.
Sanjay Lamsal, Ph.D.
Larry V. Kohrnak

School of Forest Resources and Conservation
University of Florida
Gainesville, Florida

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Nitrogen (N) enrichment is a problem of global significance; human activities have more than doubled the amount of N cycling through the biosphere over the last 200 years. A global increase in the abundance and availability of N has led to dramatic consequences for aquatic systems, particularly in the near-shore marine environment. N enrichment in Florida parallels the global problem, with loading to wetlands, rivers, springs and the marine environment increasing by an order of magnitude or more in places over the last 50 years. The consequences, both acute and chronic, of this increase in loading have aesthetic, health and economic consequences for the State, and merit the intense scrutiny they currently receive.

While neither loads from the Florida landscape nor ecological vulnerability to N enrichment in our aquatic systems are notably different from other parts of the world, two facets of the Florida environment dramatically affect the processes of N loading: first, the abundance of wetlands that act as effective sinks for N in some parts of the State, and second, the intrinsic vulnerability to N pollution and transport in karstic areas. Both underscore the need for targeted protection of high risk or high benefit lands in our effort to mitigate this problem. Perhaps the principal conclusion of this work is that the management of N pollution in Florida's springs requires solutions that focus on source reduction (e.g., land use change, management practices) rather than sink enhancement. This emerges because springs are located in areas that are vulnerable by virtue of their geologic characteristics, and where sinks typically found in surface basins (e.g., wetlands) are fundamentally absent. Further, a focus on source reduction needs to be targeted in space to those areas most likely to contribute N to the aquifer, which are, coincidentally, the areas of the State where we have made the least progress in land protection.

The source of N in the Floridan aquifer is a source of some controversy. While it is clear that human activities in aggregate have elevated nitrate-N concentrations dramatically over background levels, it is not immediately obvious which sources should be the principal target for meeting load reduction goals. A central conclusion that all sources (wastewater effluents and sprayfields; fertilizers on golf courses, lawns and agricultural fields; poultry farms and other confined animal feeding operations) require scrutiny, and that the relative loading among these sources is highly site specific. In general, however, it appears as though fertilizer applications are the principal source of nitrate-N in most of the major springs examined in this work.

One of the key findings in the groundwater literature over the last decade is that the water emerging from spring vents is from reservoirs with potentially long residence times: specifically, the age of water is typically between 20 and 40 years old, prompting concern that the nitrate-N signal in the springs is the leading edge of development that occurred 30 years before the present. This review of the literature does not dismiss this concern outright, but underscores the caveat that the water emerging in the springs is a mixture of “old” and “new” groundwater. While the resulting mixture may indicate a nominal residence time in the subsurface of decades, the residence of “new” groundwater may be dramatically shorter; travel times of dye tracers put in sinks to spring vents suggest much shorter residence times of at least a fraction of the water. If that “new” water bears most of the nitrates, as might be expected, then the inference about the age of the N from the age of the water is problematic. Regardless of the age of the N delivered, however, this uncertainty underscores the need for improved characterization of temporal and spatial loading dynamics, both for targeting load reduction strategies and for setting realistic timelines for management-induced water quality improvements. Among the tools that should be explored further are the use of ion profiling and isotopic tracers, perhaps as part of monthly water quality sampling, and the wider use of fluorescent dyes to determine links between proposed development sites and regional groundwater conduits. Moreover, the standard sampling protocol of monthly samples for basic water quality may be inadequate for understanding delivery dynamics, and at least local and/or episodic sampling at higher resolution is needed.

This work examined some of the local- and landscape-level methods that have been used to attenuate N loading to aquatic systems. In general, the areas where these techniques will work are where drainage at or near the land surface is taking place. In areas where aquifer water does not come into contact with organic matter prior to discharge in a spring, these sink enhancement measures are unlikely to yield much benefit.

Given a principal conclusion of this review regarding the need to address the N enrichment problem at the source, policies and practices that limit N loading are of paramount importance. Knowledge of subsurface conveyances is a first-order challenge in delineating areas of high vulnerability to N loading and transport, particularly given the strongly non-uniform characteristics of the aquifer matrix. Strategies that depend on land management (e.g., altered fertilization schedules) are less likely to yield strong results than strategies that regulate land use, or provide incentives for land use change. Surface flow data suggest that using lands in highly vulnerable areas (e.g., those delineated by the Florida Geological Survey's Floridan Aquifer Vulnerability Assessment – FAVA) for forestry or low intensity pasture will minimize N pollution risks. Few studies have systematically studied vertical N loading rates from different land uses, so quantitative loading rates in regions where the aquifer is unconfined remain a key uncertainty.

Estimates of N loading from urban areas are particularly important given the growth of that land use in springsheds around the state. Of particular concern has been the use of sprayfields for municipal wastewater disposal. Based on evidence of N attenuation potential in regions where the Floridan aquifer is confined, that sprayfields should increasingly be sited in areas that limit immediate vertical transport to underlying groundwater. Concerns about water-logging that prompt selection of well- to excessively-well drained sprayfields suggest the need for renewed consideration of constructed wetlands technology, where N assimilation and denitrification are well documented.

The problem of N enrichment in Florida's springs is vast – the principal sources are diffuse, arriving from the lands used for dwellings and to produce food/fiber. Links between surface activities and subsurface water quality are profoundly variable; in some areas, where the environment has high natural auto-purification potential, that link is weak. In others, where water at the surface rapidly becomes water in the Floridan aquifer, that link is strong and important. Ironically, it is the areas most at risk for groundwater pollution that have been the focus of much of the State's agricultural and urban development. Reversing this trend in a strategic and judicious way is the principal challenge facing Florida's springs.

INTRODUCTION

Nitrogen Pollution Globally

Human activities, including fertilizer use, fossil fuel combustion, and elevated use of leguminous crops now release more nitrogen (N) into the global environment than natural processes (ecosystem N fixation, lightning fixation) (Vitousek et al. 1997). Anthropogenic influence continues to grow, particularly with the relatively recent expansion in commercial fertilizer use worldwide, which now accounts for 140 Tg of N yr^{-1}, a figure that exceeds the upper estimate of the quantity fixed naturally in terrestrial ecosystems (Vitousek et al. 1997). Most of this nitrogen is delivered to freshwater and marine ecosystems via riverine transport (Howarth et al. 1996); Vitousek et al. (1997) show a strong relationship between N loading and N export in rivers globally (Fig. 1).

The effects of widespread N enrichment on the world's ecosystems are observed from biodiversity and biogeochemical consequences in terrestrial environments (Tilman 1987, Aber 1992), to profound and often non-linear effects on freshwater and marine ecosystems (Howarth et al. 1996, Rabalais 2002). Indeed, nitrogen enrichment can stimulate ecosystem production (e.g., increasing fish yields) but can also trigger catastrophic shifts in the feeding ecology of an aquatic system, leading to dystrophy and significant loss of upper trophic level production and

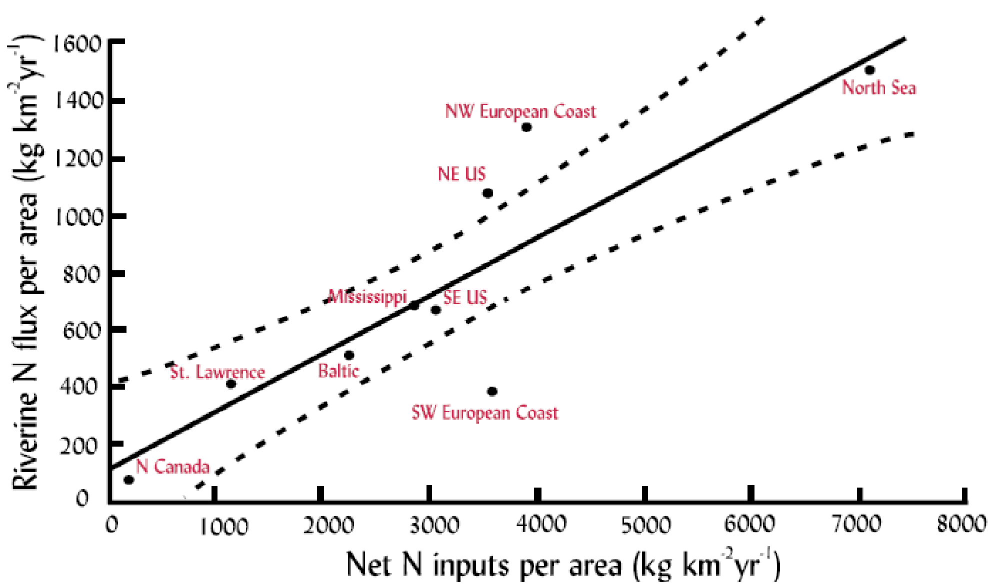


Fig. 1 – Relationship between N inputs (kg m^{-2} yr^{-1}) and riverine delivery of N. Loads in rivers have increased as much as 20 fold since the mid-1800's. Note the SE-USA, where nitrate pollution in rivers is a locally significant concern, is typical of global responses to anthropogenic loading. (From Vitousek et al. 1997a).

diversity (Cloern 2001). The global emergence of eutrophication as the primary water quality challenge is frequently linked to enrichment of N, leading to increased fixation of C and a cascade of effects on dissolved oxygen, water clarity, ecosystem energetics, diversity and productivity. Among the most charismatic examples of N enrichment include the emergence of harmful algal blooms (HABs – red tide, brown tide, cyanobacterial blooms) both in freshwater and marine systems (Anderson et al. 2002), and the hypoxic zone in the Gulf of Mexico - which has been linked to both excess N loading and the loss, at the landscape scale of wetlands and other natural N sinks (Rabalais et al. 1996).

In freshwater systems, where phosphorus (P) is typically considered the limiting nutrient for ecosystem production, there is growing evidence of both the primary and interactive effects of N on biological productivity (Smith et al. 1999). Consequently, management of both N and P from anthropogenic sources are critical priorities for managers, regulators and scientists in all corners of the globe. Aggressive management schemes that limit the quantity or improve the timing and uptake of fertilizer applications, enhance or restore the landscape assimilative capacity, reduce the load from fossil fuel combustion, and decouple human wastes from waterways are needed globally. Evidence has shown that these efforts can work, but that the probability of success in managing the problem is maximized by understanding the stores, fluxes and transformations intrinsic to the system being managed. The objective of this report is to synthesize the literature on nitrogen loads, transport and sinks in Florida, with an emphasis on understanding how the nitrate form of nitrogen arrives at spring systems at the elevated levels that are now commonplace throughout the state.

Nitrogen in Florida

Ninety-three percent of Florida's population relies on groundwater for drinking water (Fernald and Purdum 1998). In 1995, 60 percent of fresh water used in Florida was groundwater (Berndt et al. 1998). Clearly, protecting the groundwater resource under conditions of increasing demand and pollutant loading is one of Florida's first-order natural resource challenges.

There is ample evidence that the groundwater resource in Florida is declining in quality. For example, over two decades, water quality monitoring of the major rivers in the Suwannee River Basin has indicated a statistically significant increasing trend in the concentrations of nitrate-N (NO_3-N) (Ham and Hatzell 1996), which is primarily attributed to groundwater discharges in the Middle and Lower Suwannee reaches (Pittman 1997). Similar trends have been observed for the Ocklawaha River, particularly where that system interacts most closely with groundwater (Mytyk and Delfino 2004). Fig 2 shows the total NO_3-N delivered by the Suwannee River to the Gulf of Mexico, which has increased from ~3000 tons in water year 2001 to over 7000 tons in water year 2005, along with the approximate spatial distribution of load by river reach. Notably, those river segments where surface and groundwater mix are responsible for the bulk of the load, with less than 25% of the basin responsible for 65% of the load.

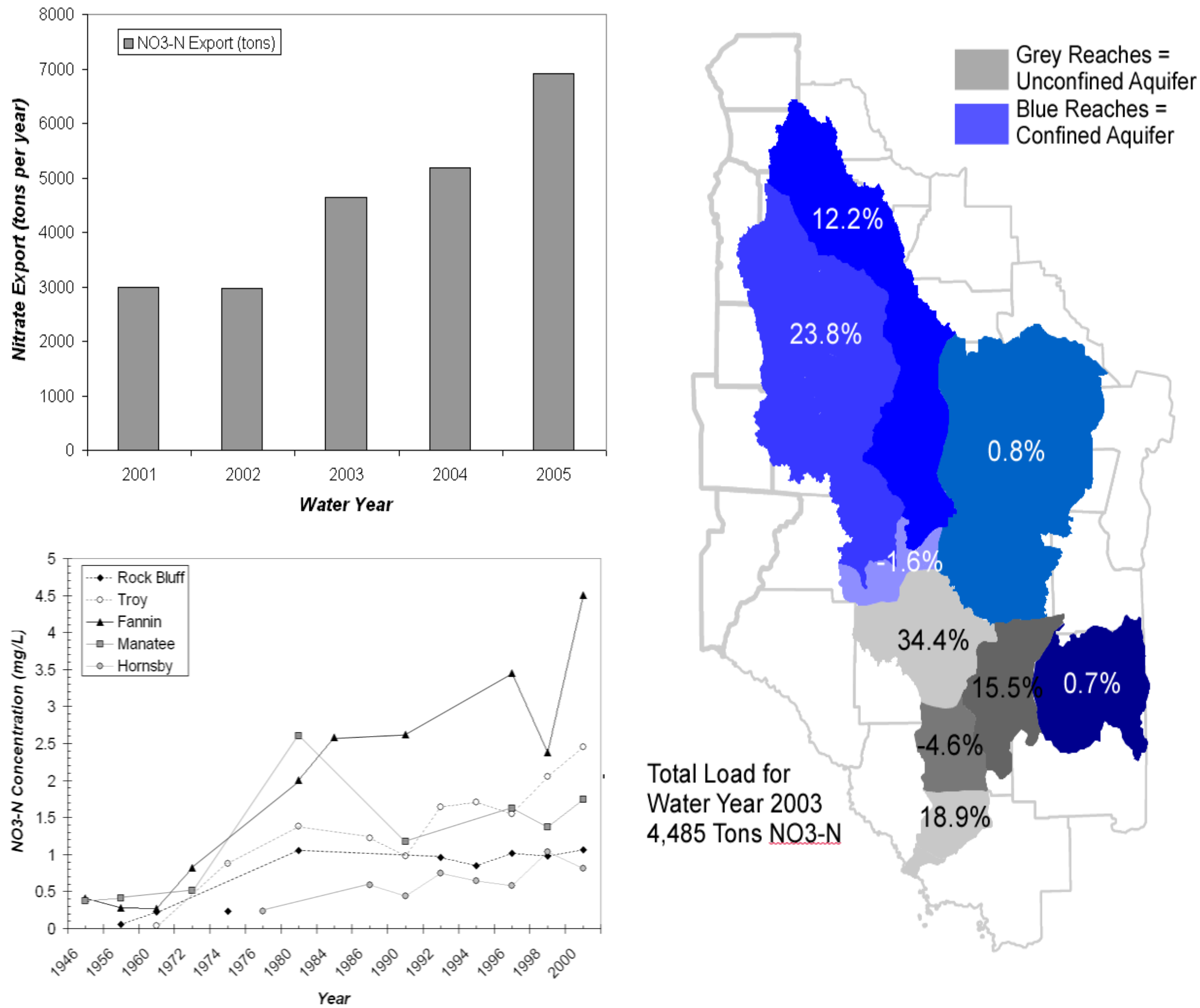


Fig 2. Nitrate loading to the Gulf of Mexico from the Suwannee River. Shown are a) recent changes in total loads between 2001 and 2005 (primarily driven by changes in water flows), b) long-time series changes in nitrate concentrations at 5 1st magnitude springs along the Suwannee River, and c) spatial estimates of nitrate loading by sub-basin. Basins where surface and groundwater mixing is limited by a regional aquitard are shown in blue; sub-basins where that aquitard is absent represent less than 25% of the total area, but contribute nearly 65% of the total load. (Data Sources: Hornsby et al. 2002, 2003, 2004, 2005; Mirti and Mantini 2006).

Nitrate-N concentrations of several springs, which are direct groundwater discharges from the upper Floridan Aquifer System (FAS), have increased substantially from near background concentrations (≤0.1 mg/L; Katz et al. 1992; Maddox et al. 1992) to more than 5 mg/L during the past 40-50 years (Katz et al. 1999) (Fig 2B); despite intermittent sampling, the signal of dramatic enrichment is unmistakable. Hornsby and Mattson (1997) highlight that the primary source of the NO_3-N is ground water entering the surface water system via springs.

Elevated NO_3-N concentrations have been widely reported in aquatic systems of the St. Johns River Water Management District (SJRWMD), and there is evidence that nitrate loads from the human-influenced landscape are growing. For example, Mytyk and Delfino (2004) summarize observations in the Ocklawaha River, a major tributary of the St. Johns, and observed significant increasing trends at 5 of 14 stations along the river, primarily at or below Silver Springs (Fig 3). Despite strong evidence for landscape N sinks (Rodman Reservoir), the data suggest a small but significant upward trend in nitrate loads to the Lower St. Johns River.

Background nitrate-N concentrations in groundwater of the SJRWMD are generally below 0.2 mg/l (Mytyk and Delfino 2002, report a median NO_3-N concentration of 0.07 mg/L for

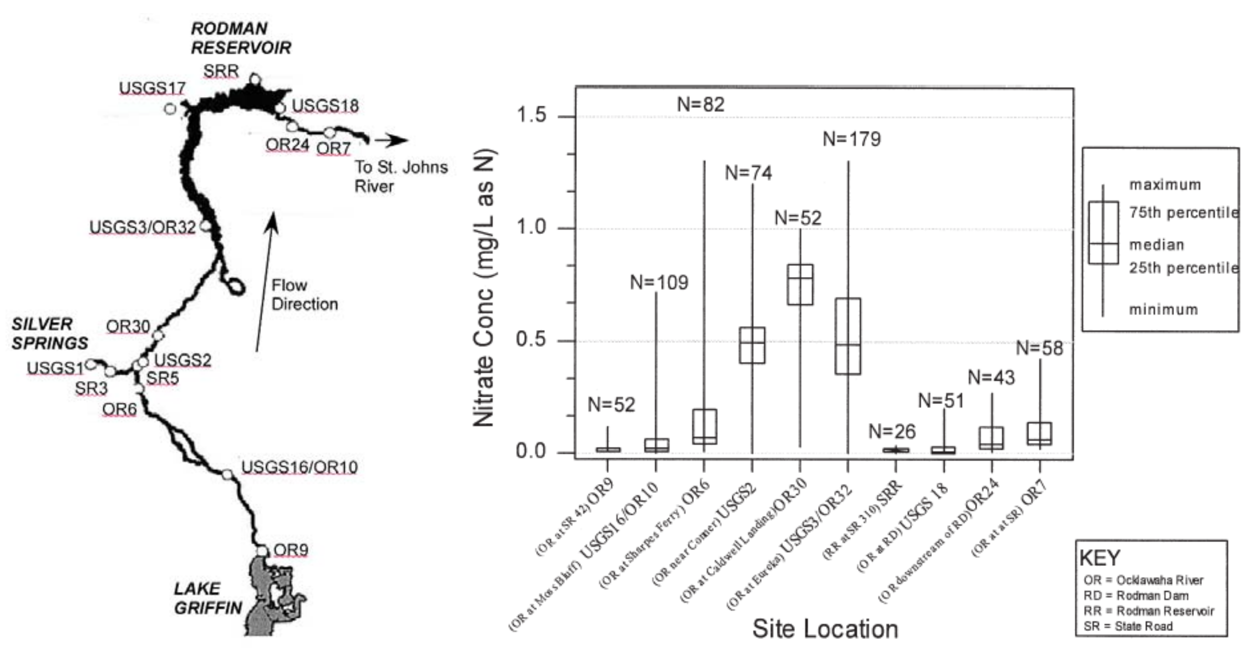


Fig. 3 – Nitrate concentrations in the Ocklawaha River system observed between 1966 and 2001. Shown are A) a map of the river and measurement locations and B) statistical summary of the observations. Significant increasing trends with time were observed for USGS1 (r^2=0.61), USGS2 (r^2=0.52), USGS3/OR32 (r^2=0.18), SR5 (r^2=0.25)and OR7 (r^2=0.08).

the Ocklawaha River); concentrations in excess of this value imply an anthropogenic source of N (Toth 1999). Elevated concentrations are most pronounced in areas where groundwater sources discharge to surface conveyances (springs and spring runs) for reasons to be discussed at length later. For example, among 17 springs sampled throughout the SJRWMD during 1995-96, total NO_3-N concentrations were found above the "elevated threshold" of 0.2 mg/l in Wekiva Springs (1.92 mg/l), Ponce de Leon Springs (0.948 mg/l), Rock Springs (1.62 mg/l), Seminole Springs (1.41 mg/l), Sanlando Springs (0.782 mg/l) , Palm Springs (0.703 mg/l), Starbuck Spring (0.447 mg/l), Blue Spring (0.617 mg/l), and Gemini Springs (0.633 mg/l). Interestingly, among the wells sampled from the Upper and Lower Floridan aquifer in the vicinity of the Wekiva River, only one well had elevated NO_3-N levels (0.672 mg/l) (Toth 1999). In another intensive study of water quality at 55 groundwater locations of the Wekiva springs in 1999, 22 samples had concentrations above the elevated concentration of 0.2 mg/l with the highest concentration of 7.5 mg/l (Toth and Fortich 2002), clearly indicating the dynamic nature of the groundwater resource in both time and space. Although the observed nitrate concentrations are below the USEPA drinking water standard (10 mg/L), the elevated concentrations are expected to have substantial ecological consequences (see below). These results imply anthropogenically elevated NO_3-N concentrations, which necessitate multiple management foci to effectively address the problem in the face of growing development pressure and dramatic local and global increases in N delivery.

NITROGEN EFFECTS ON THE ENVIRONMENT, HUMAN HEALTH, AND AQUATIC ORGANISMS

The most familiar reason cited for concern about high levels of NO_3-N in groundwater is the significant health risks associated with human consumption of water containing excess nitrates (Follet and Follet 2001),which is a known cause of methemoglobinemia. Methemoglobinemia occurs when NO_3 (nitrate) is reduced to NO_2 (nitrite) by bacteria found in the digestive tract of humans and animals (Pierzynski et al. 1994); this NO_2 can oxidize ferrous iron (Fe^{2+}) in hemoglobin to ferric iron (Fe^{3+}), forming methemoglobin, which is unable to provide oxygen transport functions provided by hemoglobin. The resulting bluish discoloration to skin and blood is most prevalent in infants (3-6 months of age) and is consequently referred to as "blue baby syndrome"; the effect can be fatal if sufficient oxygen deprivation ensues. The U.S. Environmental Protection Agency (USPEA) has established a maximum concentration of 10 mg/L NO_3-N in drinking water. Animals are also susceptible to methemoglobinemia, although the health advisory level for most livestock is much higher (~ 40 mg/L NO_3-N).

Ecological effects of NO_3-N enrichment are observed at concentrations appreciably lower than 10 mg/L. Even modest increases in NO_3 levels in aquatic system can contribute to eutrophication, particularly in near-shore marine ecosystems that are typically limited by the availability of mineral nitrogen. Eutrophication is defined as an increase in the nutrient status of natural waters that causes accelerated growth of algae or water plants, increased turbidity, depletion of dissolved oxygen, and frequently substantial changes in aquatic trophic web energy flow (Pierzynski et al. 1994); it occurs primarily in response to nitrogen (N) and phosphorus (P) additions. In many freshwater ecosystems, P is the limiting factor, which can attenuate the ecosystem-scale changes that arise due to N additions, but in many aquatic systems in Florida, the proliferation of N-fixing organisms, naturally elevated levels of P and/or addition of anthropogenic P make many river and lake systems sensitive to both nutrients. Further, most estuarine and marine systems have adequate P and respond strongly to N enrichment.

Even where ecosystem effects are not expected (for example, due to P limitation), N enrichment may cause organism-level effects, including reproductive stress, behavioral changes and increased susceptibility to disease (Edwards et al. 2004). A recent review of the literature on nitrate toxicity (Mattson et al. 2006) is now available; key findings of that report and summarized here, including their final assessment of ecologically safe concentrations.

Nitrates and nitrites can be toxic to aquatic organisms in several ways, including reproductive effects, embryonic development effects, and endocrine disruption, in addition to affecting the transport of oxygen in blood. As with all toxicity measures, thresholds for chronic and acute toxicity vary between organisms, but, in general, toxicity levels were observed well below levels set by USEPA to protect human health (10 mg/l – this and all subsequent concentrations are for NO_3-N). For example, the larvae of one species of caddisfly were sensitive to nitrate concentrations in excess of 1.4 mg/l, while others were sensitive at 2.4 mg/l. Fish toxicity also varies widely, but nitrate levels near 4 mg/l affected mosquitofish reproduction; nitrite levels above 2 mg/l are generally toxic to fishes. Tadpoles of several anuran taxa are sensitive to nitrate concentrations as low as 2.5 mg/l and nitrite concentrations near 1.0 mg/l. While bird and mammalian tolerance of high nitrate levels is well documented (no harm reported below 44 mg/l associated with consumption), some preliminary evidence of nitrate effects on the endocrine system of alligators and other reptiles has been shown at very low concentrations (< 0.1 mg/l) (Guillette and Edwards 2005).

Notably, the focal area for the Mattson et al. (2006) review was the Wekiva River, in which NO_x (NO_3^- + NO_2^-) concentrations approach and frequently exceeds levels ascertained from the literature to have organismal effects. The study concludes that, given uncertainty factors, a safe concentration level for nitrates is between 0.125 and 0.140 mg/l. Meeting these levels will require an order of magnitude reduction in loading (assuming constant flow) from current concentrations (mean from 1990 and 2006 = 1.39 mg NO_x-N/l).

NITROGEN BIOGEOCHEMISTRY

Overview of N Biogeochemistry

Nitrogen exists in multiple forms and is transformed via numerous pathways in the environment. Several attributes make the biogeochemical cycle for N unique among the major nutrients, including the presence of a large unreactive atmospheric pool (5 orders of magnitude greater N storage than other pools combined), the absence of a mineralogical pool (especially in Florida), the numerous valence states that N can assume under different reduction-oxidation conditions, and the myriad organic forms (primarily amino acids) in which N can reside. The nitrogen cycle is also unique in the degree to which human activities have altered the global availability and dynamics (Table 1). Natural sources of N are abiotic (lightning ~ 3 x 10^{12} g N/yr) and biotic (N fixation ~ 44 x 10^{12} g N/yr) (Schlesinger 1997); human activities yield N to the environment at rates that exceed these background levels (~80 x 10^{12} g N/yr from fertilizer use on agricultural fields; >20 x 10^{12} g N/yr from fossil fuel combustion). In all, it is estimated that human-derived sources contribute between 60% and 80% of the global N deposited on land annually, and it is estimated that nearly 50% of the N transported in the world's rivers (~ 36 x 10^{12} g N/yr) is of anthropogenic origin (Galloway et al. 1995).

Among the major implications of N enrichment for Florida is the extent to which groundwater has been a sink for increasingly available N; it is estimated that groundwater may receive up to 11 x 10^{12} g/yr of anthropogenically introduced N. In many areas of the world, this represents a long-term sink, but in the productive karst aquifers of Florida's peninsula, this

Table 1. Summary of global N cycle, showing the influence of human activities on total loading (after Vitousek et al. 1997).

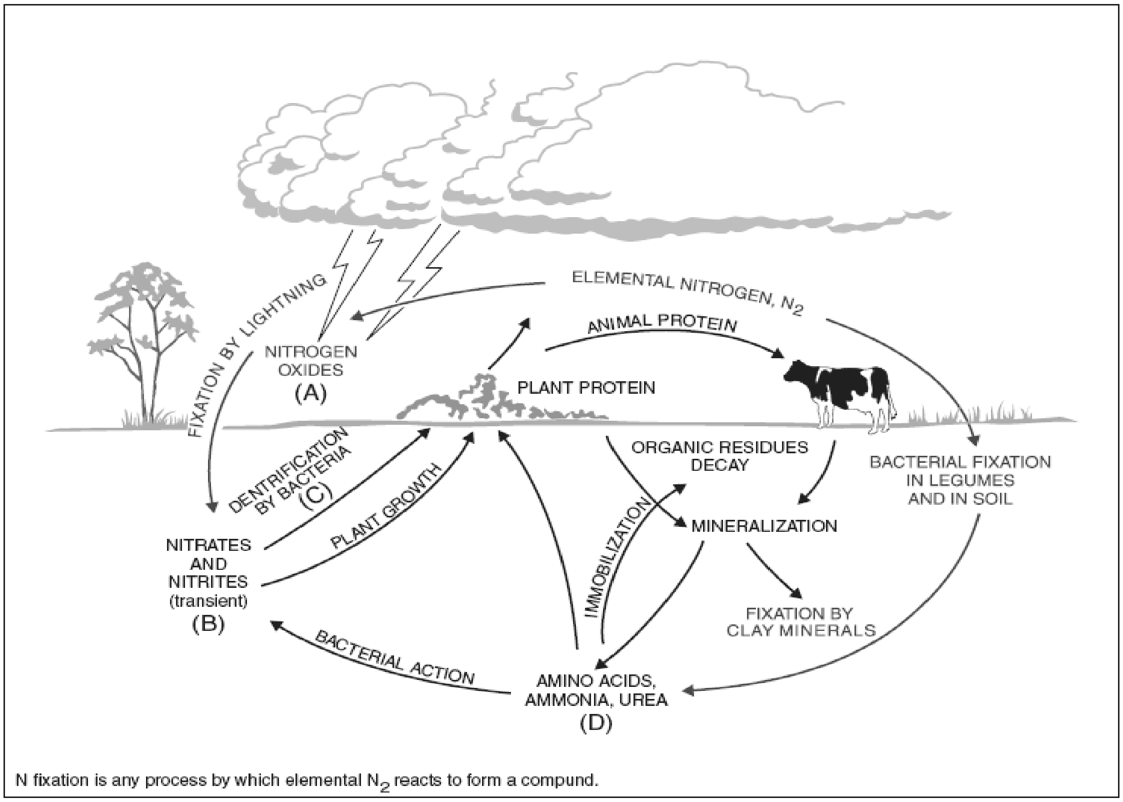
Time	Source	Quantity (million MT/yr)
Pre-1900	Bacterial Fixation	90-140
	Lightning	<10
	Total	100-150
Post-1900	Bacterial Fixation	90-140
	Lightning	<10
	Cultivation of N-Fixing Crops	40
	Fertilizer	80
	Fossil Fuel Combustion	>20
	Land Clearing/Burning	70
	Total	310-360

nitrogen may reemerge rapidly in surface waters. For reasons to be elucidated later, related to the availability of electron donors to drive denitrification, nitrates in groundwater are effectively unreactive (no biological or chemical attenuation) meaning that once nitrate enters the groundwater, it will emerge somewhere. In Florida, this location is primarily springs.

The remainder of the nitrogen contributed to ecological systems is returned to the atmosphere via microbially-mediated denitrification pathways (described below – Fig. 4). Globally, denitrification is estimated to yield up to 230 x 10^{12} g N/yr to the atmosphere. At least half of this denitrification occurs in wetlands (Bowden 1986).

Among the more important terrestrial and aquatic transformations (Fig. 4) in the N cycle are 1) transformation between organic and inorganic forms (mineralization and immobilization), 2) transformation between reduced and oxidized inorganic forms of N (nitrification), 3) gaseous loss of N (ammonia volatilization, denitrification), 4) biological N fixation, and 5) losses associated with water movement (leaching and erosion). Each pathway is discussed in greater detail below. Fig. 5 (after Schlesinger 1997) presents a simplified version of Fig. 4, depicting only the major components of the N cycle and the primary exogenous flows.

Fixation of nitrogen is an energetically expensive process that requires either strong electrical gradients (as made possible in lightning and in the Haber-Bosch process via which humans fix nearly all the mineral N used in fertilizer) or substantial biological energy. While it is frequently noted that only certain plants are capable of fixing N from the atmosphere, in fact it is certain prokaryotes, such as microbial symbionts (e.g., genus *Rhizobium*), free-living bacteria (e.g., genera *Clostridium* and *Azotobacter*), and blue-green algae (e.g., genera *Anabaena* and



EXPLANATION

(A) $N_2 + O_2 \rightarrow 2NO$
$2NO + O_2 \rightarrow 2NO_2$

(B) $2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{energy}$

(C) $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

(D) $2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2\ H_2O + 4H^+ + \text{energy}$

Fig. 4 – Schematic of nitrogen biogeochemical cycling between various pools (Bowden 1986)

Microcystis) that make this process possible. The reason that so few organisms can perform this process is that conditions under which it can occur are highly reducing, a setting created symbiotically in root nodules of N-fixing plants and in the cells of blue-green algae. Diazotrophs (microbes that fix N) use the enzyme nitrogenase, which is strongly sensitive to oxygen and 8 moles of ATP per mole of ammonia fixed to overcome the strong triple-bonds that make atmospheric N biologically unavailable. The ammonia resulting from fixation is rapidly incorporated into certain amino acids, such as glutamine or alanine, which can be transferred to other N-containing compounds by a variety of commonly occurring amino transfer reactions.

Over 90% of nitrogen in the biosphere is present in organic form, and over 1200 x 10^{12} g N/yr are cycled through terrestrial and freshwater ecosystems. N bound in these organic compounds is largely unavailable to plants (Vinten and Smith 1993); microbial mineralization processes liberate ammonium ions (NH_4^+) from organic sources under both aerobic and anaerobic conditions, making N available for plant incorporation.

Microbial decomposition of organic compounds in soils results in the release of simple amino acid compounds ($R\text{-}NH_2$) from more complex proteins. Further decomposition hydrolyzes these amine groups, releasing N as ammonium ions (or ammonia, depending on the pH at which the decomposition takes place), which is partially available for plant uptake. The oxidation of ammonium to nitrite (NO_2^-) then nitrate (NO_3^-) liberates energy; the resulting inorganic nitrogen species are readily available for plant uptake. The entire conversion process from organically bound N to inorganic mineral/ionic forms (NH_4^+ and NO_3^-) is termed mineralization. Environmental conditions conducive to mineralization are: near neutral pH, sufficient soil moisture, and good aeration, and warm temperature (25-35^{o}C).

Immobilization, the reverse process to mineralization, is the direct conversion of inorganic N ions (NO_3^- and NH_4^+) into organic forms via microbial processing (i.e., instead of via plant uptake). Microorganisms decomposing organic residues often require more N than is

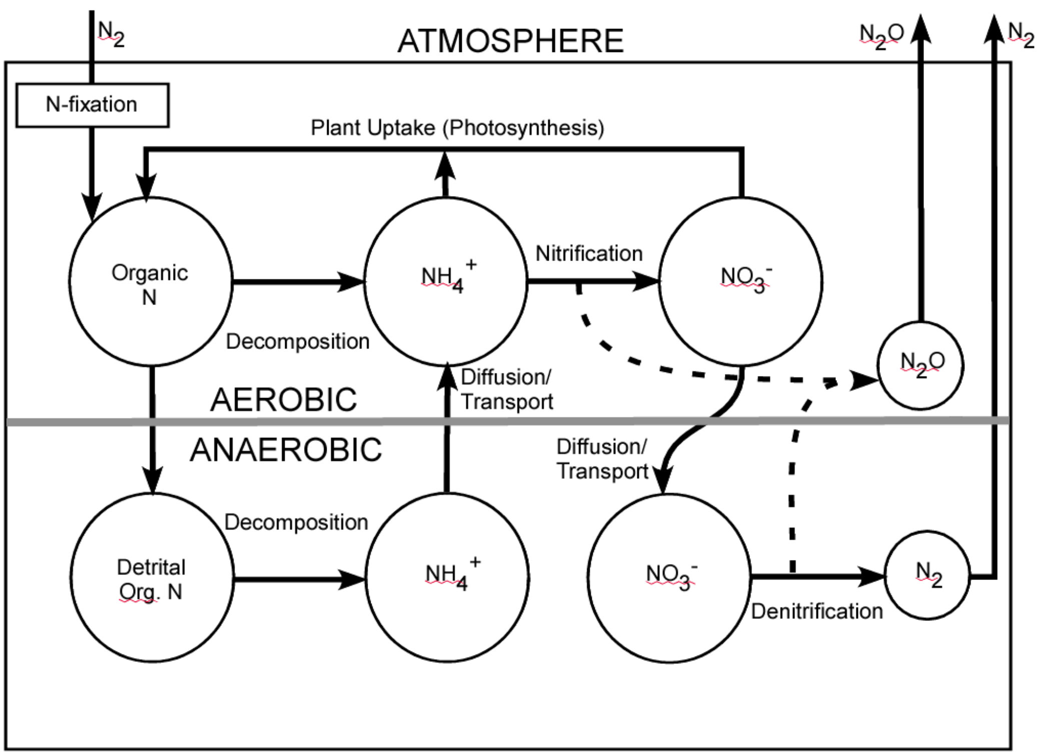


Fig. 5 – Simplified schematic of N cycling, with emphasis on the influence of redox potential on inorganic nitrogen transformations (Schlesinger 1997)..

contained in those residues as they incorporate mineral N into their cells (e.g., as proteins). One indicator of the degree to which microbial N incorporation will result in immobilization is the C:N ratio. Organic residues with a high C:N ratio cannot provide enough N, so the microbial community scavenges inorganic N from the environment, immobilizing that pool from subsequent plant uptake. The C:N ratio in organic matter typically falls between 8:1 to 15:1 (median ~ 12:1), and the C:N ratio for microbes is between 5:1 and 10:1. On average, therefore, microbes incorporate about 8 moles of C for every 1 mole N. However, since only one third of the C metabolized by microbes is incorporated into their cells, microbes ultimately use 24 moles C for every mole N assimilated into their bodies. Consequently, if an organic substrate has a C:N ratio exceeding 24:1, microbial decomposition processes will scavenge the environment for additional N, leading to immobilization. For purposes of illustration, soil humus typically has a C:N ratio of 10:1; ecosystem litter layers have a C:N ratio between 80:1 and 200:1, and wood has a C:N ratio of approximately 400:1 (Cockx and Simoone 2003). This is relevant to N transport and transformation in the environment because it underscores the relationship between ecological C fixation and storage and the relative vulnerability of an area to mineral N enrichment and transport. The opposing processes of mineralization and immobilization occur simultaneously in soils, and the direction of transformations are affected by the C:N ratio (Hallberg and Keeney 1993; Brady and Weil 1999). Organic N may be mineralized to ammonium, but some of this ammonium may be rapidly recycled back to the organic pool through microbial biomass. Mineralization of organic C to CO_2 (e.g., via long term effects of tillage) can result over time in reduced C availability for heterotrophic bacterial growth and an associated increase in mineral N (as NH_4) (Hallberg and Keeney 1993).

At high pH (> 9.3 pH), NH_4^+ ions will be converted to ammonia gas (NH_3) which may volatalize to the atmosphere. Highly alkaline conditions are rare in most of Florida's aquatic systems, which are typically acid to circumneutral, but may exist in lakes and wetlands during peak photosynthesis, where CO_2 removal by algae force the carbonate buffering system towards bicarbonate raising the pH to levels approaching those favoring ammonium dissociation.

The process of nitrification refers to the conversion of NH_4^+ to NO_2^- and then to NO_3^- by bacteria (species of the genera *Nitrosomonas* and *Nitrobacter* are primarily responsible for these steps). During nitrification, protons are produced leading to significant increase in acidity.

Provided that conditions are favorable (i.e., aerobic), nitrification is such a rapid process that NO_3-N is generally the predominant mineral form of N in most soils.

Nitrogen evolution to the atmosphere occurs when biochemical reduction reactions convert NO_3 ions to gaseous forms of N (primarily N_2O and N_2), via the process called denitrification. This process is carried out by both heterotrophic bacteria (species in the genera *Pseudomonas*, *Bacillus*, *Micrococcus* and *Achromobacter*), and autotrophic bacteria (*Thiobacillus denitrificans* is an example); numerous species, mostly facultative anaerobes, have the ability to produce nitrate reductase, the enzyme responsible for catalyzing the process, and use nitrate as the terminal electron acceptor. Denitrification in agricultural soils can be significant, particularly in areas with high inputs of N fertilizers (Velthof et al. 1997). Because denitrification must occur where there is insufficient oxygen to provide a terminal electron acceptor for all metabolism, soils must possess anoxic microsites (local zones with O_2 concentrations < 0.3% in pore-spaces – Greenwood 1962) in order to support denitrification; this condition is much more likely to exist in clay-dominated soils that maintain high moisture content. If the soil is near saturation, oxygen in the pore water needs to be below 1 ppm to make nitrate utilization as a terminal electron acceptor thermodynamically favorable (Snoeyink and Jenkins 1980). This is of particular relevance for Florida because the two conditions necessary for denitrification – anoxia and electron donor availability – vary widely in space, from wetlands that are ideal locations for denitrification, to the sandy soils (inceptisols and entisols) overlying the unconfined Floridan aquifer, where denitrification is practically absent.

Van Breeman et al. (2002) constructed a nitrogen budget for 16 watersheds in northeastern USA, and estimated that denitrification is the sink for a significant fraction (average 49%) of N inputs to the agricultural ecosystem. In most systems, denitrification is the primary sink for reducing NO_3-N concentrations in groundwater (Korom 1992). The process requires an anoxic environment (Eh = +350 to + 100 mV) to make NO_3^- ions a thermodynamically favorable electron acceptor for microbial metabolism, and a source of organic matter (electron donor in metabolism). As a result, landscape hotspots for denitrification tend to be areas characterized by high and persistent water contents (e.g. riparian zones, wetlands, heavily irrigated regions, animal-manure holding facilities - Galloway et al 2004). In Florida, presence of wetlands both in headwater areas and along flow conveyances suggests that denitrification potential of the landscape is high. The loss of wetland coverage, and changes in wetland hydrology that limit

Table 2. Nitrogen removal mechanisms in floodplain and wetland riparian forests in the southern United States (after Walbridge and Lockaby 1994)

Mechanism	Reference	Location	Rate (kg N / ha / yr)
Deposition	1	Maryland	11.0
Denitrification (potential)	2	Louisiana	350.1
	3	Little River, Georgia	31.5
	4	Coastal Plain, Georgia	224.0
Denitrification (mass balance observations)	5	Tar River, NC	130.0
	1	Maryland	47.7
	6	Coastal Plain, Georgia	1.5
NH_4+ adsorption	5	Tar River, NC	64.2
	1	Maryland	0.8
Microbial Immobilization	5	Tar River, NC	16.2
	7	Coastal Plain, Georgia	87.0
Plant Uptake	5	Tar River, NC	15.5
	3	Little River, Georgia	51.8
	1	Maryland	15.0

1 – Peterjohn and Cornell (1984)
2 – Engler and Patrick (1974)
3 – Lowrance et al. (1984)
4 – Abrams and Lowrance (1991)
5 – Brinson et al. (1984)
6 – Jacobs and Gilliam (1985)
7 – Qualls (1984)

periods of low redox conditions both contribute to reduced landscape assimilation capacity. Wetlands also provide sites for biological uptake and long-term sequestration of organic N, sediment-bound or organic particulate N deposition, ammonium adsorption to clay or organic electrostatic binding sites and microbial immobilization (Table 2). While there are few studies of comparative rates of these mechanisms in Florida, Table 2 suggests that wetlands are critical to landscape attenuation of N enrichment. Table 2 also illustrates significant uncertainty and/or site-specific circumstances that influence the degree to which a given mechanism drives N removal. This process-level uncertainty translates in management uncertainty, particularly for designation of riparian buffer widths and wetland water level regulations (MFLs). A note about Table 2 is that removal rates for biological uptake, cation sorption and microbial immobilization are not persistent. Ecosystems eventually reach homeostasis with respect to N metabolism, and uptake and immobilization will be balanced by biomass senescence and microbial degradation, both of which will result in release of mineral N. Similarly, cation exchange of ammonium can saturate, and will not provide a long term sink for N; denitrification, export in organic form and ammonia volatilization are the only persistent mechanisms for mineral N removal.

Measurement of Nitrogen in the Environment

Measuring nitrogen in environmental samples is critically important to the inference of loads, the evaluation of management and the assessment of ecological risk. As with all laboratory methods, standard protocols exist as a well as a suite of alternatives that address shortcomings of the standard method. Measurement technique is important in several ways. First, methods have differential accuracy and precision based on the sensitivity and repeatability of the chemical reactions used to indicate concentration. Many of the methods (for nitrate+nitrite, total Kjeldahl N, ammonium) are colorimetric, meaning that reagents are added to water samples to generate a color, the intensity of which is correlated with the concentration in solution. Second, as instruments and reagents have been refined over the last 50 years, measurement sensitivity has improved; this observation is of particular importance when evaluating historical time series (e.g., Mytyk and Delfino 2004).

Standard methods for N measurement are briefly described, including operational range and sensitivity; for the measurement of nitrates, some shortcomings and alternatives are discussed.

Measurement of Nitrates: The central reaction in the colorimetric determination of nitrate+nitrite (NO_x) concentrations is between nitrite (NO_2^-) and sulphanilamide under low pH conditions. The resulting diazo-compound couples with N-1-naphthyleythelene diamine dihydrochloride to yield a reddish azo dye, the concentration of which can be measured photometrically at 520 nm. A critical pretreatment to the sample is reduction of nitrate to nitrite by a copper-cadmium column; the nitrate concentration alone can be inferred from the difference between colorimetric response for a reduced and unreduced sample. Various autoanalyzers (e.g., Bran + Luebbe) are available that automate the reagent injection and measurement of colorimetric response. The range of observations is 0.05 to 10 mg NO_3-N L^{-1}, extensible with dilution, with a bias accuracy of ± 5%.

Measurement of Total Kjeldahl Nitrogen: TKN is the sum of dissolved organic nitrogen and ammonium in a filtered solution. The underlying principle is that in a sulfuric acid environment, the addition of potassium sulfate (K_2SO_4) and cupric sulfate catalyst ($CuSO_4$) will convert N in amino acids to ammonium; it will also convert any free ammonia to ammonium. In a basic environment, ammonia is distilled from solution and absorbed in a boric or sulfuric acid medium. The reaction of ammonia, hypochlorite and phenol in the presence of sodium nitroprusside catalyst yields an intense blue compound (indophenol), the concentration of which can be determined colorimetrically by absorbance at 640 nm. The detection limit is approximately 0.1 mg/l, with a bias accuracy of less than 5%. Note that the dissolved organic nitrogen (DON) component of a water sample can be determined by running the ammonium protocol before and after the TKN digestion.

Total Nitrogen: A measure of total nitrogen dissolved in a water sample can be obtained in a TN analyzer (e.g., Antek9000N, Carlo Erba CNS analyzer), wherein the sample is vaporized and combined with oxygen at high temperature (850 or 1050 °C). One of the combustion products in NO (nitrous oxide) is converted to more stable NO_2 that is chemoluminescent in proportion to the total quantity of N in the sample.

Drawbacks and Alternatives for Nitrate Measurement: The primary drawback of the standard method for nitrate measurement emerges when high temporal resolution monitoring of the environment is required. Because of the intrinsic dynamics of nitrates arising from its solubility and biological sensitivity, monthly or quarterly sampling, which is typical of most regulatory monitoring, may be inadequate to understand when and why nitrates are loaded to aquatic systems. More frequent grab samples are possible, but typically constrained by the logistical complications and personnel requirements of landscape level, high temporal resolution (e.g. daily) sampling designs. Recent instrument developments show some promise for in situ monitoring at high resolution that will obviate this limitation, and permit much greater insight into the environmental dynamics of nitrates. The new solutions have emerged along two trajectories: miniaturization and field-ruggedization of the autoanalyzer technology currently used to implement the cadmium-reduction technique in the laboratory, and optical methods. The former (typified by the YSI9600 that permits hourly sampling in various aquatic environments; http://www.ysi.com) has been demonstrated for spring systems in Florida, along with numerous other locations. The other technology relies on the optical response of NO_3^- at 210 nm (in the UV region of the spectrum); covariance with dissolved organic carbon makes spectral inference more complex, but a company (Satlantic – www.satlantic.com) has demonstrated high accuracy in a variety of marine, estuarine and freshwater environments. These emerging technologies offer an excellent opportunity to address unanswered questions about the temporal dynamics of nitrates in aquatic systems, and improve both management and attenuation of N enrichment.

SOURCES OF NITROGEN IN THE ENVIRONMENT

Overview of Environmental N Loading

As discussed above, humans have substantially altered the global nitrogen cycle, by as much as 80% of total biogeochemical cycling in some estimates (Schlesinger 1997, Vitousek et al. 1997). At the landscape scale, the delivery of nitrogen comes from atmospheric wet deposition (in mineral form – see Fig. 6), biological fixation (primarily by plant species in the *Fabacae* family, and particularly cultivated legumes) and anthropogenic applications in the form of fertilizers, imported manures and wastewater effluent. Typical fertilizer application rates are summarized in Table 3 as a means of comparison with atmospheric sources (Fig. 6) and observed wetland removal rates (Table 2). Because N is frequently the limiting factor for production in Florida's sandy soils, N applications at relatively high rates are important for maintaining yields. BMPs for reducing N loading in the environment include the use of slow release fertilizers, precision farming achieved through the use of soil testing, altered irrigation schedules to reduce leaching potential, use of organic fertilizers and micronutrient management (Cockx and Simonne 2003). Note that Table 3 is not a useful reference for estimating actual application rates for particular land uses; for example, for plantation forests, the industry standard application rate

Table 3. Recommended fertilizer application rates for Florida (UF-IFAS EDIS publications)

Crop/Land Cover	N Application Rates (kg N / ha / yr)	Source	Notes
Residential Lawns	80 - 240	Trenholm et al. 2002	
Landscape Plants	80 - 160		
Athletic fields	200 - 280	Miller and Cisar 2005	for bermudagrass fields
Dairy cow pastures	240 - 360	Sollenberger 2006	est. from recommended monthly application rates
Hay production	140 - 300	Staples et al. 2003	
Corn Silage	50 - 300	Staples et al. 2003	
Sorghum silage	60 - 300	Staples et al. 2003	
Vegetable production	180 - 200	Cockx & Simonne 2003, Hochmuth & Cordasco 2003	
Corn	150/210	Mylavarapu et al. 2002	Irrigated/non-irrigated
Sugarcane	90	Mylavarapu et al. 2002	
Wheat	80	Mylavarapu et al. 2002	
Legumes (soy, peanut, alfalfa)	0	Mylavarapu et al. 2002	
Deciduous fruit trees	140-200/200-400	Crocker and Rose 1999	mature fruit trees/mature nut trees, respectively
Citrus	140 - 200	Morgan and Hanlon 2006	
Plantation Forests (young)	45 - 55	Jokela and Long 1999	in the first year
Plantation Forests (established)	160 - 220	Jokela and Long 1999	Applied every 6-8 years

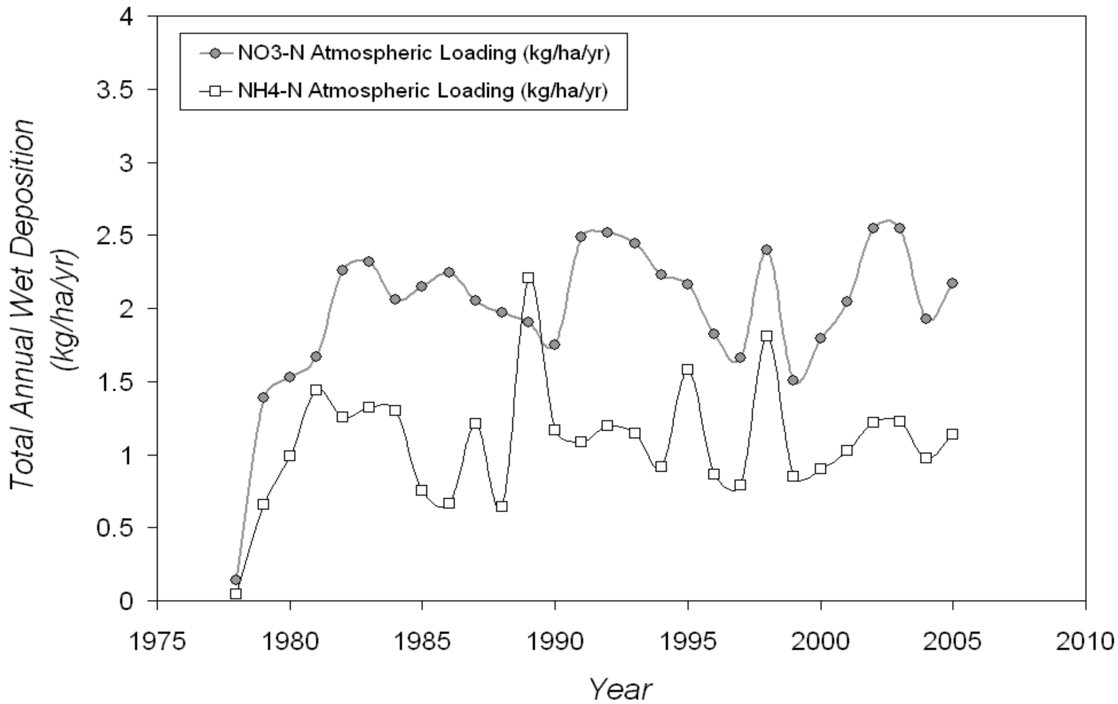


Fig. 6 – Time series of annual wet deposition in kg ha^{-1} yr^{-1} for ammonium (NH_4) and nitrate (NO_3) from Bradford Forest in Bradford County, North Central Florida between 1978 and 2005 (from National Atmospheric Deposition Program monitoring location at Bradford Forest, Florida - http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=NTN&id=FL03).

for N is between 300 and 500 kg N/ha/20 yr rotation, which makes listed rates (Table 3) effectively upper bounds. Further, while Florida's soils typically require amendments for reasonable agronomic yields, the magnitude of fertilizer needs is strongly dependent on soil type.

Sources of Nitrate-Nitrogen in Groundwater

Nitrate-N is perhaps the most widespread groundwater contaminant (Hallberg and Keeney 1993); in particular, numerous studies of water quality in agricultural areas of the U. S. have documented NO_3-N concentrations in ground water and surface water greatly in excess of the regulated water quality standard of 10 mg/l NO_3-N (Keeney 1986; Weil et al. 1990). Hallberg (1989) suggests that agriculture is the most substantial anthropogenic source of NO_3 in the environment, though the loading from urban stormwater and municipal wastewater discharges (both centralized and decentralized) are also important. The most significant problems with NO_3-N accumulation in subsurface water in the U. S. occur in response to 1) heavy fertilization in intensive row-cropping practices in rain-fed grain production, 2) the irrigation and fertilization of shallow-rooted vegetable crops on sandy soils, and 3) locally intensive animal feeding and handling operations (Keeney 1986). In the sandy soils of the southeastern US, the extensive use of fertilizers on row crops is considered by some to be the main source of NO_3-N leaching to ground water (Hubbard and Sheridan 1994). However, Galloway et al. et al. (2004) stressed that human activities, particularly food production and, additionally, use of sprayfields and septic systems, have a locally significant role in increased NO_3-N levels in groundwater. Similarly, Spalding and Exner (1993) reviewed the literature and suggest that urban and agricultural land use types are significant contributors to elevated NO_3–N levels in groundwater. Animal wastes, particularly from confined feeding operations (dairy cows and poultry in particular), also comprise a significant source of NO_3-N that contaminate surface and groundwater; this source is particularly germane to the nitrate enrichment observed in the Suwannee River Basin. Crop type appears to play a major role in nitrate loading; while rates of fertilizer application vary widely among crops, leading to source differences, Randall et al. (1997) report that actual leaching was 30-50 times higher for annual crops (corn, soy) than for perennial crops (alfalfa, pasture grasses). This is primarily due to extended nutrient uptake over the course of a year, but regardless of the mechanism suggests that fertilizer application use efficiency varies widely among crops.

Several properties of the nitrate ion make it particularly problematic as a groundwater pollutant. First, it is highly soluble (saturation of nitrate in water occurs at ~300 g/l) and extremely mobile, moving rapidly through soil profiles via leaching and contaminating groundwater. Second, once nitrate has passed out the soil/vadose zone, the absence of electron acceptors and anion binding sites in the mineral matrix of aquifers (karst or otherwise) markedly slows nitrate reactivity; in fact, some authors have shown that nitrate reactivity in groundwater is so slowed (0.013 μmol N L^{-1} d^{-1}) that its transport was comparable to a bromide tracer (Smith et al. 2004), and that nitrite production rates (0.036 μmol N L^{-1} d^{-1}) more than compensated for this attenuation rate. Others have documented enhanced nitrification of DON and ammonia in shallow groundwater (where oxygen is present) (Miller et al. 1999), resulting in greater nitrate fluxes out of surficial groundwater than was delivered to that groundwater via NO_3-N leaching. Therefore, efforts to understand and mitigate NO_3-N loading to ground water must deal with the complex interplay of numerous land uses and point loads, a variety of temporal and spatially dynamic N sinks, and surface and groundwater conveyances that link the two.

In certain regions, interflow (flows through the vadose zone) or shallow groundwater emerges in bottomland or riparian areas. Hence, NO_3-N that has moved in percolating water from upland soils into shallow groundwater may reappear in surface water bodies and, only then, become an environmental quality problem (Hubbard and Sheridan 1994). This underscores the importance or riparian buffers as a primary interception point for mobile nitrates before they reach aquatic systems. Nitrate mobility and transplanted loads via subsurface paths is magnified in areas of Florida where high NO_3 loading rates on the landscape coincide with short hydraulic residence time at the surface (before denitrification can occur); the absence of effective natural attenuation of nitrates between sources and springs is the primary cause of elevated loads at those locations and *the* major management challenge for improving spring water quality.

Loads and Yields of Nitrate-Nitrogen at the Watershed Scale

While evaluating NO_3 loading at the watershed scale integrates in situ loads, transformations and transport in the hydrologic conveyance system, and landscape-level sinks, it is this level of observation that is both most informative with respect to actual environmental consequences of NO_3 loading, and easiest to measure. Results from watershed loading studies are shown here; note that these loads are not directly analogous to measured fertilizer loads.

Nitrate-N exported from a watershed depends on concentrations and discharge volume. Chemical load, the product of discharge volume and concentration, provides a better estimate of chemical loss over time than the concentration alone. Lewis et al. (1999) estimated that the undisturbed watersheds in the Americas yield N loads of 5.1 kg/ha/year. The N yield from the undisturbed watersheds was strongly related to runoff, and runoff explained a large portion of the variance in the yield of total N (R^2=0.85). Discharges of N from watersheds, especially as NO_3-N, increase as anthropogenic inputs of N to croplands increase (Jordan et al 1997b).

Castillo et al. (2000) quantified seasonal and spatial variation in the concentrations of NO_3-N at 17 sites distributed among tributaries and along the mainstream of the Raisin River in Southeastern Michigan. The annual mean NO_3-N concentration ranged from non detectable levels to 18.1 mg/l. Mean NO_3-N concentrations strongly correlated with the ratio of agricultural to forested land upstream of the sampling locations, and the annual yield of NO_3-N was consistent with the expectations based on land use. Higher concentrations were found in small tributaries and most of the agricultural lands, suggesting the association between agricultural activities and NO_3-N levels in surface and ground waters. Based on mass balance analysis of known sources of N loading in the Mississippi Basin, Howarth et al. (1996) estimated that > 80% of river N originated from agricultural activities and sewage activities accounted for < 10% of N inputs. The NO_3-N loads transported by river reaches and streams can vary greatly across the basin depending on the discharge and the land uses upstream. In a study of NO_3-N distribution among tributaries and the mainstream of the Raisin River in Southeastern Michigan, Castillo et al. (2000) estimated a low yield of 1 kg NO_3-N/ha/yr for the headwaters in the region where the land use had the highest fraction under forest and wetland categories. However, for the entire basin, the estimated load of NO_3-N was 9 kg N/ha/yr. This discrepancy in NO_3-N loads implies that the spatial patterns of NO_3-N loads can vary greatly depending on position in the watershed (headwaters or downstream), and land use-management types. It also may reflect greatly accelerated rates of N attenuation in headwater vs. higher order streams (Peterson et al. 2001)

Fisher and Oppenheimer (1991) estimated that 40% of the N load to Chesapeake Bay comes from human waste, 33% from livestock, and 27% from fertilizer. Jordan et al. (1997a) estimated N loads generated by 17 agricultural watersheds from the Coastal Plain of the

Table 4. Area, land use distribution, NO_3-N concentrations and discharge from 17 watersheds that drain into the Chesapeake Bay (Jordan et al. 1997a).

Basin	**Area**	**Land use**						**Water Yield**	**NO_3-N**	
	Hectares	Row crop	Grass -land	Forest	Fallow	Pond	Others	Yield (m/yr)	Conc. (mg/l)	Load (kg/ha/yr)
Rhode River										
101	226	2.3	21.9	52.4	10	1.1	12.3	0.44	1	4.4
102	193	6.2	19.5	59.6	1.2	0.4	13.1	0.45	1.5	6.7
103	247	1.7	12.5	71	2.1	0.3	12.4	0.44	0.94	4.1
108	150	26.3	13.5	51.6	2.7	0.1	5.8	0.44	1.7	7.4
109	17	60.2	0	34.6	0	0	5.2	0.44	3.6	16
110	6.2	0	0	98.2	0	0	1.8	0.44	0.48	2.1
111	5.5	0	0	11.3	88.6	0	0.1	0.44	0.25	1.1
Delmarva										
301	569	0.3	0	98.3	0.7	0.4	0.3	0.45	0.19	0.86
302	971	28.1	3.3	50.6	10.2	0.1	7.7	0.46	1.6	7.4
303	478	15	56.2	25.3	1.4	0.1	2	0.44	1.1	4.8
Central Coastal Plain										
304	1077	66.3	0	30.4	1.1	0.1	2.1	0.36	2.6	9.4
305	1757	59.8	7.6	28.8	0.1	0.5	3.2	0.36	2.8	10
306	684	66.7	2.7	28.3	0	0.5	1.8	0.35	3.1	11
310	5240	67	1	27	2.2	0.3	2.5	0.37	4.1	15
Outer Coastal Plain										
307	139	1.3	0	88.8	9.9	0	0	0.35	0.52	1.8
308	1241	45.6	0	52	0.5	0	1.9	0.34	3.8	13
309	1632	41.3	0.6	56.9	0.1	0.2	0.9	0.35	2.6	9.1

Chesapeake Bay. Land use characteristics of these watersheds and its NO_3-N discharges are summarized in Table 4. Higher NO_3-N concentrations and discharge were generated from watersheds with greater land under row crops. Basins with large fractions of forested and fallow lands had lower concentrations and loads (with nearly identical water yields).

Complementary information to Table 4 is provided in Table 5, which summarizes the export/loading from various land use types, both nationally and for Florida. Notably in Florida, urban areas consistently yield greater loads of nitrogen than other land uses, but concentrations are approximately equal, a result presumably due to the increased water yields from urban landscapes. Further, it appears that landscapes in Florida yield greater quantities of N, but generally lower concentrations of N and NO_3-N than nationally observed values. Note also the dramatic water quality differences observed between production forest lands and other land uses; total nitrogen loads are ~50% less than the next largest land use (row crops), and nitrate concentrations are lower by a factor of 10. This supports the contention that forested landscapes, even those used for timber production, reduce the overall pollutant load on the landscape, and possibly sequester or at least transform N in the environment (Table 6). Table 6 summarizes the inorganic nitrogen budget for the Bradford Forest, suggesting that the total export in runoff and groundwater is less than the estimated inputs by approximately 80%. Note that the export of dissolved organic N (DON) was relatively high in these systems (3.75 kg/ha/yr), suggesting that the N is transformed rather than sequestered, but also note that the mobility and reactivity of DON is expected to be lower, particularly in karst aquifers. Note also that the areal export of N in this intensively managed forest stand is 0.7 kg/ha/yr, a figure two orders of magnitude lower than comparable yields from other land uses.

Jordan et al. (1997b) tested the effects of agricultural land use on loads of N from the Piedmont watersheds of Chesapeake Bay from December 1990 through November 1991. The watershed characteristics were diverse, with sizes varying from 52 ha to 3200 ha and differing land use compositions ranging from 0-60% cropland, 10-98% forest, and 2-30% other land use types. The linear regression of N load per ha (based on long-term regional mean rate of water flow) against percentage of cropland or non cropland (R^2 = 0.76) predicted that cropland loads were 42 kg/ha/yr. However, based on measured water flows, the regression of N load per ha against percentage of cropland or non cropland (R^2 = 0.56) predicted cropland loads of 32 kg N/ha/yr. The lower predicted N load for the year resulted partly from the study year being conducted during a dry year; the regression line was not as tight as with long-term regional mean rate of flow. Using long term regional mean water flow removed the variance introduced by differences in measured water flow among watersheds. The estimated N export varied from 1.2 kg/ha/yr for natural lands, 2.5 kg/ha/yr for managed forests, 5 kg/ha/yr for pastures, and 29-42 kg/ha/yr for cropland. Predicted values for non-croplands were similar to previous N load estimates (Beaulac and Reckhow 1982), but predicted loads from croplands were higher than median values of 9 kg/ha/yr for row crop and 15 kg/ha/yr predicted for mixed agricultural land (Beaulac and Reckhow 1982). Large regional differences suggest differences in N input, removal, storage, or transport processes in croplands, presumably due to both variation in loads and landscape transport/attenuation. Higher NO_3-N loads from croplands in 1990/91 compared to previous periods is in agreement with the growing concern of increased NO_3 loading from anthropogenic activities to the environment.

Table 5. Summary of annual land use loads and event- mean concentrations nationally and for Florida. Data are for total N load, total N concentrations and nitrate concentrations. (after Harmel et al. 2006)

		Land use						
	Location	Urban – Low Intensity	Urban – Medium Intensity	Urban – High Intensity	Pasture	Row Crops	Citrus	Prod. Forests
Total N Loading (kg/ha)	Nationally	9	11	7.8	8.7	16.1	-	2.9
	Reference	Omeric	Omeric	Omeric	Reckhow	Reckhow	-	Reckhow
	Florida	11.6	16.6	32.1	11.2	6.9	7.2	3.75
	Reference	Harper	Harper	Harper	Harper	Harper	Harper	Korhnak
Total N Conc. (mg/L)	National	2.64	1.85	1.75	4.13	7.06	-	2.73
	Reference	EPA (1983)	EPA (1983)	EPA (1983)	multiple‡	multiple‡	multiple‡	multiple‡
	Florida	2.29	1.8	2.83	1.97	2.28	1.71	1.31
	Reference	Harper	Harper	Harper	Harper/ Graves	Harper/ Graves	Harper/ Graves	Korhnak
Nitrate Conc. (mg/L)	National	0.72	0.56	0.57	0.81	4.71	-	0.32
	Reference	EPA (1983)	EPA (1983)	EPA (1983)	multiple‡	multiple‡	multiple‡	Binkley
	Florida	0.28	0.68	0.19	0.80†	0.80†	0.80†	0.08
	Reference	McConnell	McConnell	McConnell	McConnell	McConnell	McConnell	Korhnak

† - mixed land use.
‡ - References include EPA (1983), Reckhow et al. (1980), Tarabe et al. (1997), McConnell et al. (1999), Kohrnak (unpublished data), Harper (no date), Graves et al. (2004), Binkley et al. (2004)

Table 6. Inorganic nitrogen budget for Bradford Forest site. Data are for three watersheds (intense treatment, moderate treatment, control) from 1978 – 1993 (Kohrnak, unpublished data). These data imply that managed forest ecosystems are a net sink for inorganic N, but a net source of total N (primarily exported as dissolved organic N).

N in Rain (kg/ha/yr)		N in Runoff (kg/ha/yr)		
NO3-N	NH4-N	NO3-N	NH4-N	DON
2.05	1.00	0.13	0.33	3.29
Total	**3.05**	**Total**		**3.75**

Nutrient concentrations measured in rivers and springs could be influenced by numerous environmental, land use and landscape factors. Elevated NO_3-N concentrations in ground water are frequently observed around dairy and poultry operations, barnyards, and feedlots (Hii et al. 1999, Carey 2002), but land use is not the only factor that might predict concentrations in river systems. In order to identify landscape variables affecting NO_3-N concentrations in rivers, Castillo et al. (2000) employed multiple linear regression (across a single agricultural watershed) to predict nitrate concentrations from a suite of independent variables related to location in the watershed, land use and cover, geology, and nutrient discharges. The regression analysis was performed for mainstream and tributary sites separately, and identified land use and location in the watershed as primary predictors of NO_3-N concentrations. The variables – ratio of agricultural to forest land and distance from the river mouth – explained 99% of the spatial variability in NO_3-N concentrations over the Raisin River watershed. Notably, the regression parameters vary substantially by season, with spring and summer predictions dominated by land use, while that relationship was not evident during the fall, during which NO_3-N concentrations were predicted by landscape position alone. These results illustrate the complexity of nitrogen delivery, and suggest that the combined flows from surface and groundwater (which occur in the spring and summer) link land uses to river systems, while during the fall, the flows in the river are primarily baseflow (groundwater) that integrates across the land use effects. The analog of this effect in peninsular Florida would be manifest in differences between summer and fall flows, which are dominated by storm flows, and spring flows, which are more likely to be baseflow. The results of the Castillo et al. (2000) study would predict that the summer/fall flows would be more reflective of land use effects, while the baseflows in the spring would be reflective of landscape position and possibly geologic setting.

Another long term N loading study (Schilling and Zhang 2004) evaluated annual and seasonal patterns of NO_3-N loads from the Raccoon River watershed over a 28-year period (1972-2000). That watershed is primarily agricultural; in 2000, land use was primarily row crops (76.2%), with grassland (17.4%), forest (5.4%), and urban/artificial (0.5%) also important. Groundwater recharge and discharge were quantified in addition to NO_3-N export dynamics. Overall, NO_3-N loads exhibited high temporal variation but no directional trend through the study period; NO_3-N export from the watershed ranged from 1.4 kg/ha/yr (in 1977 and 2000) to more than 65 kg/ha/yr (in 1983 and 1993), with an average NO_3-N load of 26.1 kg/ha/yr (± 18.3). Annual precipitation also varied (513 mm in 2000 to 1208 mm in 1993; average = 870 mm/yr); greater NO_3-N loads are associated with periods of above normal precipitation and discharge (Fig. 7). Graphical comparison of NO_3-N load and precipitation (Fig 7) also indicates maximum loads following the second year of below normal precipitation and discharge. This could be attributed to NO_3-N storage in the soils during dry periods, which later became mobilized during periods of higher rainfall and runoff, a problem with a clear analog in Florida.

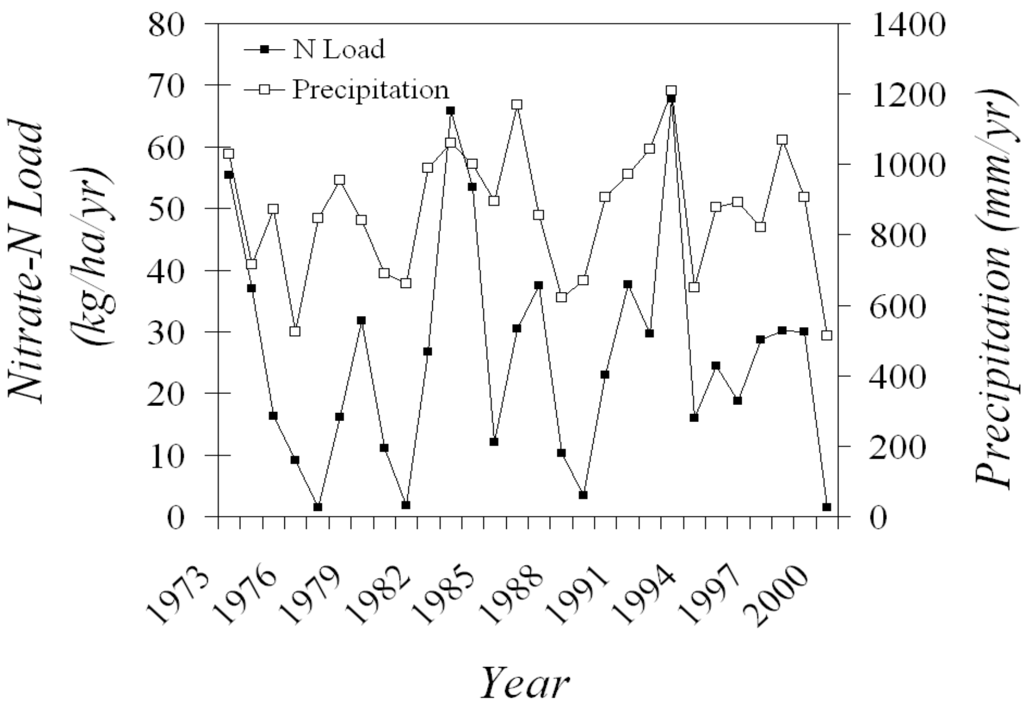


Fig 7. Nitrate-N discharge and mean annual precipitation in 28 year period in the Raccoon River watershed (From: Schilling and Zhang 2004).

Baseflow contributed 54% of the water flux from the watershed, but carried over 66% of annual NO_3-N export. Baseflow nitrate loads varied widely, with estimated loads between 0.1 to 57.9 kg/ha/yr, with an average of 17.3 kg/ha/yr. A linear relationship between baseflow export and total NO_3-N export was significant, with 94% of the variance in baseflow export explained by total NO_3-N export (Fig 8). In general, the fraction of total NO_3-N exported by baseflow increased in drier years. This situation can be observed in Florida as well, with the mixing of nitrate rich groundwater, which dominates river flows at low flow, and relatively nitrate poor surface water, which dominates at peak flows.

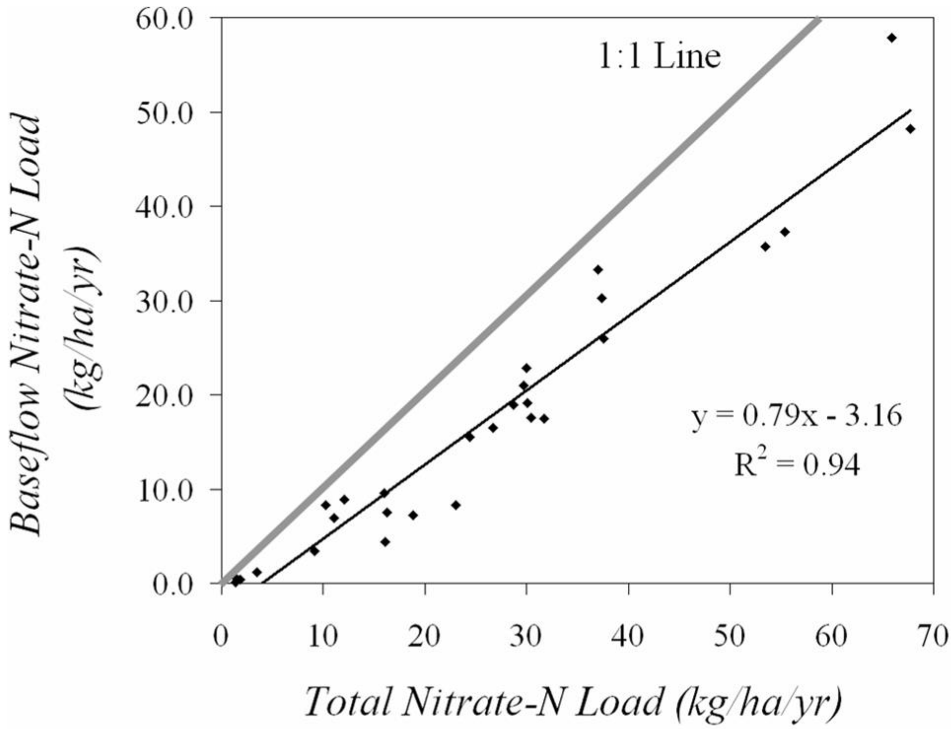


Fig 8. Relationship between baseflow NO_3-N load and total NO_3-N load in the watershed (From: Schilling and Zhang 2004).

One of the most informative long term study sites in Florida for understanding the effects of anthropogenic activities on regional N enrichment in the surface and groundwater is the Suwannee Farms site near O'Brien, Florida, in Suwannee County (Fig. 9). The site is in a region where the Floridan aquifer is unconfined and generally within 5 meters of the ground surface, and the soils have been shown to be extremely susceptible to nitrate leaching (Albert 2002). The near total absence of surface hydrologic features (except major rivers, all of which are essentially expressions of the Floridan aquifer potentiometric surface) makes this area desirable for intensive agriculture despite the fact that the deeply weathered soils necessitate large quantities (ca. 300 kg N/ha) of fertilizer application to support crop and dairy pasture production (Andrews 1992, McKinnie et al. 2003). Nitrate concentrations observed in the vadose zone and upper Floridan Aquifer System (FAS) at these sites were severely enriched, frequently exceeding drinking water standards by an order of magnitude. For example, nominal values directly below potato farms of 50-20 mg NO_3-N per liter were observed (McKinnie et al. 2003), values in surficial groundwater wells downstream of dairy farms were often as high as 130 mg/l, despite concentrations up-gradient of those sites rarely exceeding 1 mg/l (Andrew 1994). Such high concentrations have been shown to be transient (McNeal et al. 1995) in other areas of the state, but concentrations between fertilization events can remain as high as 20-40 mg/L NO_3-N, with this layer of enriched groundwater persisting 2-3 m into the aquifer (McNeal et al. 1995).

Human wastes, dairies and row crop operations are not alone in increasing N pollution; Lopez-Zamora et al. (2006) observed significant enrichment plumes emanating from poultry houses in the same area (Suwannee County, Florida), and attribute this to airborne ammonia

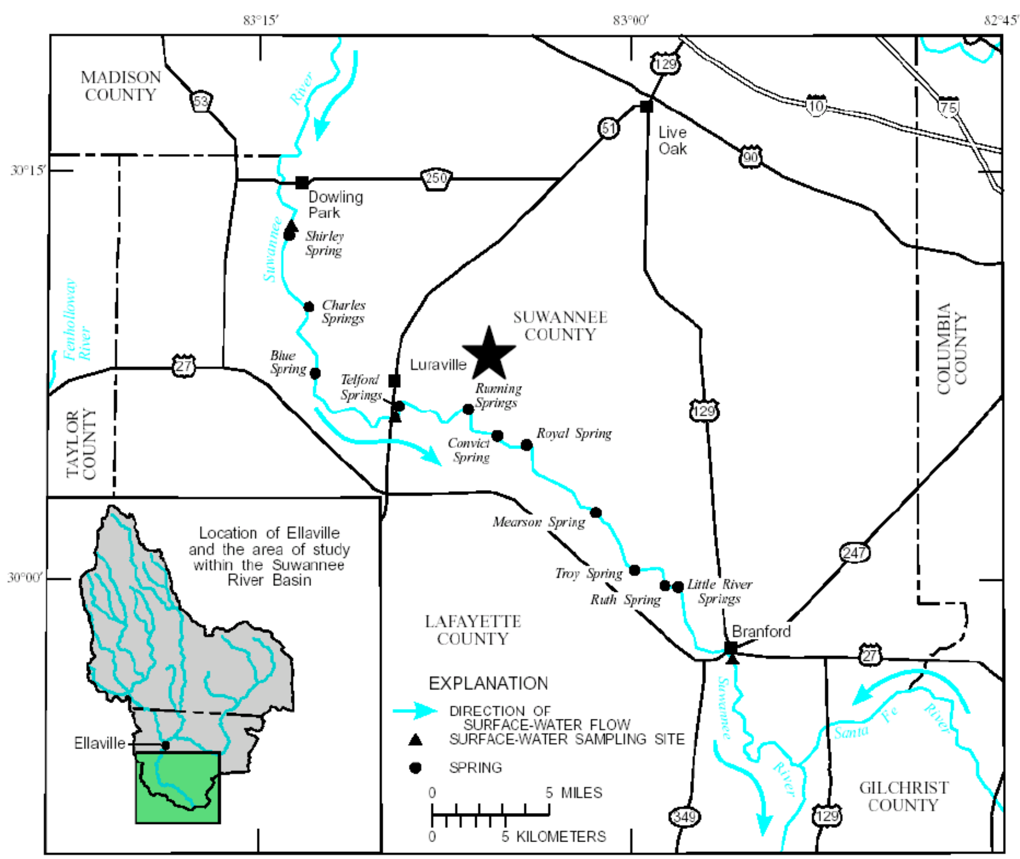


Fig. 9 – Location of Suwannee Farms study site with respect to the river mainstem and major (1st magnitude) springs. The reach between Dowling Park and Branford showed an increase in nitrat-N loads from 2,300 kg/d to 6,000 kg/d; river concentrations increased in this reach by 0.02 mg/L/yr between 1971 and 1991, underscoring vulnerability of this area to N enrichment.

emissions and subsequent microbial conversion to nitrate. The mobility of nitrates in the soils resulted in significant foliar N concentrations in slash pines over 400 m from the site; while no data were obtained for water quality in the region, the implication is that the numerous poultry operations may inadvertently be loading N to the environment via previously undocumented and currently unmanaged pathways.

Another study of N-loading (Woodward et al. 2002) examined the nitrate leaching effects of dairy manure effluent applied to forage systems in the same Suwannee Valley area. Extreme loading rates of as high as 900 kg/ha/yr were examined, and forage grass operations were shown to be capable of up to 500 kg/ha/yr of N uptake; the remainder leached to the soil water, where NO_3-N concentrations in excess of 60 mg/l were observed. Of additional BMP-related interest from this study is the strongly significant observation of reduced nitrate loading under a bermuda/ryegrass rotation than under a corn-sorghum-ryegrass receiving the same loading.

The influences of N processes within forested landscapes on biogeochemical cycles at a catchment scale have been demonstrated in experiments at Hubbard Brook Experimental Forest (HBEF), New Hampshire, USA and Coweeta, North Carolina, USA. Over a three-year period after clearcutting a hardwood forest at Hubbard Brook, forest-floor organic matter decreased by 10800 kg ha^{-1}, soil organic matter declined by 18900 kg ha^{-1} and net N loss from the soil was estimated to be 472 kg ha^{-1} with an increased export of inorganic N in the stream estimated to be as high as 337 kg ha^{-1} (Bormann and Likens 1979, Huntington et al. 1988). This response to clearcutting was attributed to accelerated rates of decomposition induced by favorable temperature-moisture-nutrient conditions and enhanced nitrification rates, a process replicated in Florida at the Bradford site (Morris 1981) where elevated nitrate export was observed after clear-cutting. Increased availability and loss of NO_3-N also increased the loss of cations from the ecosystem (Likens et al. 1977). Significant alteration of N fluxes has also been observed in a clearcut experiment at Coweeta (Swank 1988). Initially after logging, soil N mineralization increased by about 25% and nitrification increased by 200%; surprisingly, only a small fraction of available soil N was exported from the catchment via stream water (Waide et al. 1988). Ecosystem retention was due partly to rapid revegetation and related high rates of N uptake and partly to microbial immobilization (Vitousek and Matson 1985). Further evidence for the importance of the balance between mineralization and immobilization in regulating N losses in other ecosystems is given by Hornbeck et al. (1986). It is evident that net nitrification rates and associated nitrate concentrations differ tremendously across forest ecosystems due to a number of sources of variation (soil texture, temperature, inorganic N availability); Stark and Hart (1997) demonstrate that while net nitrification is typically extremely small in forests, gross nitrification is large, with rapid (< 1 day) ecosystem uptake of mineralized N explaining the low net rates.

In conclusion, the most significant enrichment of N at the watershed scale is likely to be due to mineral fertilizers, both in Florida and in general. Atmospheric N loading (wet deposition) and enhanced export due to forest clearing were small relative to increased loads observed on intensive agricultural landscapes. However, the relative influence of human and animal wastes is not well described in the loading literature; innovative use of isotopic measurements of N in nitrates delivered to water bodies (described below) is one technique that has been demonstrated to reduce this uncertainty.

Identifying Sources of Nitrates

Effective management practices to preserve water quality and design remediation plans for sites that are already polluted requires identification of the actual sources and sound understanding of the processes affecting local NO_3-N concentrations. In particular, a better understanding of hydrologic flow paths and NO_3-N sources is required to determine the potential impact of contaminants on water supplies. Determination of the relation between NO_3-N concentrations in water resources (ground and surface water) and quantity of NO_3-N released from a particular source is complicated by (Kendall and Aravena 2000):

- The occurrence of multiple possible sources of NO_3-N in many areas,
- The presence of overlapping point and non-point sources, and
- The co-existence of biogeochemical processes that alter NO_3-N concentrations

Different sources of NO_3-N often have isotopically distinct composition (Hornsby 1994), making isotope studies useful to identify the source of NO_3-N. Isotopic studies can also be used to trace the movement and fate of NO_3-N in the environment along with a suite of hydrologic tracers (Katz et al. 1999). Kendall and Aravena (2000) described the use of the stable N and oxygen isotopes of NO_3-N molecules as tracers to evaluate the sources and processes that affect NO_3-N in groundwater. The stable isotopes of N are ^{15}N (nominal abundance of 0.36%) and ^{14}N (nominal abundance of 99.64%). The wide range of oxidation numbers exhibited by N compounds, ranging from +5 (as in NO_3) to -3 (as in NH_4), results in a wide range of isotopic compositions (Kendall and Aravena 2000). Similarly, the stable isotopes of oxygen are ^{16}O (abundance 99.763%), ^{17}O (0.0375%) and ^{18}O (0.1995%).

Because differences in isotopic abundance of an element from one substance to another are small, concentrations are expressed with "delta" (δ) notation. A δ value of an isotope in a sample is the per mil (‰, parts per thousand) difference in the ratio of the less abundant isotope to the more abundant isotope relative to the same ratio in a known standard (for N, the standard is atmospheric air where $^{15}N/^{14}N = 0.0036$) and may be represented as (Panno et al 2001):

$$\delta X_{(sample)} = [(R_{(sample)} - R_{standard}) / R_{standard}] * 1000$$

where δ X is the isotope of interest ($\delta^{15}N$), and R = the ratio of $^{15}N/^{14}N$. Generally $\delta^{15}N$ values are different for different sources of NO_3-N. Nitrogen from fertilizers has $\delta^{15}N$ values around 0 ± 4%, N from animal wastewater and septic systems have $\delta^{15}N$ values ranging from + 8% to + 22%, and N from natural organic matter buried in soils have $\delta^{15}N$ values ranging from + 4% to + 9% (Heaton 1986; Panno et al 2001). Thus, determining the $\delta^{15}N$ values in sample gives an indication of the source of N contained in that sample.

In the Suwannee River basin in Florida, Katz et al. (1999) measured values of $\delta^{15}N$ in 24 springs, and observed a range between 2.7 and 10.6 ‰ (per mil) (median ~ 5.4 ‰), indicating that the nitrates are likely from both organic (manure, human waste) and inorganic (fertilizer) sources. Some of the sampled springs and nearby wells had values in excess of 9 ‰, indicating a dominance of organic sources, but over 65% of the wells sampled had values < 2 ‰, indicative of inorganic fertilizer sources. The strong evidence in that study of complex mixing dynamics among different subsurface reservoirs underscores the need for detailed monitoring and geochemical end-member determination to better understand the relative vulnerabilities of different spring systems to regional land uses, and also improved understanding of local physical geology (e.g., factures, conduits, etc.). Water samples collected from two groundwater wells in Lafayette County, North Florida showed higher $\delta^{15}N$-NO_3 values of 11.0 and 12.1 ‰, indicating the likelihood of an organic source of NO_3-N, which was consistent with the dairy and poultry farms that could be contributing NO_3-N to groundwater (Katz et al 1999).

In the Silver Springs system, Phelps (2004) observed nitrate loads and measured isotopic fractions to determine sources. Results from 37 wells and 3 of the headsprings generally indicate that fertilizer is the main source of N enrichment in the springshed, but because the range of isotopic values was between -0.5 and +11.5 ‰, a wide mixture of sources and/or significant temporal dynamics was evident. When wells were stratified by land use, the median isotopic fractions in each area (5.4, 4.9 and 4.1 ‰ for urban, agriculture and forest, respectively), were intermediate between mixed and solely mineral fertilizer sources. However, measurements at the main spring are suggestive of strongly confounded temporal dynamics, with a value of 8.5 ‰ at one sampling event (indicative of mixed mineral-organic sources) and 3.7 ‰ at another sampling event (strongly indicative of a mineral source of N). One hypothesis is that the source of spring water varies with flow regime, with low flow carrying increased total nitrates and a lower isotopic value, both indicative of dispersed fertilizer application and elevated concentrations in the aquifer matrix. At high flow, more of the water passes through aquifer conduits to the head spring, and the elevated isotopic signature is the result of movement of animal or human wastes through those conduits. While the isotopic technique for source detection is useful, it is most helpful in concert with other hydrogeochemical measurements (ionic profiles, conservative tracers); further, to interpret the signal from isotope measurements, an improved understanding of temporal dynamics in spring systems is critically needed.

Temporal and Spatial Variability of Nitrate-N loading

Environmental variability is a critical confounder of scientific inference, as seen above with isotopic signaling of nitrate sources, but also more generally when trying to understand the loading or assimilation behavior of environmental systems. For example, setting regulatory thresholds for pollutant concentrations that lead to environmental change and determining the role of land use and water management decisions on pollution discharge, all depend on strong scientific inference, which is frequently weakened by variability in time and space. Few studies address variability to the extent that perhaps they should. Those studies that have attempted to quantify uncertainty about process rates (e.g. Bruland and Richardson 2004, Dondt et al. 2003) frequently conclude that spatial and temporal variability limits the utility of scaling from small numbers of observations to landscape behavior. As an example, Dondt et al. (2003) examined N_2O fluxes (blocking full denitrification to N_2 using the acetylene block technique) from three riparian wetlands in a similar physiographic zone in Belgium and observed a range of responses from net uptake of N_2O (-0.6 ± 0.4 mg N_2O-N m^{-2} d^{-1}) to net emission (2.5 ± 0.3 mg N_2O-N m^{-2} d^{-1}). They also observe apparent stochastic temporal trends at a quarterly sampling frequency.

In a study of P sorption capacity, Bruland and Richardson (2004) observed significant short-range spatial variability, with a range of observed soil P sorption index values between 90 and 250 over an area of 900 m^2. While variability was strongly structured (i.e., predictable with sampling), the accuracy of using a single value to represent an ecosystem type at the landscape scale is suspect. Temporal variability is also problematic. For example, sampling of water quality in Florida is typically at monthly or quarterly intervals. While this may be sufficient to deduce long term trends, it is insufficient to study short term dynamics. By way of example, unpublished data from two stations in the Santa Fe River basin for flow and NO_3-N are presented (Fig. 10). The data were examined for evidence of serial autocorrelation, which describes the degree to which observations separated in time from the same location co-vary. Typically, the expectation is strong autocorrelation at short time separation, with increasingly weak correlation with time between observations. Significant autocorrelation is evaluated in comparison with white-noise time series (red lines in Fig. 10). As shown, there is strong serial autocorrelation for flow observations (daily frequency) but effectively no serial autocorrelation in nitrate concentrations (monthly frequency) at the same sites. The implication is that the protocol for monitoring nitrate-N fails to capture the intrinsic time patterns of its delivery. This observation regarding nitrate concentrations in a river system is relevant to an understanding of N loading in spring ecosystems for two reasons. First, if pollution thresholds are defined (e.g., 125 ppb NO_3-N) then knowledge about temporal dynamics and exceedance frequency/period are essential. Inference based on monthly sampling risks missing peak concentration events that may be particularly important to ecological systems. Second, if landscapes are to be managed to reduce loads, a more informed picture of the manner in which NO_3 loads arrive to springs might shed light on strategic hot-spots of N pollution and/or sources that need to be managed first (e.g. stormwater, as inferred from the relationship between nitrate and temporal flow dynamics). Note that the sampling stations (Fig.10) are from confined and unconfined regions of the Santa Fe River basin, a situation that has important analogs throughout Florida; the unconfined region is where groundwater discharges (springs) occur, and is the source of most of the N load (Fig. 2C). In general, extrapolations of localized short-term measurements to a whole-system are tenuous at best, and extrapolation of site-specific measurements to other sites even more perilous.

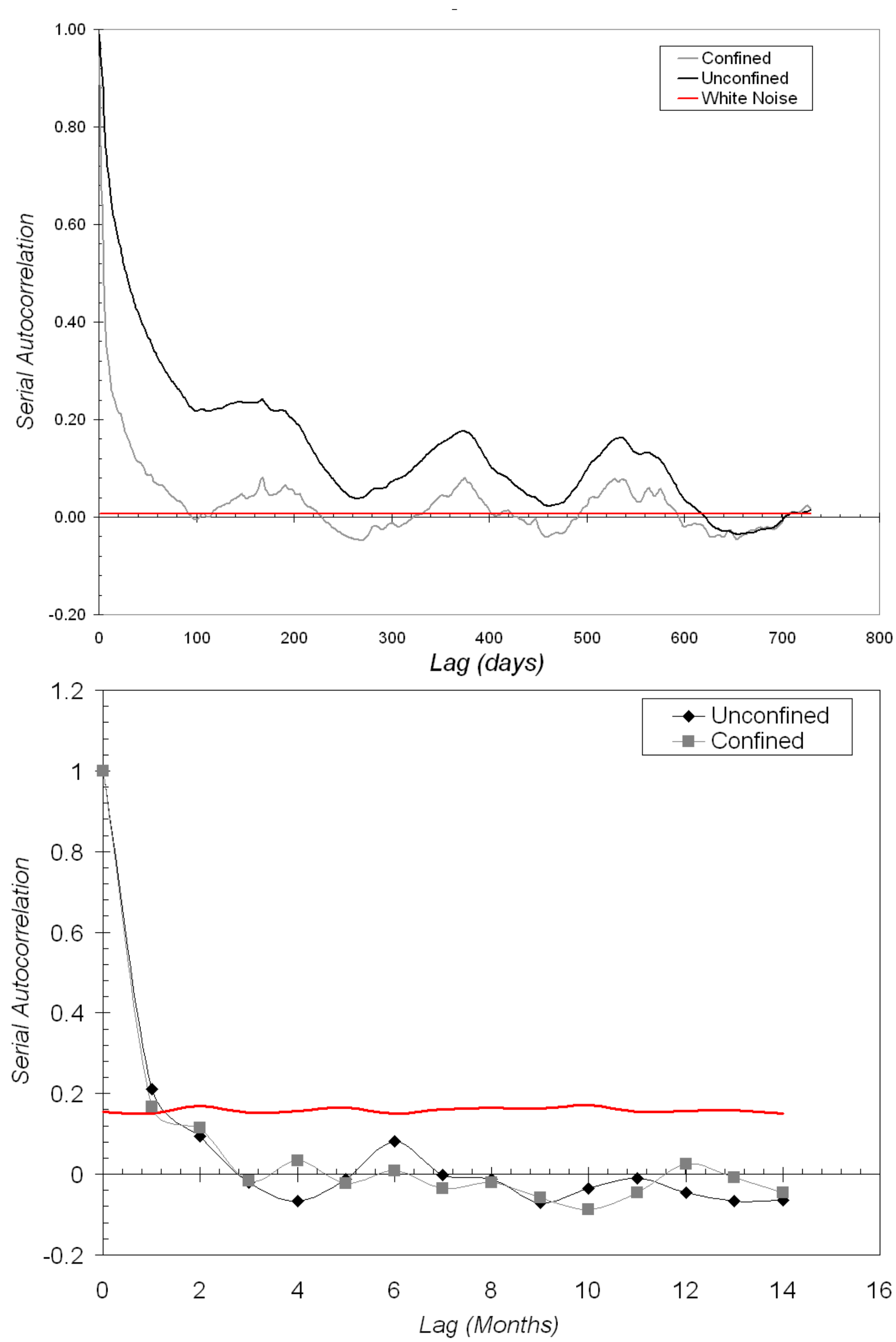


Fig. 10 – Serial autocorrelation of a) flow and b) nitrate observations at two long-term monitoring stations on the Santa Fe River. One station lies in the region of that basin that is geologically confined ("confined") and the other in the region where surface and groundwater interactions are more significant ("unconfined"); both stations are monitored monthly. The red-lines illustrate the 95% confidence bounds for significant serial autocorrelation; these data suggest that current nitrate monitoring fails to capture the dynamics of the watershed phenomena that drive nitrate delivery to aquatic systems.

Annual and Seasonal Patterns of nitrate-N loading

Discharge from a watershed can vary with seasons, with high discharge mostly following storm events (in Florida). Castillo et al. (2000) compared the NO_3-N concentrations for different seasons in the main streams and tributaries of agricultural catchments of the River Raisin, Southeastern Michigan (Table 7). Nitrate-N concentrations were highest in spring, particularly in some predominantly agricultural tributaries, although presumably some of this signal is due to snowmelt effects that are not relevant in Florida. Highest values were found in tributaries where agriculture was the dominant (>90%) land use category. High values during spring could be attributed to fertilizer applications, whereas lower values in fall season could be attributed to leaching losses with the summer precipitation. The high values of spring (April through May) corresponded with an extended period of elevated water yield.

Weekly water samples collected during July 1990 through May 1993 at the Davis Springs and Hole Basin springs in the karst regions of southeastern West Virginia showed that the median NO_3-N concentration in the springs and its temporal variability were significantly affected by weather patterns (Boyer and Pasquarell 1995). Lower NO_3-N concentration and lower temporal variability were observed during a severe drought period (250 to 550 days from June 30 1990), which coincided with the period of low NO_3-N variability; significant rainfall at the end of 1992 coincided with high NO_3-N concentrations. During drought periods, very little water flows through karst conduit systems feeding the springs. Also, lack of percolation and direct runoff into open sinkholes may have caused a build up of animal wastes and organic N on the soil surface. During dry periods, nitrification may cease because nitrifying bacteria are sensitive to water deficits. However, drought tolerant fungi can still carry out the ammonification step, resulting in a build up of ammonium N in the soil. When wet conditions return, ammonium N gets rapidly nitrified, leaching to the groundwater and appearing in springs (Power 1994).

This evidence supports an important hypothesis about how weather and climate affect delivery of nitrates to the Silver Springs system (Phelps 2004). Specifically, during low flows, nitrate delivery to springs is dominated by N already in the aquifer matrix, which is likely to be primarily of fertilizer origin (low $\delta^{15}N$) because organic sources of N are less mobile. At higher flow, source water to springs arrives through karst conduits, and is primarily carries mobilized N available at the surface, which is in organic form (DON) or ammonia, in addition to nitrates mineralized from organic sources (higher $\delta^{15}N$).

The temporal dynamics of N in Florida's springs and rivers exhibits two primary trends. First, in systems where streams flows are a mixture of surface and groundwater (where the latter has significantly higher concentrations), the relative dominance of groundwater during periods of low flow leads to higher overall NO_3-N concentrations. That is, there is a negative correlation between nitrate concentrations and flow. However, in springs, where groundwater is the only input, the correlation is reversed, with higher nitrate concentrations occurring during periods of high flow. In both cases the relationships are driven by the mixing of different sources of water. In the former case, the mixture is of low nitrate surface water and high nitrate groundwater; their relative importance in the mixture defines to resulting concentration. In the latter case, the mixture may be of old and young groundwater (or some otherwise distinct pools of subsurface waters such as matrix and conduit reservoirs). In this case, the groundwater ("old") that dominates at low flow is relatively lower in nitrates, while the groundwater that dominates at high flow ("young") is enriched in nitrates. The resulting mixture (which depends again on their relative importance to the total flow) drives nitrate concentrations.

Schilling and Zhang (2004) observed that monthly NO_3-N losses from the Raccoon valley watershed were variable, both within and between months, with the greatest NO_3-N losses occurring during the periods of high precipitation - March through June (Fig 11). Nearly 33% of the annual load occurred in March and April, and 50% of the annual load occurred in March to June. The baseflow contribution to the total load was greater during the dry periods. For karst regions West Virginia, weather patterns were found to significantly affect NO_3-N concentrations and temporal variability of NO_3-N concentrations, with lower NO_3-N concentration and lower temporal variability found during a severe drought period (Boyer and Pasquarell 1995).

Few studies in Florida have described the temporal variability of spring nitrate concentrations at a resolution to capture their dynamics. Recent work (Sickman et al. – unpublished data) showed variation in nitrate concentrations over a factor of 3 (0.6 to 1.8 mg/l) in both Ichetucknee and Manatee springs, and strong covariance with flow. Further, anecdotal

Table 7. Flow weighted mean concentration of NO_3-N (mg/l) for mainstream and tributary sites in an agricultural catchment in SE Michigan (Castillo et al 2000).

Location	Annual	Spring	Summer	Fall	Winter
Mainstream	1.4	1.6	1.3	0.9	0.8
Tributaries	3.9	4.3	3.2	0.8	0.9

evidence abounds at both springs that fertilization schedules are immediately manifest in the water quality despite other evidence that suggests that water exiting the springs is, on average, much older (Katz et al. 2004). This suggests mechanisms and rates of mixing that are, as yet, poorly understood. For example, Katz et al (1999) demonstrate the substantial differences that can arise in groundwater age estimation by changing assumptions about hydrogeologic behavior of the aquifer. Specifically, comparing a piston flow (plug flow) model with an exponential model (complete mixing) results in large (>100% in some cases) differences in inferred groundwater age. Binary mixing models (old groundwater and new groundwater) may be more appropriate for addressing matrix vs. conduit flow, but are similarly constrained by anisotropy and complexity of the karst media. Further, while the boundaries of springsheds can be delineated on average from potentiometric surfaces, the particular flow lines and travel times that link parts of the landscape to particular spring vents are highly uncertain. Underscoring that uncertainty is the dramatic variability observed in ion chemistry between water emerging from proximate vents in Silver Springs (Phelps 2004) and Ichetucknee (Upchurch et al. 2004), suggesting spatial differences in water source.

How and when loads reach the springs, where the loads are coming from, and the temporal domain of mixing dynamics are a critical unknowns that affect the manner in which these systems can be managed; continuing study of spring flows and springsheds is required.

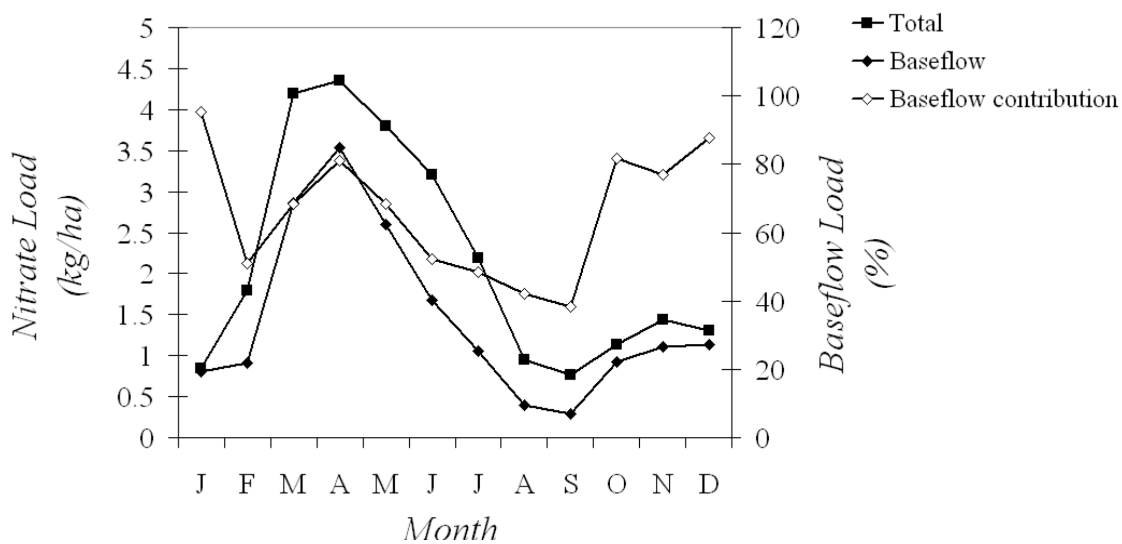


Fig 11. Monthly total and baseflow NO_3-N loads, and baseflow contribution to NO_3-N loads in the Raccoon River watershed from 1972-2000 (Schilling and Zhang 2004).

Spatial patterns of nitrate-N loading

Several studies have investigated the catchment and watershed characteristics that control the concentration and discharge of NO_3-N from surface and ground water. Spatial patterns of NO_3-N in the rivers and tributaries are found to be associated with the land use distribution. For an agricultural catchment in Southeastern Michigan, the variations in NO_3-N concentration in the streams and tributaries was highly predictable from the ratio of agricultural to forested land and upstream/downstream location in the watershed (Castillo et al. 2000). Nitrate-N concentrations increased as the proportion of agricultural land increased, and consistent with the extent of expected fertilizer use. Jordan et al. (1997a) investigated the effects of agricultural land use and nutrient loading on discharges of NO_3-N in 17 coastal plain watersheds of Chesapeake Bay. Annual flow-weighted mean concentrations of N species increased as the proportion of cropland in the watershed increased. Using linear regression, the percentage of cropland was able to significantly explain 85% of the variability in total N ($p<0.0001$) and 75% of the variance in NO_3-N ($p<0.0001$). Extrapolating the regression equation of N discharge against the percentage of cropland, N discharge was estimated at 18 kg/ha/yr for 100% cropland, and 2.9 kg/ha/yr for 0% cropland. Additionally, the percent of total N composed of NO_3 increased as the proportion of cropland increased, suggesting the association between NO_3 and land use activity.

Generally, NO_3-N concentrations in surface waters increase downstream, with marked variation between sampling sites and high variability over time. One explanation for this is that ecosystem reactivity to enriched nitrogen is much greater in headwater systems than elsewhere in river systems (Peterson et al. 2001); consequently, while land uses load river systems at the same rate throughout a basin, the ability of the aquatic system to attenuate that load varies substantially, depending upon location in the watershed. The degree to which this observation, made for watersheds in the northeastern US, holds for Florida is unknown. Van Herpe and Troch (2000) studied the spatial variation of NO_3-N concentrations in surface waters of a mixed land use catchments in the Zwalm watershed in Flanders, Belgium. Other than hydrological regime, catchment characteristics were hypothesized to control the export of NO_3 in surface waters. Correlations between catchment average NO_3-N concentrations and catchment characteristics (Table 8) showed that NO_3-N concentrations in the surface water were closely linked to land use. The proportion of agricultural land within a catchment was positively correlated with stream water NO_3 concentrations, whereas higher percentages of forested area resulted in lower NO_3 concentration. In mixed land use systems, the NO_3 concentrations measured along the streams and tributaries will exhibit high spatial variation with NO_3 concentrations related to the land use in the upstream drainage area. As such, spatial monitoring of fluxes and concentrations are necessary to target loading and attenuation hot spots and deduce processes that would aid in regulating/managing these hotspots.

Table 8. Correlation between catchment characteristics and stream NO_3-N concentrations for Zwalm watershed in Belgium (Van Herpe & Troch 2000).

Catchment characteristics		R	*p*
Geomorphology			
	Mean elevation	-0.76	0.133
	Slope	-0.76	0.137
Land use			
	Urban	-0.24	0.701
	Arable land	0.94	0.019
	Pasture	0.42	0.486
	Agricultural	0.98	0.004
	Forest	-0.94	0.017
Soil type			
	Clay	0.14	0.819
	Loam	0.67	0.219
	Sandy Loam	-0.70	0.192

R: correlation; *p*: level of significance

ASSESSING VULNERABILITY TO NITROGEN LOADING

Nitrate-N loading occurs throughout Florida from atmospheric deposition, fertilizer applications, and wastewater discharges; however, loads of nitrogen on the land surface (either natural or anthropogenic origin) have varying probabilities of actually reaching the groundwater and springs. Understanding the relative vulnerability of the various aquifer systems to pollutant loading at the surface (Fig 12, 13) is essential because, as human influence in the landscape increases, regulatory agencies can use relative vulnerability information to set conservation priorities, engage in informed municipal planning, or designate development-specific BMPs.

Geologically induced vulnerability

At the regional scale, stratigraphic variation can exert major control over groundwater flow and quality (Alley 1993). As water makes its way into the groundwater by infiltration, the soils and hydrogeologic setting play an important role in determining the extent of leaching of nutrients and other contaminants. Focusing on nitrates, soils with large pools of organic carbon will offer some biological attenuation of leaching (via immobilization and denitrification), and soils that are poorly drained will both retard the progress of water into the subsurface and also tend to provide the anoxia required for denitrification. Soils that are well and excessively well drained will have limited opportunity for denitrification. Clearly, soil and geologic substrate are related, and probably keystone variables in determining regional vulnerability to nitrate transport from the surface to groundwater. Among the most vulnerable geologic types, for reasons to be explained, is karst, which dominates large portions of the Florida landscape.

Karst systems have an interrupted surface drainage and subsurface conduit flow which gives rise to a relatively rapid and direct connection between surface and ground water. Such hydrogeologic characteristics give rise to accelerated leaching potential, making karst systems vulnerable to pollution introduced by human activities. One of the most important hydrologic features of karst systems is that water moves in systems of caves, fractures and fissures before emerging as springs, typically at karst terrain boundaries (Ford 1993). Connectivity between surface and ground waters characteristic of karst hydrogeologic landscapes makes karst aquifers susceptible to chemical contamination from land surface activities and elevated NO_3-N concentrations are frequently found in these systems (White et al. 1995, Coxon 1999). Swancar and Hutchinson (1992) illustrated how geology regulates water movement showing that the

Floridan aquifer received recharge primarily in poorly confined areas, and effectively no recharge in areas where the confining unit is thicker than 67 m.

A schematic of hydrogeologic units at Silver Springs, which is typical of the karst stratigraphy observed for many Florida spring systems (Fig. 14) shows the layers that substantially affect vulnerability to NO_3 enrichment. In particular, upper layers (undifferentiated Plio-Pleistocene materials, and phosphatic clays/siliciclastic sands of the Miocene Hawthorn group) are absent in some areas (most areas deemed high vulnerability to contamination – Fig. 13 – are unconfined). The primary risk factor for the FAS in Florida is the absence of the Hawthorn aquitard; in areas where this layer is absent, the FAS interacts directly with contaminants entrained by leaching water from the surface. Where the Hawthorn is thick and intact, mixing between surface and groundwater is minimized, and opportunities for biological removal of nitrogen are enhanced. All the major springs in Florida occur in unconfined portions of the landscape; most of the nitrate that reaches the groundwater is applied in these areas. Note that a national map (Fig. 15) of aquifer vulnerability to nitrogen enrichment and nitrogen loading (Nolan et al. 1998) depicts Florida as uniformly low intrinsic risk.

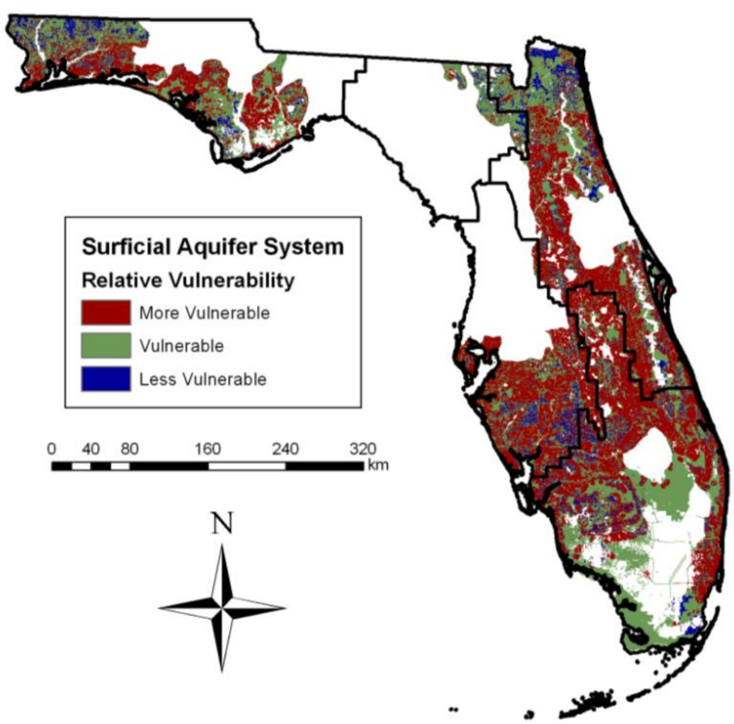


Fig. 12 – Relative vulnerability of the Surficial Aquifer System to pollution from overlying land uses (from Arthur et al. 2005). Areas in white are outside the study bounds.

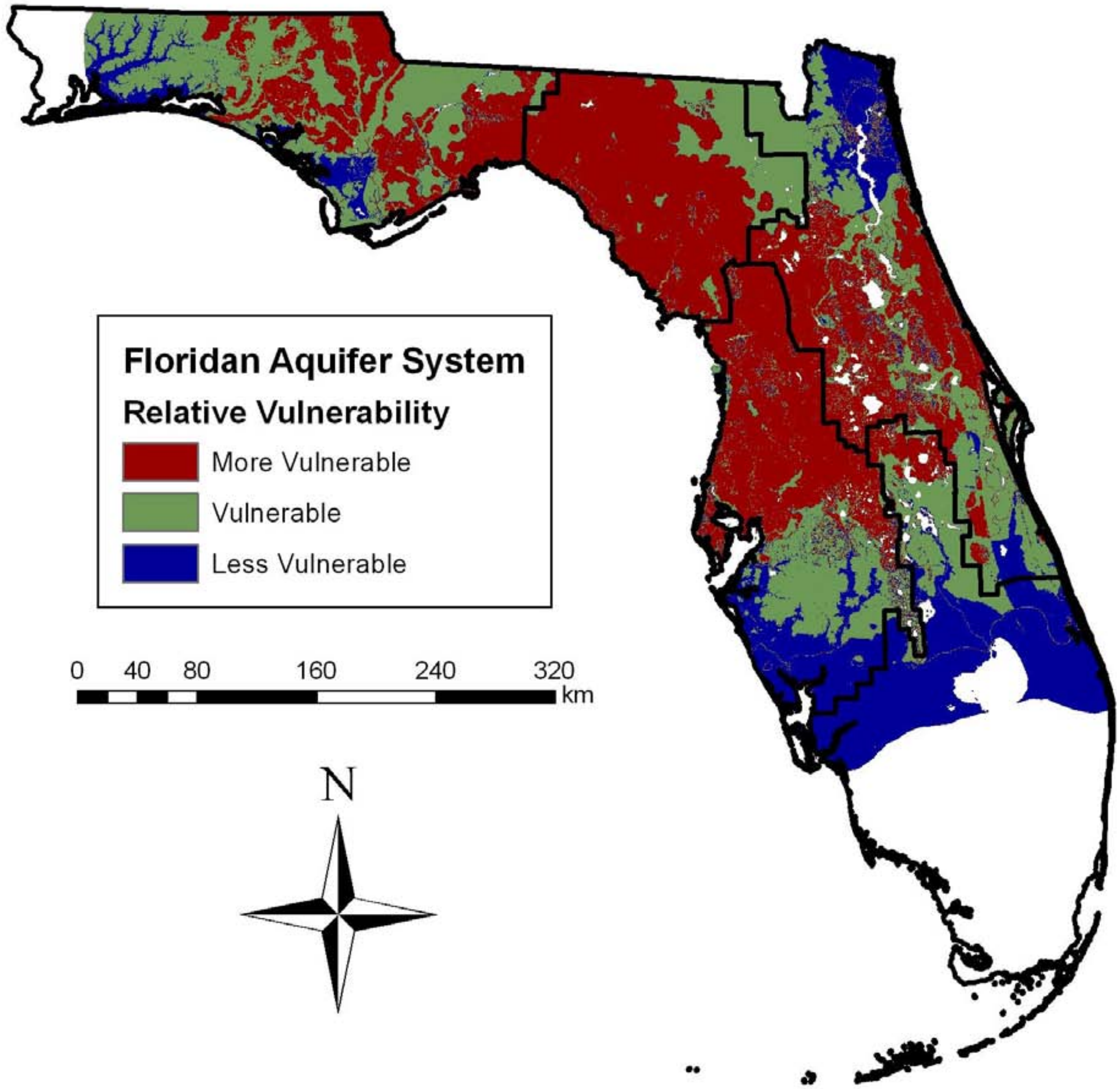


Fig. 13 – Relative vulnerability of the Floridan Aquifer System to pollution from overlying land uses (from Arthur et al. 2005). Areas in white are outside the study bounds.

The Upper Floridan aquifer is the source of water originating from most springs in Florida; exceptions include smaller seeps that emerge from the surficial aquifer and sump/sink/rise systems where surface water descends into the subsurface (and mixes variably with water of the upper FAS) and then reemerges; the most notable example of the latter is the Sink-Rise system of the Santa Fe River, but other rivers exhibit similar behavior. The upper Santa Fe River, a sinking stream, is linked to a resurgent spring, the River Rise, approximately 5.2 km downgradient.

SYSTEM	SERIES	STRATIGRAPHIC UNIT	APPROXIMATE THICKNESS (FEET)	LITHOLOGY	HYDROGEOLOGIC UNIT
QUATERNARY	Pleistocene to Holocene	Undifferentiated post-Miocene deposits	0 - 100+	Marine quartz sand. Also fluviatile and lacustrine sand, clay, marl, and peat deposits.	SURFICIAL AQUIFER SYSTEM
	Pliocene	Undifferentiated Pliocene deposits	0 - 100	Nonmarine clayey sands, red and yellow, fine-to coarse-grained to pebbly, kaolinitic, crossbedded.	
				UNCONFORMITY	
TERTIARY	Upper Miocene to Pliocene (?)	Undifferentiated Upper Miocene-Pliocene deposits	0 - 100+	Marine sands, argillaceous, carbonaceous; sandy shell marl; some phosphatic limestone. Also terrestrial-deltaic (?) interbedded deposits of clay, sand, and sand clay. Phosphatic, including a rubble of phosphate rock and silicified limestone residuum in a gray and green phosphatic matrix.	
				UNCONFORMITY	
	Middle and Lower Miocene	Hawthorn Group	0 - 140	Marine interbedded sand, cream, white, and gray, phosphatic, often clay, green to gray and white, phosphatic, often sandy; dolomite, cream to white and gray, phosphatic, sandy, clayey; and some limestone, hard, dense, in part sandy and phosphatic.	INTERMEDIATE CONFINING UNIT
				UNCONFORMITY	
	EOCENE: Upper Eocene	Ocala Limestone	0 - 180	Marine limestone, white to cream to tan and brown, granular, soft to firm, porous, highly fossiliferous, cherty in places, Lower part at places is dolomite, gray and brown, crystalline, porous.	FLORIDAN AQUIFER SYSTEM: UPPER FLORIDAN AQUIFER
				UNCONFORMITY	
	EOCENE: Middle Eocene	Avon Park Formation	800 - 1,100	Marine limestone, light brown to brown, finely fragmental, low to high porosity, highly fossiliferous (mostly foraminifers); and dolomite brown to dark brown, firm to very hard, low to moderate porosity, crystalline, saccharoidal; both limestone and dolomite are fractured. Carbonaceous or peaty; gypsum present in small amounts,	FLORIDAN AQUIFER SYSTEM: MIDDLE SEMI-CONFINING UNIT
	EOCENE: Lower Eocene	Oldsmar Formation	500 - 650	Marine limestone, light brown to chalky white, porous, fossiliferous, with interbedded brown, porous, crystalline dolomite; minor amounts of anhydrite and gypsum.	FLORIDAN AQUIFER SYSTEM: LOWER FLORIDAN AQUIFER
	Paleocene	Cedar Keys Formation	400 - 700	Marine dolomite, light gray, hard, slightly porous to porous, crystalline, in part fossiliferous, with considerable anhydrite and gypsum, some limestone.	SUB-FLORIDAN CONFINING UNIT

Fig. 14 - Hydrogeologic units in the Silver Springs basin (after Phelps 2004, Scott et al. 2001)

Dean (1999) investigated the extent of surface water and groundwater mixing in this sink/rise system. Based on water temperature delays between the River sink and River rise, the total subsurface travel time of the river ranges from ~ 12 hours to nearly 8 days at high and low stages, respectively. Physical and chemical data indicate that significant surface and groundwater mixing occurs, primarily shown by increases in electrical conductance, decline in dissolved organic carbon content and increases in dissolved calcium. At low river stage, relatively more surface and ground water mixing/exchange occurs, increasing aquifer

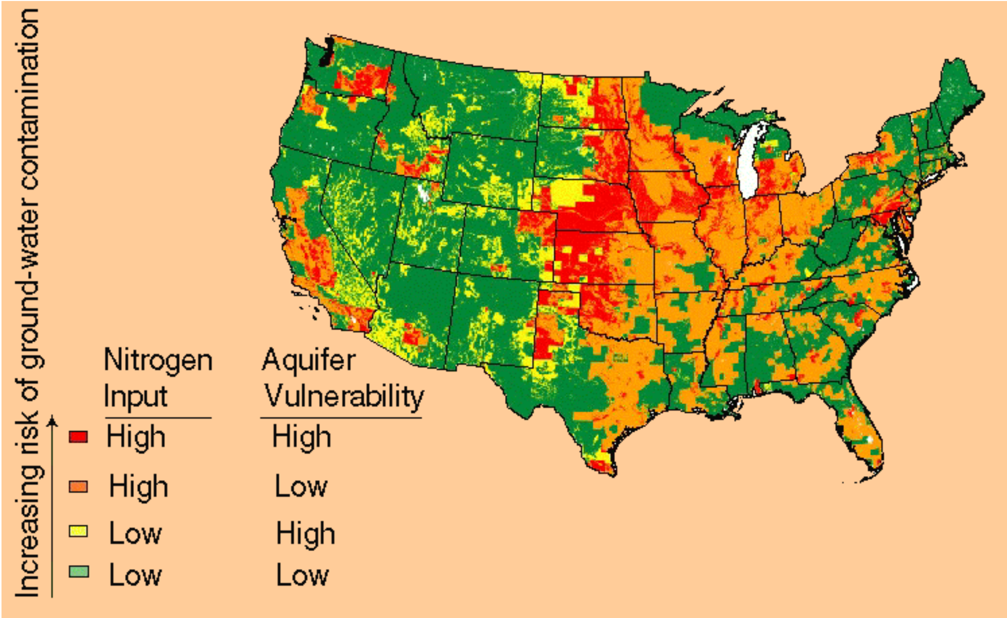


Fig. 15 – National map of vulnerability to groundwater nitrogen pollution; risk is a combination of intrinsic aquifer vulnerability and nitrogen load. (Nolan et al. 1998)

vulnerability to contamination from polluted surface water, while at high river stage, most of the throughflow of water occurs in conduits, limiting mixing rates. However, at high flow, passage of water is from the conduits into the aquifer matrix; while the total volume of water movement is small, any contaminants carried in river water at high flow are likely to remain in the groundwater for a much longer period. Katz et al. (2004) suggested that recharge of recent origin coming from shorter groundwater flow paths and/or from features that are hydraulically connected to the upper Floridan aquifer (e.g., sinkhole) could contribute a larger fraction of total spring discharge during high flow conditions. Regional simulation of groundwater flow systems indicates that first magnitude springs from the Floridan aquifer receive only a small portion of water from upward movement of deep regional reservoirs (Bush and Johnston 1988).

The importance of hydrogeology on NO_3-N concentrations in surface water is exemplified in the Santa Fe River Watershed (SFRW). The SFRW has contrasting hydrogeology, with sandy, well-drained soils connected directly to the unconfined aquifer in the western part, and poorly-drained soils separated from the confined aquifer in the eastern part by a variable thickness clay/sand matrix called the Hawthorn Group. An area of 820 sq mi in the eastern part of the SFRW where the aquifer is confined and surface water dominates transport drains into Santa Fe River (SFR) Reach 1. An area of 546 sq mi in the western part of the SFRW, where the aquifer is confined and the primary transport is via the subsurface, drains into SFR Reach 2. Nitrate-N concentration monitored in the stream water shows very low concentrations in SFR Reach 1 but elevated concentrations in the SFR Reach 2. As a result of concomitant increases in flow volume, NO_3-N loads generated by Reach 2 is substantially higher; river loads in each of the reaches over the last 5 years are summarized in Table 9. Although the SFR Reach 2 occupies only 40.8% of the watershed, it generated an average of 97.8% of the NO_3-N loads contributed by the SFRW to the Suwannee River over the last 5 years. The difference between the NO_3-N loads contributed by the two reaches is attributed to the difference in hydrogeology. The SFR Reach 2 drains the sandy well-drained portion of the watershed with unconfined Floridan aquifer, where NO_3-N in the landscape quickly drains to the groundwater, and remerges to the surface waters via springs. However, areas that drain into the Reach 1 have poorly-drained soil and the Floridan aquifer is confined. Land use activities (crops and improved pasture) and animal activities, which are the sources of NO_3-N in the SFRW (Lamsal et al. 2006) are expected to load at similar rates between reaches, the capacity of the landscape to denitrify is dramatically different, resulting in massively accelerated transport in Reach 2.

Katz et al. (2001) investigated the interaction between surface water from the Little River and ground water in karst areas in northern Florida. The Little River, an ephemeral stream that drains a watershed of 88 km^2, disappears into sinkholes along the Cody Escarpment (the transitional zone between confined regions and unconfined regions where the Hawthorn Formation is being actively eroded) and recharges the upper Floridan aquifer. During high flow conditions in the Little River, the water chemistry of some of the wells close to the sinkholes changed, indicating the mixing of groundwater with river water. Based on tracer studies, the proportion of river water that mixed with groundwater ranged from 0.13 to 0.84. Further, water levels in wells established close to sinkholes increased following recharge from the Little River, indicating rapid response and susceptibility of the unconfined aquifer to contamination.

Table 9. Nitrate-N loads (kg) generated by the two reaches of the Santa Fe River Watershed during the year 2001-2005 (Data sources: Hornsby et al. 2002, 2003, 2004, 2005; Mirti and Mantini 2006).

Santa Fe River	2001	2002	2003	2004	2005
Reach 1	4	3	29.6	15	56
Reach 2	475	581	696	1128	1302

Land use induced vulnerability

Land use and land use change has implications for NO_3-N contamination. Numerous studies (e.g., Spalding and Exner 1993, Halberg and Keeney 1993, Hudak 2000, Harter et al. 2002) have shown that agricultural activities are the main source of elevated NO_3-N concentrations in ground water. Forest and natural ecosystems are in relative balance between nutrient inputs and uptake, and allow little NO_3-N to escape from the root zone (Morris 1981, Johnson 1992). The disturbance of natural systems that affect N cycling leads to N losses, usually as NO_3-N, to groundwater. Therefore, land use change greatly influences NO_3-N concentrations in groundwater and surface waters. Deforestation leads to decreased evapo-transpiration, and as a result, significantly greater quantities of water drain from the forest system. The organic matter contained in the top layer of forest soils mineralize and NO_3-N is carried away along with draining water. However, the increase in NO_3-N loss following disturbances for most systems (e.g., deforestation) is less than 10 kg/ha/year, and soil solution NO_3-N concentrations are very rarely greater than 10 mg/L (Hallberg and Keeney 1993). While the mobility of NO_3-N leaching from forests makes it a threat to groundwater, this source is small compared to agricultural sources that involve fertilization and animal activities. Further, work by Vitousek and Matson (1985) demonstrated that microbial immobilization of elevated nitrate levels after clear-cutting was rapid and significant, limiting transport of nitrates in soil pore water to hydrologic conveyances.

Boyer and Pasquarell (1995) studied the impact of agricultural activities on NO_3-N pollution of springs in the karst region of southeastern West Virginia, where an estimated one third of the region's farm cattle and agricultural market value are located on karst terrain. The results show strong relationships between percent agricultural area and NO_3-N concentration in springs. The median NO_3-N concentration in springs increased at about 0.19 mg/l per percent increase in agricultural land, concluding that agriculture was significantly affecting NO_3-N concentration in the karst aquifer. Similarly, in areas with mixed land use systems and unconfined aquifer, Postma and Boesen (1991) found plumes of NO_3-N emanating from the arable lands and spreading through the aquifer, while the groundwater derived form forested areas was virtually free of NO_3-N. Panno et al. (2001) sampled groundwater discharging from 10 springs in the southwestern Illinois sinkhole plain during four consecutive seasons – fall (November 1998), and the winter (February/March), spring (May) and summer (August) of

1999. Nitrate-N concentrations in this predominantly agricultural basin ranged from 2.28 to 7.48 mg/l, and were above the 1.4 mg/l threshold for background concentrations. Isotopic information suggested that fertilizer was the primary source, though that signal fluctuated markedly in time.

Agricultural activities consisting of cropland farming and animal farming operations (beef and dairy cows, poultry, and swine) along with atmospheric deposition have contributed large quantities of N to groundwater in the Suwannee River Basin in northern Florida (Katz et al. 1999). In an investigation into the sources of NO_3-N in the karstic springs of Florida, Katz (2004) found that the spring waters with highest NO_3-N concentrations (Jackson blue spring with 3.1 mg/l and Fanning spring with 4.2 mg/l) had very high percentages of the springshed under agricultural land use (55 and 49%, respectively). The Jackson Blue springshed had almost 97% of the agricultural land under crops (i.e., vs. pasture), and low $\delta^{15}N$ value (2.6‰) which indicates that the NO_3-N in the spring originated from inorganic fertilizers. However, Fanning springs had higher $\delta^{15}N$ value (7.2‰) which could be related to lower percentage of cropland (about 60%) in the springshed, and a higher contribution from organic sources of N like manure, wastewater or septic tank effluent. These results suggest that elevated concentrations in the groundwater and spring water of the karst spring systems in Florida are related to agricultural land use and wastewater effluent (sprayfields, reclaimed water applications, septic tank drainfield leachate). The combination in many of these springsheds of land uses contributing high NOx loads, and extremely limited attenuation potential because of edaphic and hydrogeologic conditions makes these areas of primary importance from a management perspective. Tracing groundwater flowpaths and determining attenuation rates along those flowpaths as a means of determining direct spring effects could be an important part of the land planning process in the future, but will require substantial improvement in our ability to measure and model the transport phenomenon. Case studies of N pollution from various sources in a subsequent section are examined.

Time lag induced vulnerability

Nitrate-N released from its source (croplands, feedlots, sprayfields, septic tanks, etc) may leach to groundwater, flow as an essentially conservative solute in groundwater, and re-emerge to the land surface via springs or seeps to lakes, rivers and the near shore marine environment (submarine groundwater discharge). Where this reemergence occurs is of critical importance (springs vs. riparian wetlands), as is when it reemerges (seasonal denitrification variability). Here the implications of how long it takes that dissolved mineral nitrogen to arrive are discussed. The time between release of NO_3-N to the environment and its potential reemergence in surface water is related to the groundwater transit time, which can be defined as the nominal time between recharge and discharge. In reality, any parcel of groundwater may move at differential rates because of, first, the enormous heterogeneity in the structure of the karst aquifer, which has multiple preferential flow paths, and second, spatially and temporally variable hydraulic gradients in both surficial and karst aquifers. As a result, residence time of water in the subsurface is a statistically distributed value, and is unique to each area; tracer tests are required to estimate this transit time probability density function, but even these synoptic observations are of limited generality when considering nominal residence times under different flow regimes, even at the same location. Evidence from the sink-rise system on the Santa Fe River (Martin and Dean 2001, Martin and Screaton 2001) suggests that mixing between conduits and matrix can reverse (water from the matrix entering conduits vs. water from conduits entering matrix) under different flow regimes, substantially affecting the storage time of water in the subsurface.

However, as a general rule, groundwater transit times don't impact NO_3-N loadings directly, because the NO_3 ion is functionally inert in groundwater, and no significant attenuation occurs with additional residence time. However, water emerging in a spring is frequently a blend from numerous sources (Katz et al. 2004), all of which have characteristic nominal residence times and different nitrate loading rates. Some water may be of recent origin (days to weeks) and be of substantially different quality than other sources that might be older (months to years, and in some cases, much older). As a result, inferring an association between contemporary land use conditions and water quality may be confounded by the age of the water.

This is possibly relevant in two ways; first, if the water that has been substantially enriched is of younger origin, reflecting localized and contemporary land use conditions, the nitrate concentration will be diluted by older water, tending to mask the dynamic signal. In this case, hydrogeochemical signature analysis could be used to partition aggregate flows into constituents. The primary risk emerging from this scenario is that low-temporal resolution synoptic sampling (monthly or quarterly) could fail to measure the effects, leading to underprotection of the resource. A second scenario is where the enriched water is primarily of older origin, and the dilution in the spring discharge is from water of more recent origin. In this scenario, the implications for management are possibly more problematic because the older water will carry the signature of nitrates from the landscape some period ago (years, decades in some cases) meaning that contemporary discharges are not fully reflective of the anthropogenic influence of contemporary land use, and, further, efforts to mitigate for elevated nitrate loads might not have a measurable effect for a period similar to that groundwater transit time. Clearly, efforts to understand residence times and mixing are essential for both identifying sources and setting realistic desired management outcomes.

Katz (2004) found a statistically significant ($p<0.05$) inverse correlation between mean transit time of groundwater and NO_3-N concentrations measured in the first magnitude springs in the karsts regions of north central Florida, suggesting that elevated nitrates are found in more recent recharge.

Based on multi-tracer analysis, the nominal age of groundwaters discharging from the large karstic springs of Florida ranges from 5-35 years (Katz 2004). It is important to reiterate that this is, statistically, a mixing of multiple end-members of different ages. While this average age estimate certainly supports the contention that NO_3-N can persist in groundwater, it does not suggest that the nitrates in contemporary discharges were delivered to the groundwater system in 1971. On the contrary, the age-concentration relationship that Katz (2004) reports suggests that it is younger water that is the delivery mechanism for enrichment; anecdotal evidence from Manatee Springs in Levy County suggests that nitrate loads elevate within hours of fertilization on a nearby golf course (Dr. Jim Sickman, personal communication). Recent changes in land use in some springsheds (e.g. Apopka Springs) have resulted in systematic albeit slight declines in nitrate concentrations (from ~5 ppm NO_3-N in 1995 to ~ 4 ppm in 2005) despite age dates suggesting a nominal age of spring water of 24 to 46 years (Springs of the SJRWMD - http://www.sjrwmd.com/programs/plan_monitor/gw_assess/springs/lake/apopka.html).

Katz et al. (2001) estimated that the average ages of groundwater discharging in the springs of the Suwannee and Lafayette County (Middle Suwannee River Basin) at or near base-flow condition were between 10 and 20 years, with lower years corresponding to smaller springs. This suggests that the peak flows in springs are dominated by younger groundwater, which is expected to have higher nitrate concentrations. Katz et al. (1999) compared the long-term trends (1955-1997) of NO_3-N concentrations measured in spring waters with the estimated inputs of N from various sources in Suwannee and Lafayette counties. In Suwannee County, decreasing

NO_3-N concentrations in spring waters followed a decrease in estimated fertilizer use from the mid 1970s to the early 1990s. Similarly, increasing NO_3-N concentrations in spring waters of Lafayette County followed a steady increase in fertilizer use from the early 1960s to the mid 1990s. These findings, though inferential, suggest that knowledge of groundwater residence times can be used in association with the chemistry of groundwater to relate contemporary loads to past contamination.

Van Herpe and Troch (2000) observed a positive correlation between surface water NO_3-N concentrations and discharge, further reinforcing the hypothesis that nitrate transport is driven by short-residence time peak flows, not long residence time baseflows. Further, the NO_3-N vs. discharge relationship was characterized by hysteresis in peak concentration levels; that is concentrations during a specific hydrograph are not uniform with flow. In particular, as flow initially increases during a peak flow event, nitrate concentrations do not; increases in nitrate concentrations occur sometime after flows begin to increase. This characteristic behavior, where NO_3-N peak concentrations lag behind discharge peaks, has been observed elsewhere (Johnes and Burt 1993, Creed et al. 1996), and is called a "flushing effect". The most obvious explanation for this process is based on hydrologic delivery from the surface and vadose zone, and comparative NO_3-N concentrations thereof. Peak flow results from surface runoff as well as increased surface drainage. However, surface runoff, which contains relatively lower concentrations of nitrates, occurs rapidly compared to subsurface drainage, which is expected to transport the bulk of the nitrate. Immediately following a storm event, direct runoff will contribute to discharge more than subsurface drainage, yielding lower nitrate loads. As subsurface fluxes reach the major conveyances (aquifer conduits), increased NO_3-N leached from the soil profile will be delivered. Van Herpe and Troch (2000) observed that this time lag was longer during summer than in winter. Process-induced time lags are primarily relevant to understanding loads. Because observations of water quality are frequently done synoptically, and rarely at high resolution, there remain significant unknowns about the dynamics of loads, and particularly the relative importance of extreme events in total system loading. Vulnerability to a particular intensity of springshed land uses may be understated if the bulk of the contamination is not captured by standard monitoring procedures.

NITRATE TRANSPORT AND TRANSFORMATIONS

Transport of Nitrate-N in the Environment

The nitrate (NO_3^-) ion is negatively charged, so is not attracted to soil cation binding sites; further, it has weak affinity to anion binding sites (e.g., compared with phosphate or sulfate). Further, it is highly soluble in water (saturation of 1 g KNO_3 occurs in 3 ml of water), which makes it susceptible to leaching through soil along with infiltrating water. There are five possible fates of NO_3-N that leaches below the root zone: export in groundwater (vertical or horizontal), retention on anion exchange sites (limited), assimilation into microbial biomass, dissimilatory NO_3-N reduction to ammonium (DNRA), and denitrification (Korom 1992).

Nitrate attenuation is predicated on biological processes; as such, where there is a source of NO_3-N in excess of plant and microbial immobilization rates, water infiltrating through the soil profile will entrain nitrates and eventually reach the groundwater; passage to the Floridan aquifer will depend on aquifer confinement, which is regionally variable, but nitrates in water below the organic matter sources of rooting zone will be effectively inert and will eventually re-emerge at the surface. In areas where this occurs in wetland seeps and riparian buffers, ecological attenuation is possible before loading to aquatic systems; this tends to be in areas where the nitrates only reach the surficial aquifer because of a confining layer. Where water and dissolved nitrates percolate down to the Floridan aquifer, emergence will occur in springs, where limited organic carbon availability will constrain attenuation, and aquatic systems will receive the load.

As such, the key processes regulating nitrate transport in the environment are related to the soil; soils that are well drained and/or have low organic carbon content will tend to permit more rapid and complete transport of any nitrate loads, while landscapes with poor NO_3-N leaching (due to poor drainage and elevated levels of soil biological activity) will generally show dramatically higher nitrate retention. In landscapes with the latter qualities, attributes such as distance to streams, slope, transmissivity of the soil/vadose zone material and hydrologic inputs will markedly affect water movement, and NO_3-N mobility. In general, management can accelerate nitrate removal (see section in this document on landscape sinks); however, management interventions are most feasible in areas where the geology permits surface water retention. In areas where this is not the case (unconfined karst aquifers), many of the conventional off-site solutions to nitrate management (Mitsch et al. 2001) will not work.

While on the surface, NO_3-N moves dissolved to surface water bodies (streams, rivers and lakes); because the nitrate ion does not bind effectively to organic or mineral surfaces, there is no particulate load, as there is with phosphates. However, because of biologically-induced transformations between N species (e.g., DON, ammonium, nitrate), there is active nitrate removal in surface waters. For example, Kellman and Hillare-Marcel (1998) showed that denitrification can play an important role in reducing NO_3-N levels during stream transport, with up to 50% *in situ* NO_3-N losses over a 600 m distance downstream in a headwater (1st order) stream. Denitrification in streams tends to be higher during late summer and early fall when water levels are reduced, contact time between stream waters and streams sediments is increased, and senescing leaves provide an ample carbon source (Kellman and Hillare-Marcel 1998). Peterson et al. (2001) used isotopically-labeled nitrogen in stream systems to show that headwater streams in particular were reactive with respect to N, but that even in these systems, nitrate transport was an order of magnitude greater than for other species of N (spatial turnover was on the order of hundreds to tens of thousands of meters).

Nitrate in water recharging surficial or deep aquifers is expected to re-emerge at the land surface along with discharge waters in springs and lakes. This is due to chemical inactivity of the nitrate ion in geologic substrates (negligible absorbance to anion binding sites) and biological inactivity below the root zone due to the absence of organic matter to drive denitrification (Canter 1996). In the absence of transformations, delivery of nitrates from groundwater sources to surface water sources depends on the hydraulics of the particular aquifer. Groundwater flow patterns and velocities are highly sensitive to hydraulic conductivity of the medium (Alley 1993).

Stainton and Stone (2003) summarized the effect of aquifer substrate on nitrate transport. Their study, which primarily was focused on investigation of the effect of riparian buffers and adjacent land use on NO_3-N transport in shallow groundwater at the stream-riparian interface, demonstrated (Table 10) that high porosity materials tend to accelerate transport of nitrates; the relative influence of reduced contact time vs. increased DO or reduced organic matter content was not discussed. Similarly, Groffman and Tiedge (1989) showed that permeable substrates tend to result in reduced denitrification rates; Gillham (1991) showed that sandy substrates increased the rate of NO_3-N movement in shallow groundwater, and reduced residence times (Willems et al. 1997) relative to other study sites.

Table 10. Daily NO_3-N loading at the stream riparian interface at stream-riparian interface of an urbanizing catchment in Laurel Creek catchment, Ontario (From: Stainton and Stone 2003).

Magnitude of loading	Site	Substrate	NO_3-N loading (mg/d)
Very low	5A	Silt / clay	< 0.1
Very low	5B	Silt / clay	< 0.1
Very low	5C	Silt / clay	< 0.1
Very low	6C	Silt / clay	< 0.1
Very low	7A	Silt / clay	< 0.1
Very low	7C	Silt / clay	< 0.1
Low	6A	Mixed	0.4 – 6.0 (2.6)
Low	6B	Organic	0.0 – 0.5 (0.1)
High	9A	Sandy	489.9-1869.5 (946.2)
High	9B	Sandy	324.6-1362.1 (690.7)

Transport of Nitrate-N in karst landscapes

The term karst is used to describe a geologic matrix comprised of limestone or other highly soluble rock (dolostone), in which the origin of landforms is predominantly the result of dissolution processes, and in which drainage is primarily underground in fissures and conduits that have been created and are enlarged by dissolution (Drew 1999, Copeland 2003). The dissolution process begins as acidified rainwater percolates downward through the soil. Soil also contains CO_2 generated during the decay of organic matter, which makes the percolating water weakly acidic (pH ~ 5.1) by formation of carbonic acid ($H_2O + CO_2 \rightarrow H_2CO_3$). Further, dissolved organic matter created during soil humification is weakly acidic and can drive the dissolution of carbonate minerals. The action of acidic rainwater and dissolved organic acids dissolves the limestone and produce fissures in rocks (Johnson and Quinlan 1995). Features such as sinkholes, springs, conduits and caves may be present in a karst terrain but not obvious. When karstified rock is overlain with non-carbonate strata or unconsolidated deposits, it is termed a covered or mantled karst. Material overlying a karst matrix that is a weathered derivative thereof is called epikarst; in portions of Florida where aquifer confining units have been eroded away, epikarst is the geological source material for the surface soils (Inceptisols).

In karst systems, surface water readily enters the groundwater via sinkholes, sumps and solution features, and the groundwater emerges to the surface via springs, and such free exchange between surface and groundwater enhances mobility of NO_3-N in the environment. The upper Floridan aquifer (UFA) is a karst system comprised of a limestone aquifer mantled by a thin layer of highly permeable sand. Recharge water along with contaminants can infiltrate rapidly through the highly permeable sand that mantles the UFA. The high degree of interactions between ground water and surface water typically result in a single dynamic flow system in many watersheds in Florida (Katz et al. 1997).

The transport of NO_3-N in groundwater greatly varies in karst landscapes, and is related to groundwater transit time; our discussion of groundwater age (in Time Lag Induced Vulnerability, above) presented evidence that the mixing of water of different ages that occurs in the subsurface is an important component of understanding the loads that emerge. In an unconfined aquifer, groundwater transit times can greatly vary based on fracture vs. matrix vs. conduit flow paths and the dynamic interplay between these as a function of potentiometric surface. Using multiple tracer techniques, the average ages of groundwater discharging from the first magnitude springs (discharge $\geq 2.8\ m^3/s$) springs of the Suwannee River Basin at or near base-flow conditions were between 10 and 20 years, with lower ages corresponding to smaller springs (Katz 2004).

In the Woodville Karst Plain (WKP) in northwest Florida, the estimated age of groundwater in the spring is between 4 and 90 years (Katz et al. 2004); as before, however, this is a composite of water of different ages, and the source of contamination may be younger water, diluted by much older water (Katz 2004). Dynamics of variation in groundwater age indicate the relative contribution of water flow from conduits, fractures/fissures, and limestone matrix.

The implications of these temporal mixing dynamics on nitrate loading are not clear. An inverse relation ($r = -0.17$) between groundwater NO_3-N concentrations and mean age is suggestive of a mixing dynamic that blends high nitrate young water with lower nitrate old water, but the residuals to this relationship are large and unexplained. Part of the uncertainty arises from incomplete knowledge of transit times for water from various parts of the springshed, and possibly from a poor understanding of the transport links between surface and subsurface water. Further, changes in the way the landscape modulates interactions between the surface and subsurface (e.g., via increases in impervious surfaces) alters the relationship through time.

Nitrate-N Transformations

In aquatic systems, net productivity may be double that of terrestrial ecosystems. Furthermore, utilization and turnover of N in aquatic systems is more rapid than that of terrestrial systems (Heathwaite 1993). A crucial difference between aquatic and terrestrial ecosystems is that N additions do not commonly stimulate growth in freshwater aquatic systems, as seems to be the case in many terrestrial systems (Stoddard 1994), where N is frequently the constituent most limiting production. Fig 16 illustrates N speciation and transformations in an aquatic system. The transformation processes involved are: fixation, nitrification, assimilation, denitrification, and mineralization or ammonification.

These general processes were previously presented (Fig. 4). In brief, during N fixation, molecular N is converted to NH_3 by bacteria. On an annual basis, total N fixation in aquatic systems rarely exceeds 20 kg N/ha (Royal Society 1983). Microbial decomposition converts organic N to ammonia forms by the process of mineralization or ammonification. Ammonium is the dominant form of N assimilated and immobilized by microorganisms (Recous et al. 1988). Ammonia is converted to NO_2-N and NO_3-N through a two stage oxidation process of nitrification, which is mediated by species of bacteria of the genera *Nitrosomonas* and *Nitrobacter*. These organisms are strict aerobes, requiring minimum oxygen concentrations around 2 mg/l to function efficiently (Heathwaite 1993). Consequently anoxia can limit nitrification leading a buildup of ammonia and dissolved organic N. Nitrates are highly soluble and move along with surface or groundwater. Under anaerobic conditions, NO_3-N can be converted to biologically inert N_2 gas by the microbially mediated process of denitrification. Denitrification is an important mechanism for NO_3-N removal from the aquatic system, but is limited by its requirement of anaerobic conditions and labile carbon supply.

Denitrification is affected by availability of labile organic matter, because that is what sustains the microbial population, providing the electron donor for heterotrophic production. Davidson and Ståhl (2000) compared denitrification rates under different levels of organic matter content. Highest NO_3-N removal rates were found in organic soils and lowest rates were found in sandy soils, indicating the stimulatory effect of peat C source on denitrifying bacteria. Denitrification is a heterotrophic process, and several studies have reported positive correlation between denitrification and NH_4^+ production (Davidsson et al. 1997, Davidsson and Stahl 2000). As such, high NO_3-N removal rates can be coincident with high dissolved organic N and NH_4^+ release on a short-term basis; however, in the long term, denitrification is a permanent N sink.

In the karst matrix and conduits of the Floridan aquifer, there is a paucity of organic C, in part because of congruent dissolution of limestone by organic acids. This absence of electron donors, which is demonstrated visually by the clarity of spring water under nearly all flow regimes, is the primary limiting factor for denitrification in the groundwater. As such, NO_3-N has to be removed from enriched waters at the surface prior to percolation into the Floridan aquifer. In some parts of the state (i.e., where an aquitard between surface water and the Floridan exists), this occurs naturally; in other regions (i.e., where the Floridan is unconfined), there are no natural zones for denitrification to occur, suggesting that either they need to be engineered into these vulnerable landscapes, or excessive N loading needs to be avoided.

Denitrification tends to be substantially enhanced in flooded soil, wetlands, and riparian zones. Tidal wetlands, which become alternately anaerobic and aerated as the water level rises and falls, have particularly high potentials for converting N to gaseous forms (Brady and Weil 1999). This beneficial ecosystem function protects estuaries and lakes from eutrophication; many authors have pointed to the loss of wetlands (both inland and coastal) as the ultimate cause of prolonged and spatially extensive hypoxia in the Gulf of Mexico.

Several factors can lead to changes in NO_3-N concentrations along a stream length. NO_3-N can be assimilated by plants during transport; NO_3-N concentrations may drop if stream water is being diluted by groundwater with low NO_3-N concentrations; further, NO_3-N may be reduced due to transport into anoxic system sediments zone where denitrification occurs. Denitrification can also occur in stream sediments during transport; however, relatively high O_2 diffusion rates into the sediments from the overlying water may limit denitrification rates in stream sediments (Knowles 1982). Denitrification is highest in headwater streams and wetlands (Peterson 2001), likely because of the higher surface area per flow volume in small stream, and also contact with zones where carbon availability due to allochthonous inputs are high, and canopy shading limits photosynthetic contributions to DO concentrations.

Organic sequestration of N, another path for transformation of nitrates, takes place by uptake and metabolic use of mineral N (either ammonia or nitrates) by plants and soil microbes. Terrestrial assimilation is a major form of N removal in watersheds and may be sufficient to prevent all atmospherically derived N from reaching receiving water bodies (Vitousek 1977). However, during winter months, most forested watersheds undergo a dormant period, or at least a period of reduced growth, leading to reduced ability of watershed to retain N. This seasonality is responsible for the commonly observed pattern of higher surface-water NO_3 concentrations in winter and spring than in summer and fall. On the other hand, concentrations of NH_4^+ in surface waters are rarely elevated at any season because soil cation exchange, low mobility, and competition among vegetation, mycorrhizal roots, and nitrifiers all contribute to watershed NH_4^+ retention (Stoddard 1994). Smith (1987) observed that during long-term aerobic incubation of soil with periodic leaching, dissolved organic N (DON) was produced between leaching episodes, although most of N was removed as NO_3. Further, DON was not susceptible to mineralization, which could imply that DON is stable in soil, and possibly in streams and rivers.

Although there is a general trend relating net mineralization/immobilization to the C/N ratio, there is no critical value that marks the point at which reversal from immobilization to mineralization occurs (Vinten and Smith 1993). The C/N ratio of the decomposing organic matter has a major influence on the balance between mineralization and immobilization, with low ratios resulting in net mineralization and high ratios resulting in net immobilization.

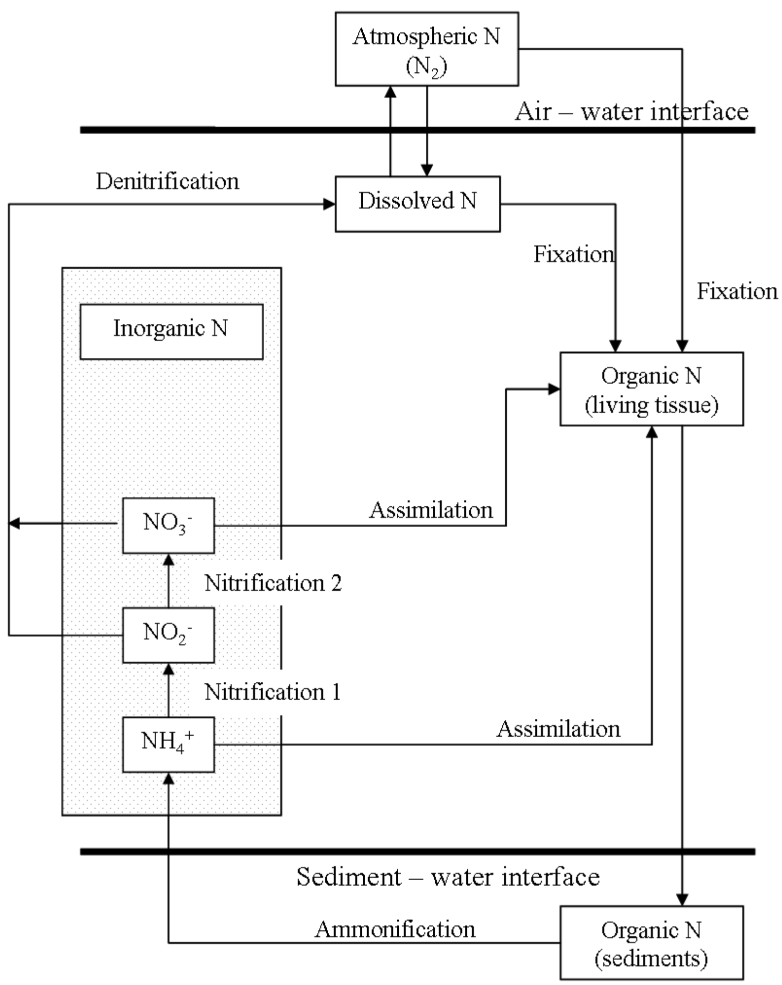


Fig 16. The aquatic N cycle (Adopted from Heathwaite, 1993).

Overall, transformational processes are limited to areas with high ecosystem reactivity. In Florida's groundwater, where organic matter is characteristically absent, there is extremely limited transformation potential, and transport is generally rapid and unattenuated. Transformation of nitrate in wetlands, another hallmark feature of the Florida landscape, is rapid and, thus, important for basin-scale biogeochemistry; nitrate loads are dramatically lower in areas where wetlands are dominant features of the landscape. It is landscape division into areas where surface water persists (confined regions) and where it does not (unconfined regions) that drives transport and transformational processes that ultimately affect nitrate delivery in springs.

SINKS FOR NITROGEN IN THE LANDSCAPE

N input to a watershed can end up in groundwater, soil organic matter, or biomass, or be converted to gaseous forms and released to atmosphere, or discharged to lakes, streams and rivers. From the perspective of a total landscape nitrogen budget, N removal from agricultural lands by harvest of crops and by grazing animals is among the most important fluxes; however, much of this material is returned to the landscape in the form of manures, composts, and wastewater effluent (sprayfields, septic tanks, etc.). From a water quality management perspective, the most important sinks for N are those that represent terminal sinks (e.g., atmospheric sinks, long term depositional sink in peat and/or sediments). For example, nitrogen in livestock waste can be lost by volatilization as NH_3 before or after application to croplands, but this typically represents a small fraction of the total load. Similarly, long-term sedimentary sinks in the Florida environment are limited; wetland peat accretion may represent a small sink, but compared with the total loads, stocks are small (Mitsch and Gosselink 1993). There are no deep lakes that will store organic N in lacustrine sediments, and geochemical sinks for nitrate are negligible. As such, the relevant sinks for N management are of biological origin (mineralization, immobilization, denitrification).

Among the most active sites for denitrification are wetlands; in particular, riparian (streamside) areas and isolated wetlands are significant sinks for NO_3-N because of their combined characteristics of anoxic conditions and carbon source availability. Research has shown that riparian forests located on the lowland sides of agricultural fields in the mid-Atlantic Coastal Plain have been shown to retain and/or denitrify up to 70 to 90% of the total N inputs (Jordan et al. 1993). Because nitrates are highly soluble and highly mobile, their propensity to readily leach into the groundwater is large. Once there, their fate is related to groundwater residence time, aquifer geochemistry, interactions between groundwater and surface water, and N source type (Hallberg and Keeney 1993, Katz et al. 1999). In Florida, these variables coincide to make subsurface sinks small compared to load, which leads to significant export rates.

Ecosystem Reactions

Denitrification is a naturally mediated reaction of the ecosystem to increased NO_3 concentrations, where NO_3 is reduced to N_20 then N_2 (in fact, the rate of intermediate nitrous oxide gas production is the basis of one type of denitrification measurement – Yoshinari et al. 1977). The four general requirements for denitrification are (i) N in oxidized mineral form (NO_3, NO_2, NO, and N_2O) as terminal electron acceptors, (ii) suitable electron donors (primarily heterotrophy using organic C; negligible autotrophy), (iii) the presence of bacteria possessing the metabolic capacity, and (iv) anaerobic conditions or restricted O_2 availability to permit thermodynamically favorable conditions for use of mineral N as terminal electron acceptor.

Once NO_3-N is leached below the root zone, there are four possible fates for NO_3-N: soil retention, assimilatory reduction into microbial biomass, dissimilatory NO_3-N reduction to ammonium (DNRA), and denitrification (Korom 1992). In most cases, denitrification dominates, and is increasingly recognized for its ability to eliminate or reduce NO_3-N concentrations in groundwater. For substantial NO_3-N reduction to take place in aquifers there must be adequate reduction potential within the sediments. Organic matter is the primary substrate necessary for this reduction; autotrophic denitrification can proceed with pyrite, and Fe(II)-silicates as the electron donor (Postma and Boesen 1991); while these compounds are found in abundance in some aquifers, the karstic aquifers of the Florida peninsula are not rich in these materials. Consequently, autotrophic denitrification is negligible.

Reactivity in the Subsurface

As has been discussed already in this report, aquifer processing of nitrates is limited strongly by availability of labile organic carbon that is a necessary ingredient for heterotrophic denitrification (Groffman et al. 1992, Lowrance 1992). Further, autotrophic denitrification relies on electron donors that are rare in the Florida environment.

Several authors have demonstrated that, under certain conditions, aquifer processing can be significant. For example, McMahon and Böhlke (1996) examined denitrification and hyporheic zone mixing in a South Platte River alluvial aquifer in Greeley, Colorado, and effects on NO_3-N loading to the river by ground-water discharge. The aquifer depth ranged from 0-2 m below land surface in the floodplain deposits to 5 to 15 m deep in the terraces. Median NO_3-N concentrations in adjacent floodplain deposits (6.80 mg/L) and riverbed sediments (6.45 mg/L) were lower compared to the median concentration in terrace deposits (26.0 mg/L), primarily because of denitrification activity. Results indicate that denitrification and mixing within alluvial aquifer sediments substantially decrease NO_3-N load to rivers from ground water.

In contrast, denitrification rates in the karst matrix underlying a citrus operation in west Florida were attenuated compared with surface rates (McNeal et al. 1995), reinforcing the general conclusion of this document that nitrates are effectively inert when outside the organic-rich soil and vadose zones. Nolan (1999) used a survey of wells sampled between 1993 and 1995 throughout southeastern USA to examine nitrate-attenuation processes in aquifers. That study found oxidizing conditions (evaluated using DO concentrations) and DOC were negative covariates with nitrates, and that iron, manganese and ammonium are similarly negatively associated; all of these variables with the exception of oxidation-reduction status (which is highly variable) are expected to be low in Florida waters, resulting in limited nitrate processing in the aquifer. Denitrification was inferred to be inversely correlated with calcium, alkalinity, specific conductance and pH, all of which are expected to be high in Florida's groundwater.

Zones of Enhanced Reactivity: Wetlands

Wetlands are among the dominant features of the Florida landscape in areas where infiltration of rainfall is restricted by subsurface confining layers; the combination of high rainfall, reduced infiltration and low relief means that the landscape stores water in numerous locations on the surface. The resulting wetlands are critical components of the landscape nitrogen budget. For example, studies have demonstrated that riparian zones can be highly effective at nitrate removal, with removal efficiencies greater than 80% (Simmons et al. 1992; Jordan et al.1993). In this section, the role and rates of wetland N attenuation is examined. However, it is critical to be clear at the outset: the absence of wetlands in areas where the confining layer is absent limits denitrification potential there. These areas are desirable for agriculture (low risk of flooding) but generally possess soils that require substantial nutritional amendment for agronomic production. As a result of the lack of impedance of infiltration by geologic confining layers, nutrients entrained by leaching water are delivered directly to the aquifer; these areas are the presumptive source of most of the nutrients emerging in springs. As a result, despite their elevated reactivity with respect to nitrogen, wetlands are unlikely to be a part of nutrient load management options in unconfined regions of the state.

Nitrate-N present in water moving through wetland systems zones are subjected to plant uptake, denitrification, and microbial immobilization, which results in significant attenuation of NO_3-N concentrations. Wetlands are so effective at removing N that many believe that it is the loss of wetlands as much as the elevated use of fertilizers that has led to anoxic conditions predominating over large near-shore areas of the Gulf of Mexico (Mitsch et al. 2001). In a wetland ecosystem, denitrification varies in response to water levels, sediment C content and quality, and the nature of ecosystem N cycling (Groffman 1994). Because assimilation into plant and microbial biomass is eventually released as that organism senesces, denitrification is the primary loss pathway in wetlands (Bowden 1987). Soil storage may be locally significant in areas accreting peat, but generally, rates of N accretion in soils are slow relative to the flux of N through ecosystems. Wetlands are ideal settings for N removal because of the preponderance of aerobic and anaerobic micro-sites that facilitate nitrification and denitrification, respectively, and the potential assimilatory sink in accreted peat.

All wetlands are expected to be active sites for denitrification, if nitrate loading occurs. Mitsch et al. (2001) summarized the literature on wetland processing rates (Fig. 17) to determine the area of wetland restoration necessary to attenuate the N loading to the Gulf of Mexico. Despite the expected potential reactivity, nitrates are not delivered to wetlands at equal rates. For example, isolated wetlands might be uniquely valuable sites for denitrification because of long contact times and oxic-anoxic zones in close proximity, but typically loads of nitrogen to these systems are small by virtue of their landscape position. Whigham and Jordan (2003) report, however, that the hydrologic modification of isolated wetlands results in significantly elevated nutrient export, indicating that their role in landscape protection of water quality might be understated, an important point given the relatively low regulatory protection accorded them.

More widely cited for their water quality effects are riparian wetlands/buffer zones. Buffer zones are vegetated strips of land located between streams and catchment areas; they regulate the transfer of material in both surface runoff and groundwater, and represent important areas for the exchange of energy and matter between terrestrial and aquatic systems (Vought et al. 1995). The importance of riparian zones to water quality is now widely recognized (Hill 1996, Lowrance et al. 2002). They have also been shown to affect both surface runoff and subsurface fluxes of nitrates (Hanson et al. 2004; Jordan et al. 1993; Nelson et al. 1995; Gold et al. 2001). The physical, chemical and biological processes occurring in the riparian zone can function to assimilate and transform contaminants before they reach streams (when water flows laterally from the land surface and perpendicular to stream flow) and they play a role in mitigating effects of floods and flood-water transport of pollutants when the river overflows its banks. The effectiveness of riparian wetlands for nutrient removal is a function of local hydrology, buffer width, location, slope, vegetation characteristics, soil types and degree of saturation (Hill 1996, Gillian et al. 1997). An effective riparian zone generally permits interaction between the nitrate-enriched shallow groundwater (and surface water, if present), an active plant community, large and dynamic soil microbial pollution, and hydric soils (to create conditions where nitrate is used as the terminal electron acceptor). However, variability in hydrological and biological conditions necessary for denitrification yields enormous variation in denitrification rates of riparian zones.

In the riparian zone, NO_3-N is removed either by plant uptake or through denitrification. The potential for denitrification is large where there is a supply of organic matter and a source of NO_3-N. Riparian forests located on the lowland sides of agricultural fields in Coastal Plain retained up to 70 to 90% of the total N inputs (Jordan et al. 1993); this figure does not distinguish between N fixation and denitrification as the terminal N sink. Also, NO_3 was removed from shallow groundwater flowing through the forest soils. In contrast, Bohlke and Denver (1995) found that the riparian zone had little effect on groundwater NO_3 when groundwater flow was too deep to pass through the rooting zone. Lack of carbon in deeper soils could be a limiting factor for denitrification. The removal of NO_3-N from the point of entry into the riparian zone to the point of stream entry can be more than 90% (Lowrance et al. 1995).

While denitrification is considered a major N removal process for the entire riparian zone, there is considerable variation from one area to another with significant hotspots and zones of high and low activity (Hill et al. 2000). Hunt et al. (2004) measured denitrification activity of soils from a newly planted forested riparian zone contiguous to a spray field heavily loaded with swine lagoon wastewater in North Carolina between 1994 and 1997. Soil samples were collected

Reference	Rates g N m^{-2} day^{-1}	g N m^{-2} yr^{-1}	Conditions
Wetlands			
Dieberg and Brezonik (1985)		28	Nutrient-enriched swamp (FL)
Koerselman et al. (1989)		6	Discharge fen, Netherlands
		20	Recharge fen, Netherlands
Johnston (1991)		0.002–0.34 (av. = 0.19)	Low-nutrient natural wetlands
		16–134 (av. = 60)	Nutrient-enriched wetland
Jørgensen (1994)		20–92	Wetlands, Denmark
Phipps and Crumpton (1994)		171	River-fed constructed wetlands (IL)
Kadlec and Knight (1996)		280	Treatment wetland, theoretical rate
Kadlec and Knight (1996)		801	Treatment wetland, based on I/O analyses
Comín et al. (1997)	0–3.46		Agricultural runoff, *Phragmites* marshes in Spain
Spieles and Mitsch (2000)		62–66[1]	River-fed constructed wetlands (OH)
Lane et al. (1999)		10	Mississippi River diversion at Caernarvon (LA)
Riparian systems			
Peterjohn and Correll (1984)		4.5–6.0	Riparian forest, Chesapeake Bay (MD)
Groffman et al. (1991)	0.22		NO_3 + glucose, buffer zones
	1.58		NO_3 + glucose, grass strips
Hanson et al. (1994)		0.5–1.6	Riparian maple swamp (unenriched)
		2.0–3.6	Riparian maple swamp (enriched)
Lowrance et al. (1985)		6.9	Restored riparian wetland
		4.3	Young hardwood riparian forest
Groffman and Hanson (1997)	0.87–1.3[2]		Moderately well-drained soil
	2.6–24.4[2]		Very poorly drained soils
Groffman and Hanson (1997)		1.5–15.5[2]	Alluvial soil
		1.0–2.0[2]	Light till

Notes: Studies listed here do not generally include wetlands exposed to wastewater, except for Kadlec and Knight (1996); av., average.

Figure. 17 – Summary of measured N loss rates from selected wetland and riparian zone studies (from Mitsch et al. 2001). To convert g N/m^2/yr to kg N/ha/yr, multiply values in this table by 10.

from four sites at three depths - the soil surface, midway between the soil surface and water table, and above the water table across two transects. The measured denitrification enzyme activities (DEA) ranged from 4 to 372 µgN_2O-N /kg soil/ha, and showed a gradient with highest levels next to the stream and lowest next to the spray field. Further, DEA generally decreased with depth but with substantial spatial variability. Based on regression analysis, total N was the single factor highest correlated to DEA ($R^2 = 0.65$) suggesting that denitrification rates are higher with greater NO_3 concentrations, and perhaps N limited. This suggests that, for this situation, carbon was not the limiting factor. In the NO_3-N enriched aquifers in Florida, however, where the aquifer matrix is karst or sand, the absence of electron donors would suggest that denitrification is C limited. Because springs discharge directly to the surface water and not through the root zone of wetlands, denitrification potential at the discharge point is negligible.

Spatial variability of denitrification is a significant impediment to estimating the landscape assimilative capacity, with or without wetland buffers. For example, Kellogg et al. (2005) measured *in situ* groundwater denitrification rates at three different depths (65, 150, and 300 cm) within hydric soils at four riparian sites. Surprisingly, denitrification rates did not differ significantly with depth for three of four sites, but between-site and between-season variability was extreme (mean values for four sites by season were: Fall - 29, 8, 96 and 16 µg N $kg^{-1}d^{-1}$; Spring – 118, 20, 66, 10 µg N $kg^{-1}d^{-1}$). There was some evidence of a systematic effect of distance from stream (denitrification rates rose closer to the stream, with mean rates ranging from 30-120 µg N $kg^{-1}d^{-1}$ within 10 m vs. < 1 to 40 µg N $kg^{-1}d^{-1}$ 30 m or more from the stream) but these effects were somewhat confounded by time and evidently random depth variability.

Some spatial variability may arise due to preferential flows of N enriched water from the landscape. For example, Hanson et al. (1994) compared denitrification rates in riparian forest sites located on the east and west sides of a stream. The sites had similar soils, vegetation, and hydrology, but differed in that the eastern side of the stream was below an intensive residential development with on-site septic systems, while the upland above the western side was undeveloped. Denitrification rates were found to be higher ($p< 0.01$) on the enriched developed site than the control site. Soil and groundwater NO_3 were also consistently higher in enriched sites. Comparison of measured denitrification rates with estimates of groundwater NO_3-N loading suggested that denitrification may have removed up to 50% of the groundwater NO_3-N that entered the enriched site. Denitrification rates varied across soil drainage gradient, with higher rates at the wetland end of the riparian zone where soils were poorly and very poorly drained, compared to uplands where soils were moderately well and somewhat poorly drained.

Water table dynamics and soil wetness are critical components of groundwater NO_3-N removal in riparian areas (Gold et al. 2001). Nelson et al. (1995) showed that while hydric soils have uniformly high capacity for NO_3-N removal, the capacity of upland/wetland transition zone soils is more variable. Further, riparian zones dominated by upland or transitional soils may be less effective at preventing groundwater NO_3-N movement into streams or wetlands than sites dominated by hydric soils. Nelson et al. (1995) found a significant but weak inverse correlation between NO_3-N removal rate and depth to water table ($r = -0.41$, $p < 0.05$), and a weak inverse relationship between NO_3-N removal rate and dissolved oxygen ($r = -0.37$, $p < 0.05$). When the removal rates were pooled by season, November (with the highest water table) had the highest removal rate, while the lowest removal rate was noted in June, when the water table was deepest; median removal rates in November were more than double than those observed in June. This result (low denitrification when photosynthetic activity is highest) suggests that microbial processes (immobilization and denitrification) were responsible for more of the observed groundwater NO_3-N removal than plant uptake. Seasonal differences in ET, which strongly affects the likelihood of saturated conditions, which in turn affects the redox state of the soil, are clearly important in Florida as well. Simmons et al. (1992) observed similar results where NO_3-N attenuation in a riparian forest was lower (< 36%) during the growing season and higher (50-78%) during the dormant season. Plant water consumption effects on water table elevations are a potentially important feedback effect that is not well documented for wetland processes.

Zones of Enhanced Reactivity: Lakes

The distinction between wetland and lakes in the shallow relief of Florida is likely to be of limited utility. However, several authors have documented the reactivity of lakes in N mineralization, primarily as a result of oxygen stratification. Seitzinger (1988) compared rates of denitrification in estuarine, lake and stream sediments and observed rapid rates and substantial variability in each. Lake systems removed between 2 and 171 μmol N/m^2; in contrast, rates in estuarine systems range from 50-250 μmol N/m^2 and rates in stream sediments are between 0 and 345 μmol N/m^2. Interestingly, the rate of N losses via denitrification were lower in all measured cases than rates of N fixation, suggesting that anthropogenic inputs both directly (in water discharges and leaching) and indirectly (via elevated atmospheric deposition) are changing ecosystem dynamics on a broad scale. Jansson et al. (1994) examined the role of lakes on landscape water quality protection and conclude the nitrogen assimilation/removal capacities of lake systems is achieved via both denitrification from the sediments and the deposition of organic materials to low-oxygen lake bottoms, where they remain relatively recalcitrant to mineralization. They conclude that lakes can remove more N per unit area than wetlands because of these parallel removal processes, despite the abundant evidence that ecosystem reactivity rates (denitrification per unit area) are much higher in wetlands.

Zones of Enhanced Reactivity: Headwater Streams

Peterson et al. (2001) used sites from throughout the country (with Florida a notable exception) to compare nitrogen processing across different scales. They observe a strongly significant positive trend between stream discharge (a continuous proxy for stream order) and uptake length for mineral nitrogen species (distance over which the nutrient is transformed). This suggests that headwater streams are more biogeochemically active; given limited protection status accorded these systems, the findings are particularly salient. One important aspect of their work is that uptake lengths for ammonium (via nitrification and assimilation) were nearly an order of magnitude shorter than for nitrates (removed via denitrification and assimilation), suggesting that long-range transport of the latter is more problematic.

Holmes et al. (1995) measured denitrification in an arid-land stream system where N limitation was demonstrated. Despite ample DO availability in the water column and low DOC concentrations, denitrification was estimated to be as high as 40% of the total nitrification rate. In Florida's low DO/high DOC systems, the rate of instream denitrification is expected to be even more pronounced, though these rates are poorly documented. Hyporheic and in-stream N removal in a temperate stream (Duff and Triska 1990) showed that denitrification was N limited in both locations, and that the hyporheic zone is a primary location for nitrogen activity. Steinhart et al. (1998) showed significant (up to 100% of the total input loads in experimental cores) in-stream nitrogen removal in 5 streams in the northeastern US, with primary locations for denitrification occurring in organic sediments, and less in sandy or gravel beds. They also conclude that in-stream processing appears nitrate limited (i.e., anoxic zones and carbon availability were sufficient). Using $\delta^{15}N$ as a marker, Kellman and Hillare-Marcel (1998) showed (using a $\delta^{15}N$ shift of 10 ‰ over 600 m) that instream denitrification was responsible for as much as 50% of total N losses. This is a largely neglected part of the nitrogen budget, and one important to consider for both spring runs and river systems. It also suggests that estimates of loading to stream systems are systematically lower than actual rates because the assumption of nitrate stability in lotic systems is invalidated.

A statistical model developed to predict denitrification in streams and rivers (Seitzinger et al. 2002) suggests that between 37% and 76% of nitrogen is removed during transport through an entire river network; more than half is removed in headwater systems (which given reduced volumetric flow rates strongly corresponds with the findings of Peterson et al. 2001), while most of the load is derived in mid-basin reaches. They conclude that the reactivity of streams makes reservoir contributions to N removal negligible, which contrasts with the spatial findings of a study done by Mytyk and Delfino (2004), which shows for the Ocklawaha River in Florida, that the Rodman Reservoir is the primary location for basin denitrification.

Ecosystem N saturation

N saturation in an ecosystem has been defined as the availability of NO_3-N and ammonium in excess of the demand for plant and microbial nutrition (Aber et al. 1989); while this neglects organic N accretion (in peats), the conditions under which long term accretion are symptoms of N saturation that may be seen in an ecosystem include increased rates of nitrification in soils, increased N leaching to groundwater, species composition changes etc. Analysis by Ågren and Bosatta (1988) shows that there are no large sinks for N that will not be saturated. Nitrogen saturation can occur by two mechanisms – the input rate of N is larger than immediate system uptake, or by addition of such large amounts of N that the internal cycling of N becomes saturated. Nitrogen saturation should show up at the interface between the mineralization of soil N and the uptake of soil inorganic N by the plants (Ågren and Bosatta 1988).

N saturation in the soil system means that mineralization rate is high and the excess of NO_3-N generated will leach out of the soil system, and degrade the ground and surface water quality, assuming no net accretion of organic soils. Because of its unique position in the landscape, riparian forests are subjected to high inputs of N from the upland areas, making these ecosystems susceptible to saturation. Riparian wetlands potentially act as filters for much of the water draining from upland sources and act as water quality regulators in agricultural watersheds.

Hanson et al. (1994) measured potential net N mineralization and nitrification, soil inorganic pools, microbial biomass carbon and N content, and N content of litter as indicators of N saturation in two riparian zones on the opposite sides of a stream, but with different rates of groundwater NO_3-N loadings. Soil inorganic-N levels, litter N content, and potential net N mineralization and nitrification were significantly higher on the enriched sites relative to the control site, suggesting that the enriched site was N saturated. However, input-output analysis was computed for the enriched riparian zone which indicated that the enriched riparian zone was still a sink for upland derived NO_3-N (Table 11). Groundwater loading was estimated to be 63 g/m of soil interface between the upland and riparian zone per year, and nearly half of this input could be accounted for by induced denitrification (enriched site denitrification minus control site denitrification). Inorganic and organic N pools also accounted for large amounts of extra N, while microbial biomass was not a major sink for extra N. Processes like denitrification in the wetlands, and storage of N **in soil organic matter appeared to moderate N saturation on the enriched site.** Aber (1992) highlighted that N retention requires effective conversion of mineral N to organic form, and to organic forms that will reside with the system for an extended period.

Table 11. Excess inputs, outputs, and pools of N in a 1 m width of riparian zone (1 m wide x 31 m long x 15 cm deep) in the enriched site compared to the control site.

Inputs (g m^{-1} yr^{-1})		
	Ground water NO_3-N input	63
Outputs (g m^{-1} yr^{-1})		
	Denitrification	37
	Hydrologic exports	small
Pools (g m^{-1})		
	Inorganic N	66
	Microbial biomass	< 1
	Soil total N	177

Anthropogenic Enhancement of Nitrogen Removal

Denitrification Walls: Denitrification walls have shown to be a practical approach for decreasing nitrate pollution of surface waters where groundwater is near the surface (Robertson and Cherry 1995, Robertson et al. 2000). Denitrification walls are constructed by incorporating organic matter (e.g., wood mulch, sawdust) in a porous wall perpendicular to the groundwater flow path. The organic matter serves as a carbon source to microbial heterotrophic production, which removes oxygen from the groundwater, providing an anaerobic environment, and provides the electron donor for heterotrophic denitrification. Denitrifying bacteria use the carbon to convert nitrates in groundwater to nitrogen gases that escape to the atmosphere. Nitrate concentrations of groundwater exiting the denitrification wall are measurably lower than concentrations entering; the degree of removal varies with design, environmental conditions and flow velocities, but removal in excess of 90% have been reported (Robertson et al. 2000 - Fig 18; Schipper and Vojvodic-Vukovic 2001).

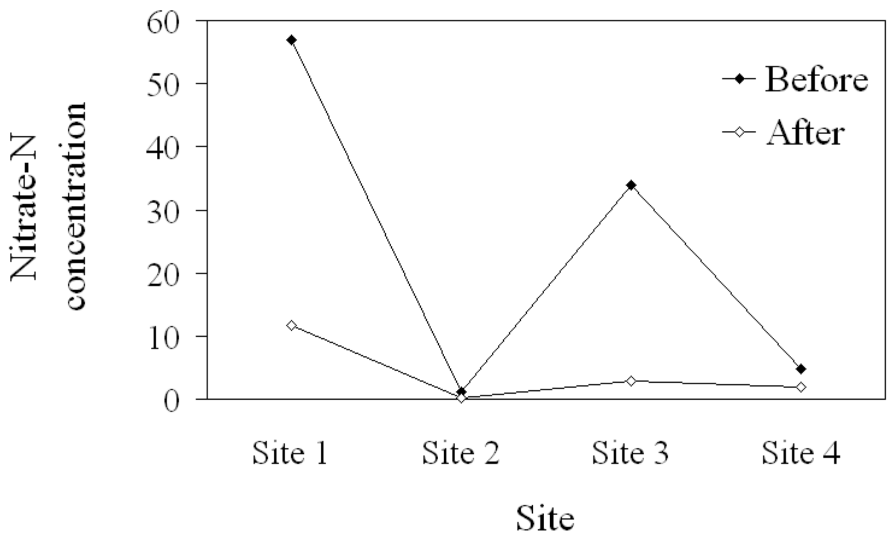


Fig 18. Six to seven years average values of Nitrate-N concentrations in water before and after treatment in the denitrification barriers derived from six to seven years of operation (From Robertson et al. 2000)

Schipper et al. (2005) estimated that maximum nitrate removal rate by a denitrification wall at 1.4 g N m^{-3} d^{-1}. Schipper et al. (2004) measured performance of a denitrification wall in aquifers characterized with high nitrate loading resulting from rapid groundwater flow rates (1 m per day) and high nitrate concentrations (often in excess 30 g N m^{-3}). Nitrate-N concentrations in the wall were generally less than 2 g N m^{-3} but no differences between nitrate concentrations upstream of the denitrification wall (21.2 to 38.9 g N m^{-3}) and downstream of the denitrification wall (15.8 to 43.9 g N m^{-3}) were observed, suggesting either that the majority of the groundwater bypassed the denitrification wall or that reactivity rates in the wall were insufficient to influence mass fluxes. The potential for bypass flow was supported by tracer test (Fig. 19), which underscores the challenge in designing walls for use in Florida. In a sandy aquifer (as the surficial aquifer is in Florida, where one exists), lower hydraulic conductivity of the denitrification wall compared to the surrounding material causes groundwater to pass under rather than through the denitrification wall. In areas where the aquifer has a shallow confining layer, denitrification walls could be implanted to the depth of the impermeable confining layer, ensuring that all groundwater flows through the wall. The efficacy of this approach to denitrification is currently under review at the University of Florida for application to high nitrate concentration runoff from horticultural operations (E.J. Dunne – personal communication). The setting for the test is restricted to areas where the Hawthorn confining layer is near (<3 m) from the surface).

Employment of denitrification walls in the karst aquifer is likely to be ineffective. Even where the Floridan aquifer is near enough to the surface to consider use of this technique, transmissivities are such that by-pass flow is inevitable. Further, the depth of nitrate enriched upper aquifer is tens to hundreds of meters, which is impractical for this approach.

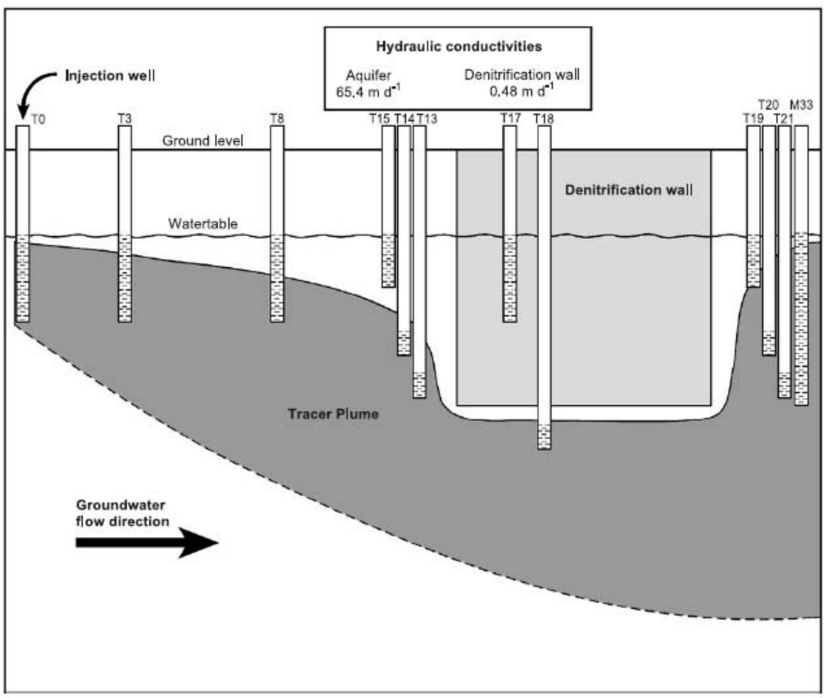


Fig 19. Schematic of the flow-path of the tracer plume underneath the denitrification wall (From Schipper et al 2004).

Treatment wetlands and lagoons: As previously discussed, wetlands and lagoons are among the most reactive landscape features with respect to reducing nitrate concentrations in surface waters. The engineered implementation of wetland systems and lagoons into the landscape for water quality improvement also has a long and successful history (e.g., Kadlec and Knight 1996, Stockdale 2001). Engineered wetlands have shown predictable and sustainable N removal capacity, primarily by providing conditions that allow both nitrification and denitrification. Among the techniques employed to optimize N removal include redox oscillations, whereby a repeating pattern of oxic conditions (wherein organic and ammonia forms of nitrogen are nitrified), then anoxic conditions (facilitating denitrification) are generated.

However, in karstic systems the aquifer is unconfined and, consequently the system lacks surface water features (wetlands, lagoons, lakes) because percolation is so accelerated. Opportunities to retain enriched water at the surface to facilitate denitrification are few unless systems are lined to restrict infiltration. There are generally wetlands associated with littoral areas of spring systems and spring-run river floodplains where denitrification can occur, but these are small in total area and generally in only episodic contact with the water flow.

Rutherford and Nguyen (2004) investigated the potential of engineered riparian wetlands to remove nitrate from spring water upwelling into the wetlands. Results showed substantial nitrate removal provided water remains in contact with microbially active soils for about 1 day. Similarly, Burns and Nguyen (2002) estimate >90% and >99% nitrate removal after water traveled for 2 to 8 hours and 3 to 13 days in subsurface (10-20 cm) wetland soils. However, the ultimate reduction of nitrate concentrations would depend on what proportion of the high nitrate water delivered to the surface of the wetland by the upwelling spring remains in contact with microbially active soils and vegetations of the wetlands. The nitrate concentrations in the spring water can also be reduced as spring water flow along the streams. However, the efficiency of stream ecosystems to remove nutrients via retention (also expressed as uptake length) has limitations because it can be significantly altered by the quantity and quality of receiving water, with low efficiency of nutrient retention in polluted streams (Marti et al. 2004). Lowrance and Hubbard (2001) estimated that the maximum possible denitrification rate from a liquid swine manure application system on Coastal Plain soils is 200 kg N ha^{-1} yr^{-1}. Given the N load emerging from Wakulla Springs (270,000 kg N/yr - Chelette et al. 2002), this translates into 1,350 ha of wetland necessary to process the effluent, which at least an order of magnitude larger than wetlands surrounding that spring. By way of comparison, sprayfields serving Tallahassee (the Southeast and Southwest sprayfields) are 910 hectares combined, with evidence of high levels of nitrates (> 5 mg N/L) in many of the test wells installed (Chelette et al. 2002).

Regional Case Studies of Nitrogen Contamination in Florida

Nitrogen contamination in freshwater and marine environments is a global water quality challenge (Rabalais 2002) that requires and receives substantial attention. Because the primary mechanisms for N control prior to discharge into sensitive aquatic ecosystems are almost exclusively biological in mechanism (microbial assimilation, dissimilatory reduction to ammonia, denitrification) and controlled in part by landscape residence times, it might be expected that the nitrogen management challenge in Florida (with long hydrologic residence times and sub-tropical biological activity) would be relatively minor. As the previous discussion of aquifer vulnerability illustrated, this is not the case in a number of regions in the state, for reasons primarily pertaining to geology; direct and rapid connectivity between surface water, which can become nitrate enriched due to anthropogenic activities, and groundwater, in which nitrates are profoundly stable. This section presents several case studies of N pollution in Florida in an effort to extract commonalities and differences that might be useful for planning or management. First, a recent study of nitrate loading in an area of the state that exhibits the characteristic geologic variability (confined vs. unconfined aquifer conditions) is examined. Inference from this study leads to a discussion of the relevant data on nitrate loading the Floridan Aquifer System (FAS) and, subsequently, some of the major spring systems that have been studied in detail (Silver Springs, Suwannee Basin springs, Rainbow Springs, Wekiwa Springs, Wakulla Springs and Ichetucknee Springs)

Nitrate Loading in the Santa Fe River Basin

Recent work (Lamsal et al. 2006) in the Santa Fe River basin in north Florida focused on sources of nitrates in a mixed use landscape. A stratified random sampling of the surface soils (0 – 2 m) from throughout the basin was used, in concert with continuous thematic layers (land use, elevation, soil type, physiographic divisions) to develop prediction surfaces of nitrate loads using advanced geostatistical methods (regression kriging). The final map (Figure 20A) shows an interpolation of point-based synoptic soil (< 2 m deep) nitrate concentrations. The results indicate that the highest *in situ* concentrations are observed along the New River, the northern stem of the Santa Fe above the Cody Escarpment that delineates the confined reaches (to the east) from the unconfined reaches (to the west). This map should be viewed as a potential load, subject to variable landscape assimilative capacities between the soil and the river; this fact is

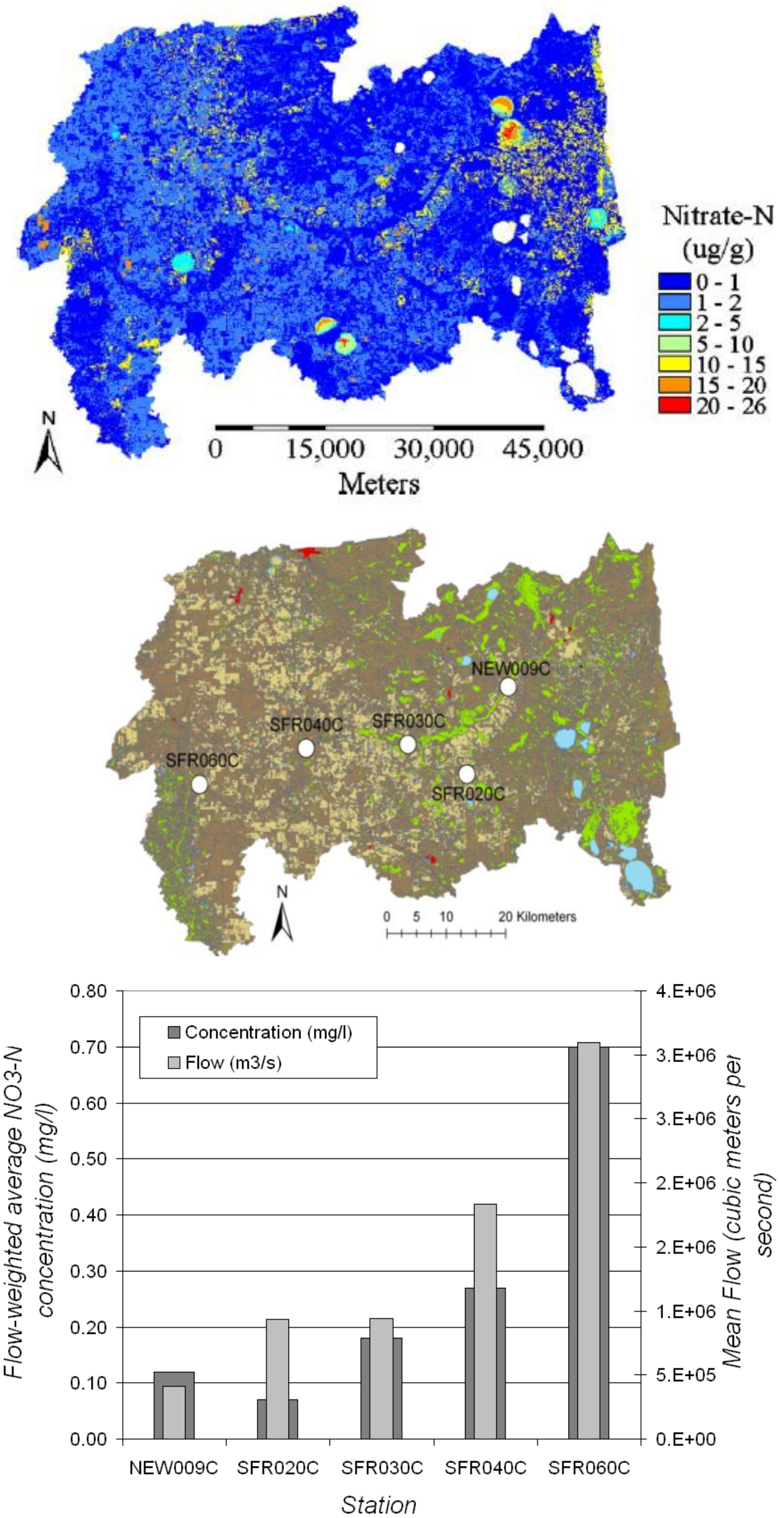


Fig. 20 – A) Regression kriging predictions of nitrate-N concentrations (mg/g) for the Santa Fe River Basin for January 2004 (after Lamsal et al. 2006); B) location of surface water quantity and quality stations from USGS National Water Information System and USEPA STORET data (underlying layer shows 1995 land use); C) flows of water and concentrations of nitrate.

underscored by Fig. 20B and C that show the location of 5 critical monitoring stations and the mean flow (water) and concentrations (NO_3-N) at each of those stations. Notably, areas to the west (SFR060C and SFR040C), where nitrate loading to the landscape is lower (based on Fig. 20A) is where nitrate concentrations are highest (and loads are markedly higher due to increases in flow). Further, nitrate concentrations in Ichetucknee Springs, which drains to the Santa Fe River in the lower basin (near SFR060C), are between 0.05 and 1.45 mg/l with a median value in recent observations near 0.8 mg/l; this value is representative of Floridan aquifer water in the region. To the east (SFR030C, SFR020C and NEW009C), stations nearer the major loading regions exhibit lower concentrations and loads, presumably because these areas are in confined reaches whereas the stations to the west are in unconfined reaches. The natural mechanisms of denitrification and biological uptake are more prevalent in confined reaches, whereas in areas that are unconfined, there are effectively no opportunities for nitrate removal, and loads to the river are greatly enhanced, despite the fact that *in situ* concentrations appear lower. Note that there are few studies that have documented rates of N attenuation in wetlands and streams that can be used to assess assimilation capacity (i.e. nitrate fluxes that can be removed without markedly changing river concentrations). There is strong reason to expect significant attenuation of nitrate both in the riparian zone, isolated wetlands, and in-stream; improved understanding of how quickly nitrates travel and transform between terrestrial and aquatic systems is essential.

The Floridan Aquifer

The Floridan aquifer system is a carbonate aquifer that underlays over 300,000 km^2 of Florida, southern Georgia, extreme southern Alabama and a small parts of Mississippi and South Carolina (Fig. 21). In many regions, it is an artesian aquifer and among the most productive karst aquifers in the world. The combination of high quality water, large yields, and shallow depth has resulted in municipal water supply in central, northwest and north Florida being almost solely dependent on this resource. Moving south from Lake Okeechobee, the FAS is both extremely deep, with a complex mosaic of surficial (e.g., Biscayne) and intermediate aquifers above it, and increasingly saline. However, municipalities in that region of the state are also increasingly considering using the Floridan as a major component of their water supply plan.

While the Upper Floridan aquifer is the primary source of public and private water supply, intermediate and surficial aquifers are also important reservoirs for surface water processes, and for some consumptive uses. For example, an intermediate aquifer exists in the northeast portion of the Suwannee Basin within the complex units of the Hawthorn formation, which lies above the karst layers that contain the Floridan aquifer. The surficial aquifer lies at the land surface in Plio-Pleistocene sand sediments that overly portions of the Hawthorn and Floridan aquifer system. Where this overlying material is actively eroding away is called the Cody Escarpment, which represents the transition from a confined Floridan aquifer to areas where that aquifer is unconfined. Aquifer vulnerability, which has been estimated by the Florida Geological Survey's Floridan Aquifer Vulnerability Assessment (FAVA), is maximized in the unconfined regions.

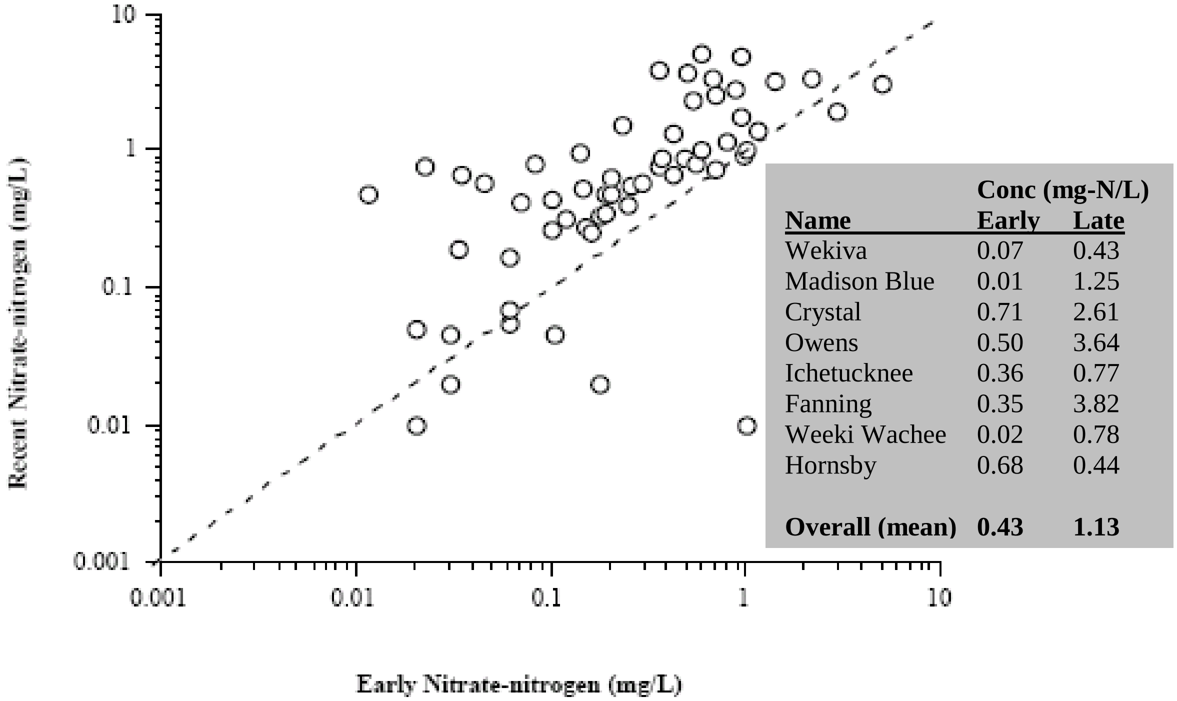
The Upper Floridan aquifer has well-developed secondary porosity, and is highly transmissive, which provides opportunity for contaminated groundwater to travel long distances in a relatively short period of time. Indeed, the Floridan aquifer is among the most productive aquifers in world as a result of generally abundant recharge and high transmissivities; as a result, Floridan aquifer springs discharge groundwater of relatively young age (e.g., < 50 years). The transmissivity of the Upper Floridan aquifer depends on both primary (matrix) and secondary (conduit) porosity of the aquifer, and varies greatly. Martin and Dean (2001) document significant mixing between these dynamic reservoirs. High rates of recharge occur in areas where

Fig. 21 – Extent and confinement of the Floridan aquifer in the Southeastern US. The Floridan is among the most productive karst aquifers in the world and the source of most of Florida's drinking water (after Miller 1990)

the Upper Floridan aquifer is at or near land surface, or is only confined by a thin semi-confining unit. Further, the dynamics of mixing in the subsurface are driven both by the fracture and matrix porosities, and the potentiometric surface that imparts geopotential energy. The complexity of the subsurface groundwater dynamics has made modeling of mixing, solute transport, contaminant attenuation and water yields problematic in the Floridan Aquifer system.

In much of north-central Florida, the Floridan aquifer is unconfined (unburied – Fig. 21). When the aquifer is unconfined, nutrients leached at land surface easily percolate vertically into the aquifer. In areas where the aquifer is vulnerable, the choice of land use practices is critical to protect the groundwater quality. However, it must be noted that the chemistry of groundwater sampled from the upper Floridan may be influenced by past land use activities as well as contemporary processes, depending on the groundwater residence times. Because of this, estimating the actual quantity of NO_3-N contributed by atmospheric deposition, livestock and agricultural fertilization becomes complex and non-static. That is, determining where nitrogen pollution and water is coming from in the mixture of water that emerges in springs requires substantial tracing and age dating evidence that has only been collected at a few springs.

This has implications for both assessing the landscape response lags due to enrichment, and, ultimately, the degree to which contemporary changes in land management will have an effect on spring water quality. For example, few studies have systematically examined temporal trends in Floridan aquifer water quality. One (Strong 2004) examined 69 Florida springs, which can be considered a statistical sample of the upper Florida aquifer, and observed strongly significant enrichment across almost the entire sample. Fig. 22 shows the relationship between baseline data (pre-1977) and present nominal concentrations for each spring. Systematic positioning of each spring above the 1:1 line suggests illustrates broad scale enrichment (higher NO_3-N concentrations today vs. early measurements); for many of the springs, modern values are an order of magnitude higher than baseline values, though for a small number of springs evidence for reduced concentrations over time is present. More interestingly from a management perspective is the strong positive correlation between pre- and post-data, suggesting that there are natural site-specific hydrogeochemical controls on local groundwater quality that persist even with anthropogenic enrichment. Notably, the two sites that were most enriched in early observations are lower in the modern measurements. This strong relationship suggests that a detailed understanding of the springshed, conduits therein, changes in land use, and temporal



Name	Conc (mg-N/L) Early	Late
Wekiva	0.07	0.43
Madison Blue	0.01	1.25
Crystal	0.71	2.61
Owens	0.50	3.64
Ichetucknee	0.36	0.77
Fanning	0.35	3.82
Weeki Wachee	0.02	0.78
Hornsby	0.68	0.44
Overall (mean)	**0.43**	**1.13**

Fig. 22 – Plot of baseline nitrate concentration vs. recent concentration for 87 springs (after Strong 2004). Points falling on or below the 1:1 line (dashed) indicate the absence of enrichment or decline in concentration; most springs exhibit evidence of enrichment and some show an order of magnitude increase in concentration.

dynamics of water and nitrate delivery are critically important to management, since these are some obvious factors that would create such intrinsic spring-specific responses.

Springs along the Suwannee River

The Suwannee River flows through areas of north-central Florida where groundwater has elevated NO_3-N concentration (Pittman et al 1997). The Lower Suwannee basin is characterized by riparian wetlands and lowland topography, limited surface drainage features, and an abundance of springs discharging water from the upper Floridan aquifer (Katz et al. 1997). In this portion of the river basin, precipitation infiltrates directly into the Upper Floridan aquifer; all rivers, including the Suwannee, become losing streams as they flow across the escarpment that divides the upper (confined) reaches from the lower (unconfined) reaches. In the Upper Suwannee basin, strongly contrasting hydrogeology results in the confinement of the aquifer and the proliferation of surface drainage and storage (lakes and wetlands); Floridan aquifer springs are almost entirely absent from this part of the basin. The Suwannee River ultimately drains to the Gulf of Mexico, where NO_3-N loadings can lead to ecological impairment. The source of elevated NO_3-N concentrations in the ground water is a mixture of organic sources (wastewater, manure) and inorganic sources (fertilizers), and almost entirely derived from lands in the lower basin. During periods of low rainfall inputs, the large volume of groundwater stored in the karst matrix maintains relatively high flows in springs and riverbed seeps. As a result, the influence of Floridan aquifer water on river water quality is more pronounced during periods of baseflow than during high flow events, when runoff from upper parts of the basin where more surface runoff occurs (confined regions) dominate river volume. These surface-derived waters (including water that has resided in the surficial aquifer) have lower nitrate concentrations because of elevated rates of denitrification in the soil and in wetlands that intercede before discharge to the river.

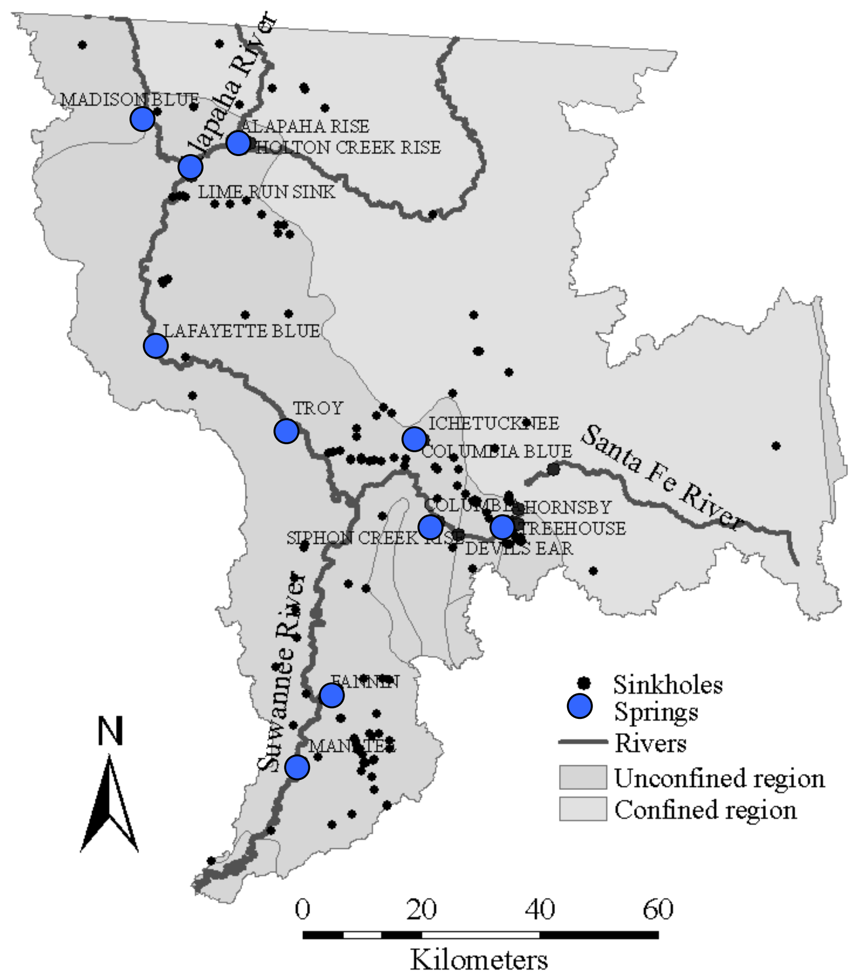


Fig 22. Hydrogeologic features of the Suwannee River Basin in Northern Florida. The two grey areas are divided by the Cody Escarpment, which is the erosional edge of a hydrogeologic confining layer. Nitrates deposited above the escarpment are much more likely to encounter conditions leading to denitrification than sources below the escarpment.

During a twenty year period (1971 – 91), NO_3-N concentrations in the Suwannee River near Branford increased at a rate of 0.02 mg/l/year (Ham and Hazell 1996). Septic tanks, synthetic fertilizers, and animal waste are the potential sources of NO_3-N in groundwater (Andrews 1994). Pittman et al. (1997) investigated how springs and other groundwater inflow affect the quantity and quality of water in the middle Suwannee River on a 33 mile reach of the river from just downstream of Dowling Park, FL to Branford, FL. Water samples were collected at 11 springs and 3 river sites during a 3-day period in July 1995 during baseflow in the river. Table 12 summarizes discharge, NO_3-N concentrations, and NO_3-N loads generated by springs and rivers. Along the study reach, springs contributed 13% of river discharge (measured at Branford) while diffuse groundwater inflow contributed an additional 19% of the total river flow. Increases in NO_3-N loads in the study reach were related to effects of land use on groundwater (Pittman et al. 1997). Because of the unconfined Floridan aquifer, any NO_3-N generated from fertilizers, septic tanks and animal wastes can readily enter groundwater via infiltration.

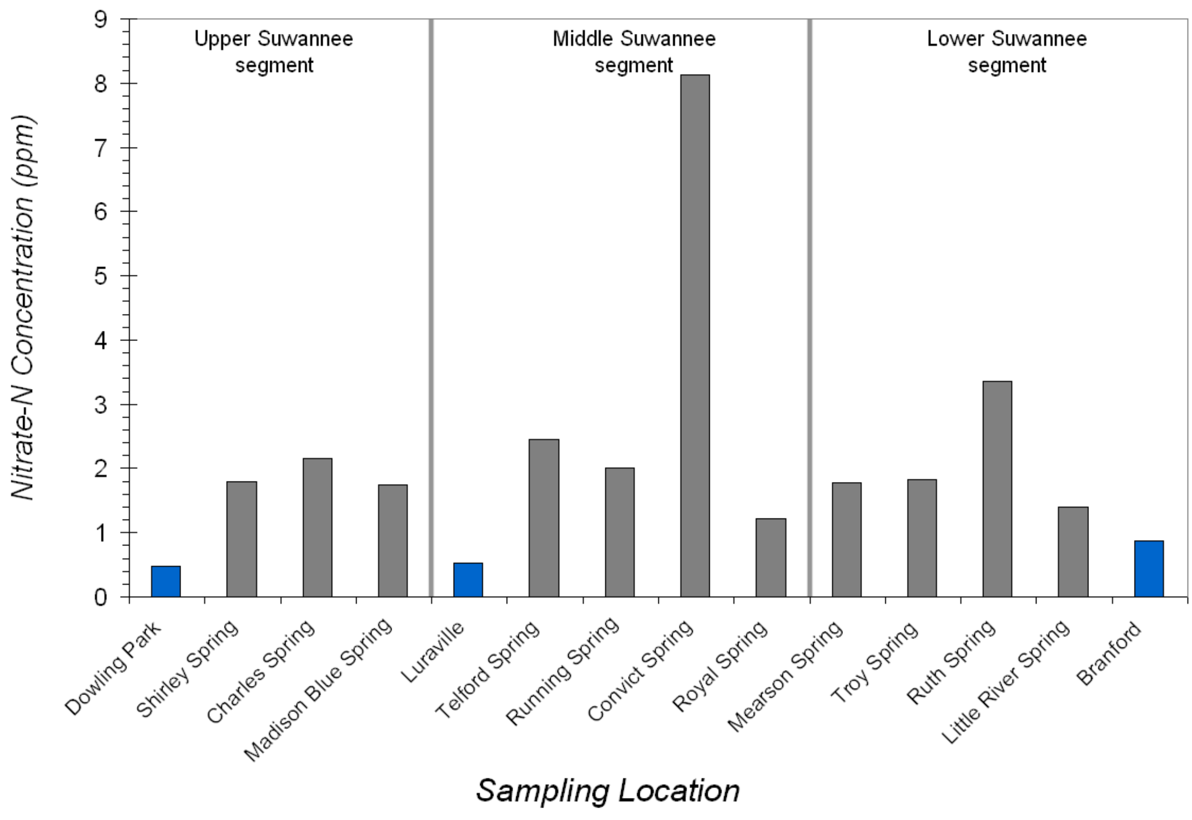


Fig 23. Nitrate-N concentrations measured in the springs along the Suwannee River; locations in blue are river sampling locations(From: Pittman et al. 1997)

Despite relatively minor hydraulic loading, springs had substantially elevated concentrations of nitrate-N; however, concentrations measured in springs varied tremendously, with values ranging from 1.3 mg/l at Royal Spring to 8.2 mg/l at Convict Spring. Convict Spring has a history of higher NO_3-N concentration than other springs in the area (Hornsby and Mattson 1997); the putative source may be septic tanks at development surrounding the spring, or from fertilized cropland several hundred feet to the south (Andrews 1994); detailed examination of the springshed and isotopic characterization would be necessary to determine sources more certainly. Overall, NO3-N concentrations in springs were higher than NO_3-N concentrations at river sites (Fig 23). Concentrations at upstream river sites close to Dowling Park were 0.46 mg/l, the same concentration observed at Luraville; however, substantial concentration increases were observed in the reach to Branford where nominal river concentrations were 0.83 mg/l. Despite this increase, springs along the two reaches were generally of comparable concentration (median concentrations of 1. mg/l and 1.8 mg/l in Dowling-Luraville and Luraville-Branford reaches, respectively). The most substantial difference between upper and lower reaches was in the

Table 12. Discharge, NO_3-N concentrations, and NO_3-N loads contributed to the Suwannee River during July 25-27, 1995 (From: Pittman et al. 1997).

River Segment	Location	Discharge (ft^3/s)	NO_3-N conc. (mg/L)	NO_3-N load (kg/d)
Upper	Suwannee River near Dowling Park	2,020	0.46	2,300
	Shirley Spring	1.5	1.7	6
	Charles Spring	7.5	2.2	40
	Madison Blue Spring	77	1.7	320
	Other groundwater inflow	264	0.05	34
Lower	Suwannee River near Luraville	2,370	0.46	2,700
	Telford Springs	33	2.5	200
	Running Spring	17	2.0	83
	Convict Spring	1.7	8.2	34
	Royal Spring	16	1.3	51
	Mearson Spring	30	1.7	120
	Troy Spring	132	1.7	550
	Ruth Spring	9.9	3.4	82
	Little River Spring	67	1.4	230
	Other ground water inflow	293	2.7	1,950
	Suwannee River at Branford	2,970	0.83	6,000

concentration of diffuse groundwater discharge to the river; comparable volumes of diffuse contribution were observed (264 vs. 293 cfs), but their concentrations differed by 3 orders of magnitude (0.05 mg/l vs. 2.7 mg/l). This observation suggests that although groundwater and riverbed seepage contributed NO_3-N to the Suwannee River, diffuse riverbed seepage may be the more significant load, and clearly the more challenging to manage.

With regard to total nitrate loading (as opposed to concentrations), Pittman et al. (1997) report substantial NO_3-N loads from both springs and river seeps. Comparison of NO_3-N loads across springs reveals that while Convict Spring had the highest NO_3-N concentration (8.2 mg/l), its discharge was so small (1.7 ft^3/s) that the resulting load was a relatively minor 34 kg/day. In contrast, lowest NO_3-N concentration measured at Royal Spring (1.3 mg/l), resulted in higher loads (51 kg/d) because of higher discharge (16 ft^3/s). In fact, the cumulative NO_3-N loads (1,277 kg/day) generated by the seven springs with lower than average NO_3-N concentrations was nearly three times the NO_3-N loads generated by the springs with NO_3-N concentrations above the median. Generally speaking, protection of the aquatic ecosystems will require reducing loads, which means focusing attention on those springs with less obvious nitrate enrichment, but with large total loads.

Along the study reach, NO_3-N loads increased from 2,300 to 6,000 kg/d, of which springs contributed 1,716 kg/d (46%), and diffuse groundwater inflow from unmeasured springs and riverbed leakage contributed to the remaining 54%. Most of the increase in NO_3-N loads occurred in the lower segment with 89% (3,300 kg/d). In the upper segment (which contributed 11% of 400 kg/d of nitrate), Madison Blue spring was the major source (load of 320 kg/d). In the lower reach, diffuse ground-water flow was the major source of NO_3-N loading (1,950 kg/d).

Silver Springs

Silver Springs in Marion County, north-central Florida, consists of the Main Spring, the Abyss, and the Blue Grotto. Numerous other springs along the edges of the spring run occur downstream (Phelps 2004). Together, these springs form the headwaters of the Silver River, which supports a diverse ecosystem, and has significant recreational, cultural and economic value. The Floridan aquifer system supports the spring discharge and is the sole source of potable water within the basin. In much of the basin, the Floridan aquifer is at or near the land surface (unconfined) and therefore, recharge into the aquifer is rapid.

Historically, land use in the Silver Springs springshed has been agriculture; however, rapid population growth in Ocala and its surroundings has resulted into major land use change. Fertilizers are applied to crops, and also to residential turf grass and golf courses. In the Silver Springs basin, nutrient loads from agricultural practices generally decreased from 1975-2000, while nutrient loads from wastewater increased because of increase in population (Phelps 2004). Based on a GIS coverage of land use for 1977 and 1995, urban and residential land use in the springshed increased from 38 mi^2 in 1977 to about 164 mi^2 in 1995. While this land use change has occurred, the water quality in the spring has been systematically declining (Fig. 24). Concentrations of nitrate-N during the 1950s, when Howard Odum did pioneering whole-ecosystem studies at this location (Odum 1957), were ~ 0.2 mg/L (Fig. 24), which though high vis-à-vis expected ecological effect thresholds, is substantially lower than current observations.

In 2000-2001, 56 groundwater wells were sampled from basin and analyzed for NO_3-N (Table 13) (Phelps 2004). The NO_3-N concentrations in 2000-2001 were greater compared to the NO_3-N concentrations from 1989-90 (Phelps 1994 – Fig. 24). Median NO_3-N concentrations in the groundwater samples increased from 1.04 mg/l in 1989-90 to 1.2 mg/l in 2001-02, and maximum NO_3-N concentrations increased from 3.6 mg/l to 12 mg/l.

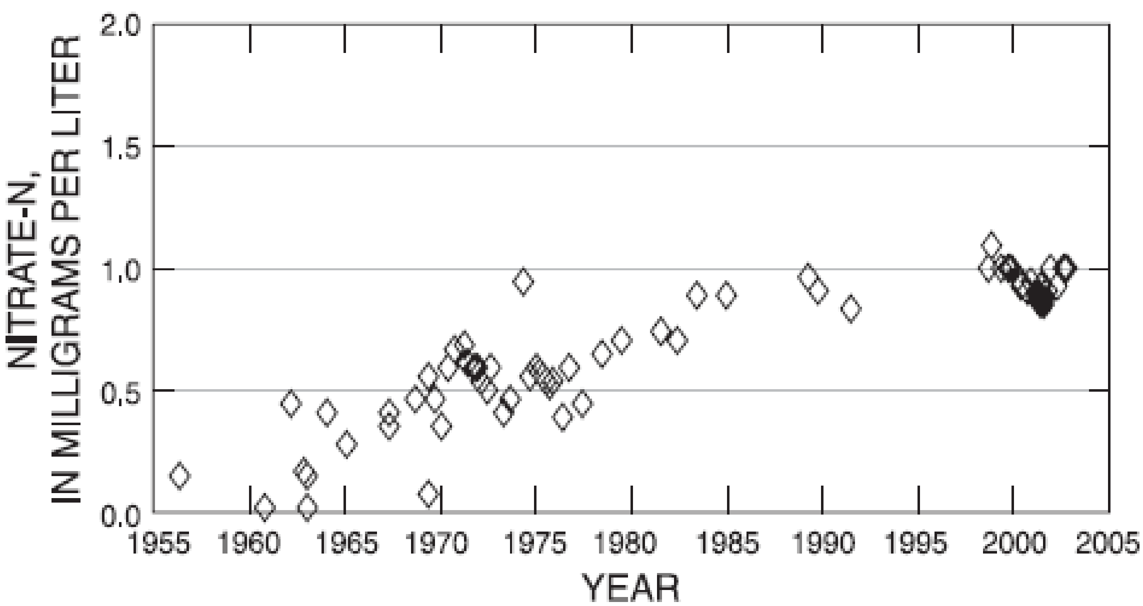


Fig. 24 – Concentrations of NO_3-N in Silver Springs from 1955 to 2004 (after Phelps 2004).

As fewer wells were located in rangeland and forest land use categories, those land-use categories were grouped together. The difference in NO_3-N concentration by land use distribution was significant at $P<0.05$ levels. The highest value of NO_3-N concentration was above the regulatory threshold for the drinking water standard and found under agricultural land use. The highest median NO_3-N concentration was found under agricultural land-use areas (1.70 mg/l) and the lowest median NO_3-N concentration was found under rangeland and forest land use category (0.09 mg/l); further partitioning of these observations into pasture sites (where fertilizers and indirect nitrogen inputs in feed are applied at higher levels) would permit an improved understanding the role of certain land uses, including managed forest, in protecting water quality.

Higher values observed under transportation / utilities (1.57 mg/l) could reflect effects of stormwater runoff for road rights-of-way or could be affected by nearby land-use activities (e.g., wastewater land application sites). Groundwater samples with higher NO_3-N concentrations generally had higher DO values (Phelps 2004), suggesting less potential for heterotrophic denitrification. Following grouping of NO_3-N concentrations for environmental interpretations by Madison and Brunett (1985) (Table 14), the groundwater quality of Silver Springs varies greatly from no contamination, to contamination levels from agriculture and animal activities that exceed the safe drinking water limit.

One of the main proposed sources of N to the environment has been on-site domestic wastewater treatment systems (septic tanks). A detailed survey (Kuphal 2005) reports that there are nearly 100,000 septic tanks in Marion County which yield 1.1 million kg NO_3-N annually. Of this total, the quantity discharged within the delineated Silver Springs springshed is nearly 300,000 kg NO_3-N annually; Kuphal (2005) contrasts this mass flux with the flux from centralized facilities in the same geographic boundary (~ 40,000 kg NO_3-N yr^{-1}).

Table 13. Nitrate-N concentration in ground-water samples grouped by land use at well locations (From: Phelps 2004).

Land use	N	Minimum	Maximum	Median
Urban	29	<0.02	5.9	1.15
Agriculture	13	0.05	12	1.7
Rangeland & forest	11	<0.02	2.2	0.09
Transportation and utilities	3	0.88	4.0	1.57

Table 14. Nitrate-N values and its environmental interpretation (From: Madison and Brunett 1985).

NO_3-N (mg/l)	Environmental interpretation
< 0.2	Assumed to represent background concentration
0.2-3.0	Transitional; concentrations may be may not represent influence from human activities
3.01-10.0	May indicate elevated concentrations resulting from human activities
> 10.0	Exceeds Maximal contaminant Level (MCL) for NO_3-N set by US EPA

Phelps (2004) analyzed the $^{15}N/^{14}N$ ratio in water samples collected from 37 wells and 3 springs of the Silver Spring groups (Table 15). In general, $^{15}N/^{14}N$ values less than 6‰ are indicative of the effects of inorganic N (fertilizers), values between 6 and 9 per mil are representative of mixed inorganic and organic source or a soil organic source; values greater than 9 are indicative of organic N (for human and animal wastes) (Coplen 1993; Katz et al. 1999). The median $^{15}N/^{14}N$ value for all groundwater samples was 4.9‰, which lies within the upper range of inorganic sources. The median $^{15}N/^{14}N$ ratio for urban land uses was slightly higher indicating more organic N (possibly septic tanks or pet waste), while the median for agriculture and rangeland/forest were within the range of generally inorganic sources. One of the high isotopic ratios observed for agricultural land use resulted from a location within a spray field for wastewater application ($^{15}N/^{14}N$ ratio = 8.9), which is close to the range indicating organic N.

Table 15. The ratio of $^{15}N/^{14}N$ (‰) in groundwater samples under different land uses (From: Phelps 2004).

Land use type	Minimum	Maximum	Median
Urban	-0.5	10.8	5.4
Agriculture	1.9	8.9	4.8
Rangeland and forest	2.2	11.5	4.1

The main spring of the Silver Springs group was sampled four times for $^{15}N/^{14}N$ ratio, which showed two distinct N isotope ratios: two values indicating inorganic N source (3.7‰ and 3.8‰) and two values indicating mixed sources with a strong influence of organic sources (8.1‰ and 8.7‰). One explanation is that the influence of inorganic sources dominates periods of low flows, when discharge is derived mainly from flows through the porous matrix, which could have inorganic N that was added continuously to the basin over longer periods of time by fertilizer applications. During periods of high flow, more of the spring discharge is due to rapid connectivity between the land surface and the spring vents via flow through conduits in the limestone; this water might mobilize organic nitrogen and nitrates mineralized at the surface. Time-series data collection of isotopic ratios would permit testing of this hypothesis, and would help in identifying the temporal dynamics of loading for the purposes of improved management.

Based on tritium-helium age dating, the estimated age of spring waters is 10 years (for Abyss spring), 18 years (Blue Grotto), and 27 years (Main Spring). The age of water rising from the spring also depends on whether water comes from shallow flow paths (which contain younger water) or deeper flow paths (which contain older water). Results indicated that recharge occurred in the early 1990s for water from the Abyss, where water follows a relatively simple, shallow flow path and is not affected by mixing or dispersion. Again, the temporal dynamics of measured groundwater age is required to improve estimation of where the nitrates are from and when they were released into the environment; if, as these nominal ages suggest, the water exiting the spring carries with it the signature of land use ~20 years ago, water quality would be expected to continue to decline, even with aggressive management. If however, the bulk of the nitrate flux is in much younger water (days to months) that mixes differentially with much older deep aquifer water to create a mixture that appears to be 20 years old, then management efforts may be immediately fruitful. Further, understanding where the sites are the preferentially contribute to this mixture would be essential for meeting any pollutant load reduction goals.

Rainbow Springs

Rainbow Springs basin lies in southwestern Marion County and southeastern Levy County in north-central Florida. The basin ranges in size from ~ 645 sq miles during the dry season (May) to ~ 770 sq miles during the wet season (September) (Jones et al 1996). Seasonal variation in basin size illustrates that intra-annual variation can have a subtle but important impact on loading and water chemistry. It is estimated that between 1965 and 1993, approximately 684 tons/year of NO_3-N was discharged from Rainbow Springs complex (Jones et al. 1996). Throughout most of the basin, the confining layer is absent and the Floridan aquifer is rapidly and directly recharged from the surface when it rains. The Floridan aquifer is the principle source of water for the springs and also for domestic, agricultural, and industrial supplies in the area.

Jones et al. (1996) measured NO_3-N concentrations in water samples collected from 66 groundwater wells in the basin. Much of the basin showed NO_3-N concentrations well above the naturally occurring limit of 0.01 mg/L (Table 16). The highest NO_3-N concentration occurred just west of Ocala, in an area of high recharge, where N applied to the surface as fertilizers or animal waste quickly enters the flow system, which results in enriched ground water NO_3-N concentrations. There appeared to be a linear zone of elevated NO_3-N that extended southwest to the head spring area. This zone corresponds to the trend of the fractures in the aquifer, which may serve as a conduit to transport NO_3-N from the area west of Ocala, directly to the Rainbow Springs. In addition, numerous large closed depression features along the zone serve as entry points for NO_3-N enriched surface runoff across the entire length of the zone. High NO_3-N concentrations are also found in the western portion of the basin in a linear zone extending to the northwest from the head spring area. This zone was previously identified as a possible fracture zone that connects numerous, large, closed depressions. The areas with low NO_3-N concentrations were in the east region under forests and wetlands, which are not significant sources of N. The lowest NO_3-N concentrations were found in the north central portion of the basin, where the Hawthorn clays overly the Floridan aquifer. Clay confinements are responsible for the low NO_3-N concentrations because N applied to the surface is prevented from infiltrating into the Floridan aquifer. These findings suggest hydrogeology as an important contributor to high NO_3-N concentrations measured in the groundwater wells of the basin.

Table 16. Summary of NO_3-N concentrations in study area wells (Jones et al. 1996).

NO_3-N concentration range (mg/l)	Percentage of wells
<0.01	14
0.01-0.1	3
0.1-0.5	30
0.5-1.0	24
1.0-3.0	23
3.0-5.2	6

The study area has many areas that are proven sources NO_3-N : septic tank effluent, treated sewage effluent, commercial and residential landscape fertilizers, and agricultural fertilizers. Nineteen wells were sampled for δ^{15}N isotopes, and the values ranged form -0.5‰ to +7.7‰ with an average value of +2.4‰. Except for the sample with the highest value (+7.7‰), all of the wells had δ^{15}N ratios within the range of natural decay in unfertilized soils, but too low for the values to have originated from organic sources. However, the NO_3-N values in the samples are too high to have originated from natural sources. It was concluded that agricultural fertilizer is the principal source of NO_3-N in ground water in the study area.

Kuphal (2005) tabulated the loads from septic systems and centralized treatment facilities in the Rainbow Springs springshed and concluded that septic tanks contribute nearly 40 times the load (91 tons NO_3-N/yr) that the centralized plants do (2.7 tons NO_3-N/yr). As a result, diffuse wastewater discharges are likely to be more efficient targets for regulation and water quality protection programs than efforts to reduce loading from centralized facilities. This value for septic tanks is similar, but higher than other estimates of the septic load (Jones et al. 1996); this diffuse flux is notoriously difficult to estimate because it depends heavily on design and age of the system, and local characteristics of the drainfield.

Jones et al. (1996) estimated that approximately 684 tons of nitrate-N is discharged each year in groundwater emanating from the Rainbow Springs Complex. While it is difficult to ascribe a particular source to that flux, the loads applied under various land uses are informative about the potential sources of that N. The caveat is that the loads applied to the land from septic tanks, urban runoff and agriculture are not necessarily the same as the fluxes to and through the Floridan aquifer because of variable capacity for attenuation in space. Table 17 is a summary of N loads to the springshed, which was divided into three regions (eastern, central and western). The N loads contributed to each region were computed based on estimated fertilizer application rates and published N concentrations in wastewater. This indicates, based on the land use loadings and the spatial extent of each land use in the springshed, that the largest N loads were generated by pasture lands, and that the contribution by row crops was minimal. Another N load of significance was the background load in atmospheric deposition; it is unlikely to have a substantial effect on groundwater because it arrives in diffuse form and in small quantities, and is used by plant communities. The overall load from septic tanks is a small fraction of the total (~1%) which would suggest a limited threat to regional ground water quality. It could be argued, however, that septic tank loads to the environment are acutely problematic because they discharge directly to groundwater. If septic tank loads (80-90 tons) are transported to the spring unattenuated, that source would represent roughly 12% of the total flux; isotopic investigations and tracers would be needed to establish that. Because at least 5,000 septic tanks were identified in the immediate recharge area of the spring based on aerial photos, and with continuing population growth, septic tank loading deserves ongoing scrutiny. Conversion to centralized water treatment might have a water quality benefits, but creates the indirect problem of biosolid disposal that is already estimated to be a substantial load in the springshed. Per capita loading from septic tanks is estimated to be between 2.4 and 2.9 kg dissolved inorganic N (DIN) per year (including both nitrate and ammonium; Reay 2004), with drainfield concentrations of DIN between 40 and 120 mg N L^{-1} (Reay 2004). While the DIN load was dominated by NH_4^+ at or next to the drainfield (>99% of DIN), nitrate was the dominant form of DIN at distances greater than 20 m, suggesting greater mobility and strong oxidation gradients.

While current contributions from turf fertilizer were insignificant, as development increases, residential turf and golf course loads could become a more significant source of N.

Table 17. Total N loadings (tons/yr) into groundwater in Rainbow springshed

Source	Regions			% of total loads
	Eastern	Central	Western	
Atmospheric	431	504	467	16.8
Septic tanks	22	17	24	0.7
Turf Fertilization	50	11	18	0.9
Golf courses	84	0	35	1.4
Sewage	13	3	1	0.2
Septage spreading	58	0	24	1.0
Row crops	0	0	44	0.5
Cattle production	410	439	407	14.7
Horse farms	991	510	< 1	17.5
Improve pasture	1,728	1,364	871	46.3

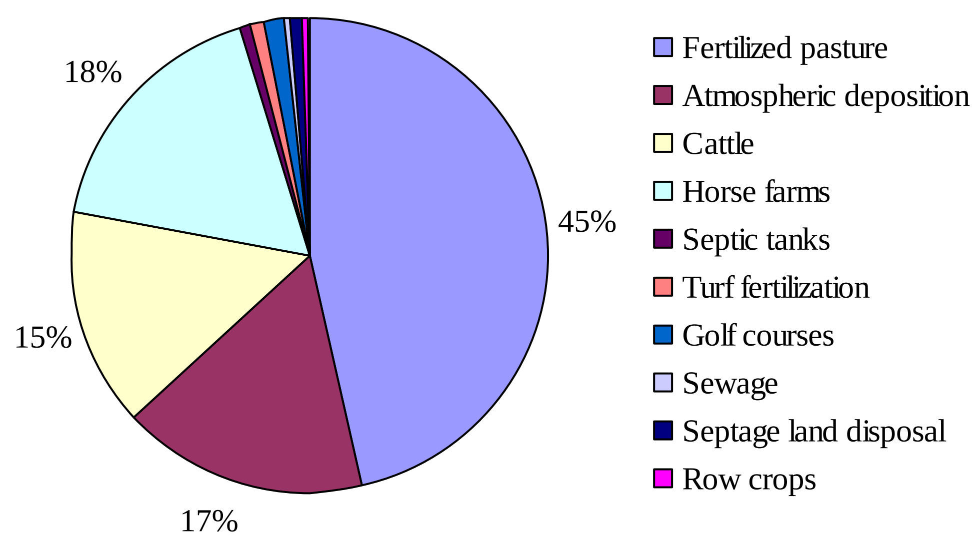


Fig 25. Relative contribution of N loads different sources to the groundwater discharging from the Rainbow Springs (After Jones et al. 1996)

Wekiwa Springs

Wekiwa Springs is a 2nd magnitude spring located in the Middle St. Johns basin (Fig 26). It forms the headwater of the Wekiva River, which is a tributary of the St Johns River. The Wekiwa springshed lies in western Orange County and includes small portions of Seminole, Lake, and Polk Counties (Fig. 27). The hydrogeologic units in the springshed consist of the surficial aquifer system, the intermediate aquifer system, and the Floridan aquifer system.

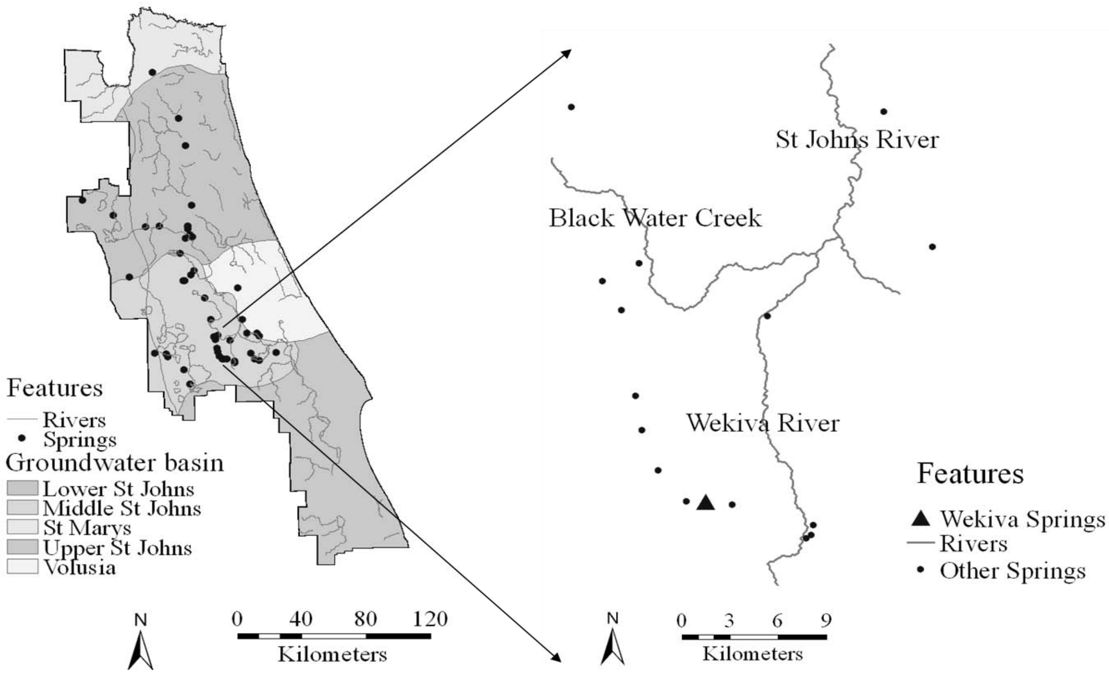


Fig 26. *A - Springs, rivers and groundwater basins in the SJRWMD.*

The NO_3-N concentrations in various springs in the Wekiwa springshed have varied over time, with many having elevated NO_3-N concentrations (greater than 0.2 mg/l) (Toth 1999). In 1999, the highest concentrations of NO_3-N in groundwater were found west and south west of Lake Apopka, where concentrations above 5 mg/L occurred (Toth and Fortich 2002). Water quality in the Wekiva River has been relatively consistent since 1990 with respect to the major constituents of concern (total organic carbon and nitrogen) (Winkler and Ceric 2006), but existing concentrations of nitrate (~ 1.4 mg/l) in the spring is indicative of substantial enrichment over natural background conditions.

During the last 15 years NO_3-N concentrations in the Wekiwa Springs have not trended up or down; however, they varied considerably, between 0.81 mg/l (in July 2001) to 2.0 mg/l (in January 1995) with a mean 1.39 mg/l and median 1.40mg/l. During the same period (1990-

2006), discharge from the Wekiwa Spring varied from 38.60 cfs in 1998 and peaked at 87.81 in 1995, with a mean of 67.02 and median of 67.65 cfs. The average annual discharge of the spring ranged from 58.86 cfs in 2001 to 73.03 cfs in 1995. Time series variation of NO_3-N concentrations and discharge measured on the same day in the springs (Fig 28) shows that NO_3-N concentrations covary positively (r =0.59) with spring discharge. There are two implications of

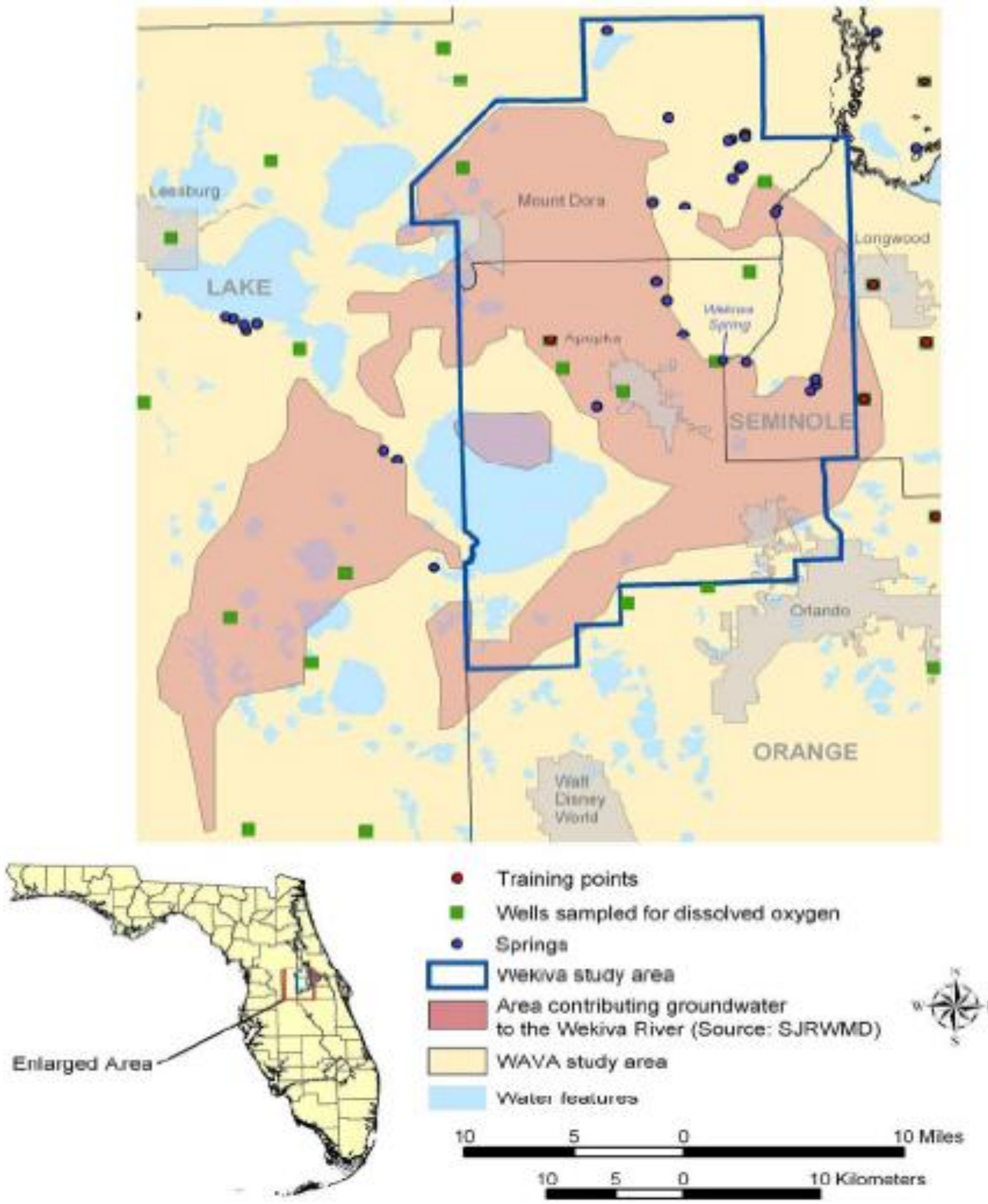


Fig. 27 – Location of the Wekiva Springs study area and springshed (from Cichon et al. 2005)

the hydrological covariance: first, increased concentrations of NO_3-N during early and mid 90s could be related to the flushing effect of surface runoff that drains to the spring. Second, and more importantly, the nitrate load to the spring is dominated by groundwater with a short subsurface resident time. This inference is based on a conceptual two-end member mixture model. A two-end member mixture model makes the simplifying assumption that the discharge is a mixture of two distinct reservoirs, namely a deep and old groundwater source, and a shallow, young source. While it is probably substantially more complex than this, with waters of various ages and depths mixing dynamically to generate vent flow, this two-part mixture is illustrative. Two assumptions are made; first, the younger source is primarily responsible for flow variability. That is, during periods of high flow, the proportion of water that is derived from recent discharge goes up. This is borne out by evidence of drought related flow declines during 2001-2002. Second, the younger source is also more enriched with nitrates compared with the flow-static older source. Evidence for this assumption is observed in the fact that the covariance between flow and concentration is positive. The overall hypothesis, therefore, is that the nitrate delivery is primarily driven by groundwater of recent origin. Only a series of age-measurements as a function of flow will yield conclusive evidence, but the observed covariance is suggestive.

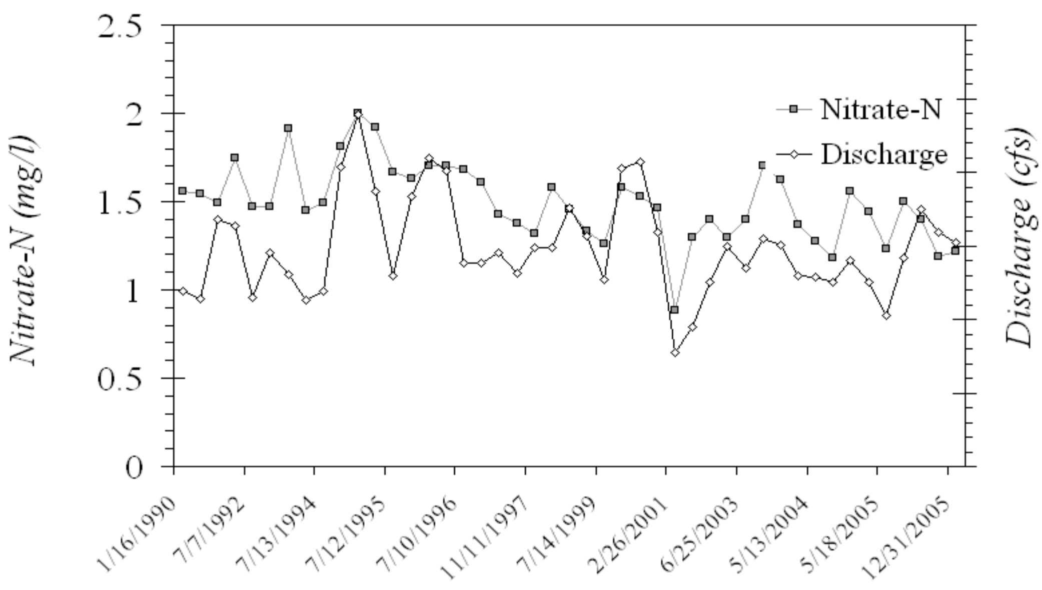


Fig 28 Time series measurements of NO_3-N and discharge in the Wekiva Springs.

The $\delta^{15}N$ values in Wekiwa Springs are between +5.3 and 6.8‰, suggesting that NO_3 is from a mixture of organic and inorganic sources (Toth 1999). However, in wells distributed throughout the Wekiwa springshed, areas with high NO_3-N concentrations have $\delta^{15}N$ values below 5.0‰ (Toth and Fortich 2002), suggesting a fertilizer source. The sources of nitrates in the spring are likely from the high recharge areas just south and south west of the spring. The estimated age of groundwater in Wekiwa Springs is 17.1 years (Toth 1999). As the groundwater is young, a significant fraction of spring water comes from the nearby sources, and could be related to historical land use changes in the high recharge areas to the south of the spring. Therefore, a more locally developed flow system from the Upper Florida aquifer in the vicinity of the springs could be the source of NO_3-N in Wekiwa Springs.

The Wekiva springshed extends south and southwest of the spring with the most vulnerable recharge areas in Orange County, just north of Lake Apopka (Fig. 29 – note, the study area in Fig. 29 is not the springshed, *per se*). The increase in nitrate concentrations in the early 90s is related to historical land use change in the Wekiwa springshed. In 1973, land use in the springshed was primarily pasture and urban; by 1990 most of the land was under urban and

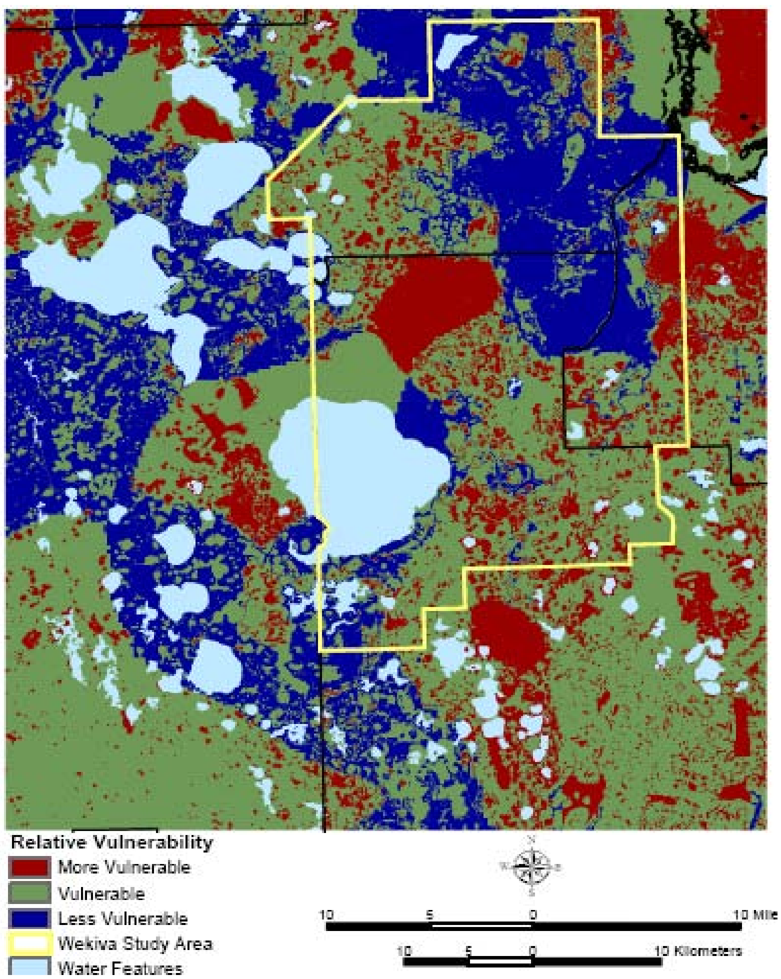


Fig. 29 – Wekiva Springs study area (yellow box) and aquifer vulnerability to contamination from surface activities. From Cichon et al. (2005).

residential land uses, indicating that the sources of NO_3-N are likely a mixture of leachate from septic tanks and recharge from fertilized lawns (Toth and Fortich 2002). In an estimated 24,600 ha area of Orange and Seminole Counties that recharge the Wekiwa Spring groundwater basin, residential and urban land use increased from 5,574 ha in 1990 to 7,370 ha in 2000. This shift in land use in the high recharge areas corroborates evidence about nitrate sources based on $\delta^{15}N$ values.

Wakulla Springs

Wakulla Springs is a 1st magnitude spring located near the western edge of the Woodville Karst Plain area in north Florida and includes southeastern Leon County and eastern Wakulla County (Barrios 2006). It is a large regional discharge point for water (nominal flow ~ 9.6 m^3/s) from the Floridan aquifer. The output forms the Wakulla River, which flows 9 miles south before merging with the St. Marks River, which discharges to the Gulf of Mexico.

Wakulla Springs has experienced a significant increase in NO_3-N concentrations since 1971 (Chelette et al. 2002). Between 1970 and 1977, the median NO_3-N concentration was 0.26 mg/L. From 1989 through 2000, the median concentration increased to 0.89 mg/L, with concentration peaking in the early 1990s and declining slightly thereafter. In February 2001, the spring was ranked “poor” in stream condition index (SCI) and the periphyton community in the spring was dominated by taxa tolerant of nutrient enriched conditions (FDEP 2001).

Katz et al. (2004) investigated the sources of nitrates observed in Wakulla Springs. The water samples had $\delta^{15}N$ values between 5.3 and 8.9 ‰, indicating that the nitrogen originates from a blend of organic and inorganic sources. The quality of water discharged from Wakulla Springs is predominantly determined by the quality of ground water in the Floridan Aquifer. While the springshed for Wakulla encompasses a large area that includes portions of southern Georgia and much of Tallahassee, land use in the unconfined regions of the springshed to the south appear to influence the water quality to a greater degree (Chelette et al. 2002). Under low flow conditions, discharge from the Wakulla Springs is composed entirely of groundwater. Under high-flow conditions discharge is still primarily Floridan aquifer water, though surface runoff (e.g. sinking streams) conveyed via a complex conduit system from the confined regions of the springshed to the vent becomes increasingly important. For example, Ames Sink is located about 5.5 miles due north of Wakulla Springs, and receives water from Lake Munson, which is part of the urban drainage system that drains much of the southern part of the City of Tallahassee. Given the proximity of the sink to the spring and the high hydraulic conductivity zone lying north of the spring, the water that enters Ames Sink rapidly discharges from Wakulla springs. This underscores the substantial if indirect connectivity between the urban areas of southern Tallahassee and water discharged from Wakulla Springs.

Variation in specific conductivity of spring discharge indicates a high degree of interaction between surface and groundwater (Chelette et al 2002). In September 2000, the River Sink station at Wakulla Springs received greater than 19" of rain due to Tropical Storm Helene. Prior to September 2000, specific conductance in Wakulla Springs was > 300 µmhos/cm; similar values were observed the previous year, and in numerous springs around the region. These elevated conductance values are largely due to saturated export of inorganic carbon (carbonates) due to karstic weathering. During September 2000, conductivity measurements in Wakulla Springs decreased from 310 to 250; however, 3 weeks after the tropical storm, conductivity rebounded to 320 µmhos/cm. The decrease in conductivity results from elevated surface water contributions to the discharge of the spring. Since rainfall and surface runoff have characteristically lower conductance values, their inflow via sinking streams will undoubtedly mix and dilute Floridan Aquifer waters discharging from the spring, reducing conductivity of the spring water. What is perhaps more surprising is the limited effect of such a tremendous inflow of low conductance water (a decline of ~ 60 µmhos/cm). This is suggestive of complex mixing dynamics that include an element of piston flow dynamics.

The high degree of interaction between surface and groundwater results in seasonal variation of nitrate concentrations in the spring water. Results from Katz et al. (2004) showed that during high-flow conditions, spring waters have *decreased* nitrate concentrations (notably different from the flow vs. NO_3 relationship in Wekiwa Springs – Fig. 28) and increased dissolved organic carbon (DOC) concentrations that resulted from mixtures of 20-95% surface water. Further, higher NO_3-N concentrations were associated with shallow wells, and elevated NO_3-N concentrations resulted from mixtures with relatively more water from these shallow sources vs. water from deeper zones in the Floridan aquifer.

Average aggregate load of nitrate-N from different sources to the contributory area of the Wakulla Springs between 1990 and 1999 are summarized in Table 18. Based on discharge measurements made between 1907 and 1999, Wakulla Springs had a median flow of 340 cfs, and between 1989 and 2000, the median nitrate-N concentration was 0.89 mg/L. Thus, the Wakulla Springs discharges an estimated load of 270,000 kg-N/yr. The highest nitrogen loads were contributed by wastewater treatment facilities, which contributed 55% of the nitrate-N loads to the contributory area of Wakulla Springs. This indicates the impact of increasing population on NO_3-N discharged from the Wakulla Springs and the importance of the WWTP location relative to the spring. However, as it reacts with the landscape and hydrosphere, the estimated loads are subjected to denitrification. Chelette et al. (2002) estimated that the N removal efficiency within the Wakulla Springs contributory area is approximately 78%. Assuming the removal efficiency remains the same, the NO_3-N loads discharged from the Wakulla Springs are likely to increase as the population of Wakulla County and the city of Tallahassee increase. Fig. 30 shows estimated loads by source for the springshed where the aquifer is unconfined or semi-confined, which are different primarily in the influence of atmospheric deposition and commercial fertilizer.

Table 18. Ten-year average and median annual nitrogen loads to the Wakulla Springs Contributory Area (From Chelette et al. 2002)

Source	Average N load (kg/yr)	Median N load (kg/yr)	% of Total
Waste water treatment facility effluent	360,000	345,000	40
Atmospheric deposition	232,000	229,000	26
WWT facility residuals	130,000	126,000	15
On site disposal system	56,000	56,000	6
Commercial fertilizer	60,000	65,000	7
Sinking streams	33,000	33,000	4
Livestock	14,000	14,000	2
Total	**885,000**	**868,000**	100

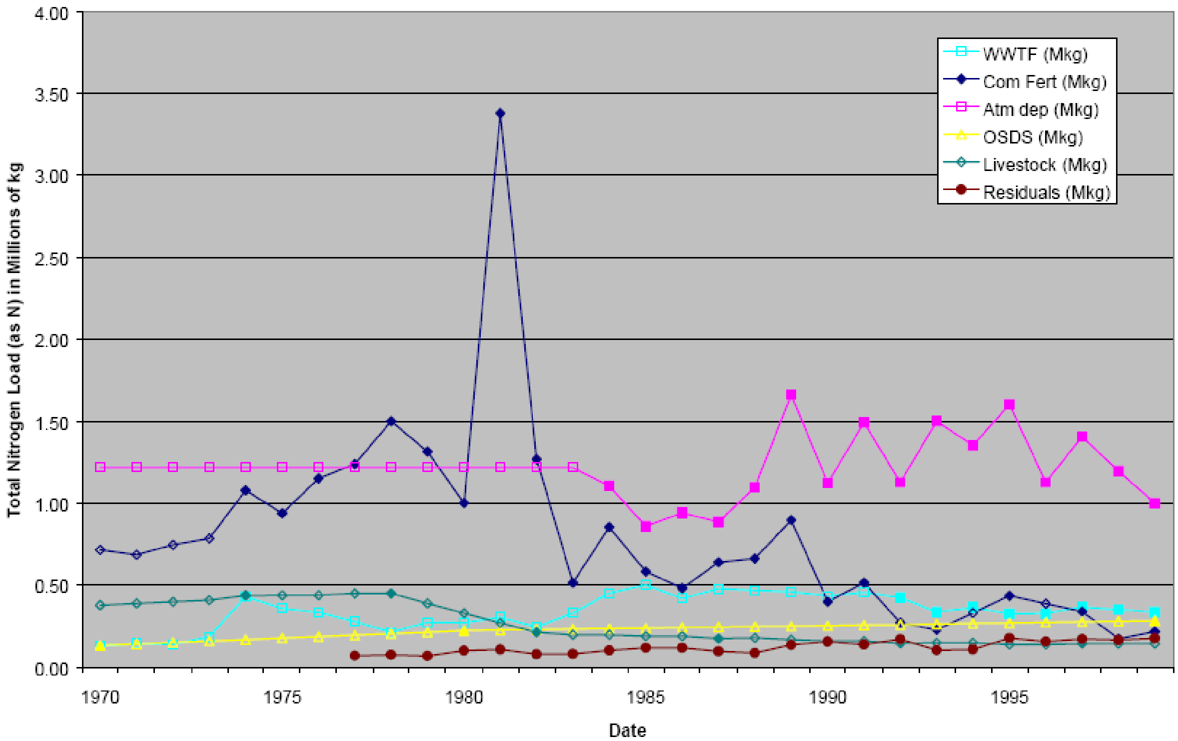


Fig. 30 – Estimated temporal loading of Wakulla Springs from different sources in the semi-confined and unconfined contributing area (note that Table 17 is for the entire area, including the confined region).

Ichetucknee Springs

Ichetucknee Springs consists of 9 springs, with 6 springs in Columbia County and 2 springs in Suwannee County. It consists of 1 first magnitude, 6 second magnitude, and 1 third magnitude spring; many have shown elevated concentration of NO_3-N. Hornsby and Ceryak (1998) surveyed the sources of nitrates in the Suwannee River Basin and reported that nitrate-N concentrations in the Ichetucknee Springs group ranged from 0.04 to 1.45 mg/L with a total flow of 345.72 cfs, yielding a total load of ~ 150,000 kg N per year.

The Suwannee River Water Management District and the U. S. Geological Survey evaluated sources of nitrates in the spring waters of the Upper Floridan aquifer in the Suwannee River Basin (Katz et al. 1999). The δ^{15} N-NO_3 of the Ichetucknee Blue Hole Spring was 4.4 indicating that the nitrates are primarily of inorganic sources, with limited contribution of organic sources. This suggests that the spring receives recharge water from an area dominated by agricultural lands that is fertilized with chemical fertilizers and manure spreading or waste disposal; further it indicates that septic systems and the sprayfield used to dispose of treated wastewater from Lake City provide limited contribution of total N load.

Nitrogen inputs from different sources in Columbia County during 1940s to late 1990s are shown in Fig 31. Fertilizer use increased from 1950s to late 1970s, then decreased until 1993, and again increased substantially from 1993 to 1997. Nitrogen inputs from all non-point sources peaked in the late 1970's corresponding to the peak in fertilizer use during this time, and heavy use of fertilizer in the past is also corroborated by $\delta^{15}N$ data. During 1954-1997, the total estimated N inputs ranged from 2.19-5.77 x 10^6 kilograms per year. The relative contribution of estimated N inputs from animal wastes (dairy and beef cows, poultry, and swine) to total estimated N inputs varied from about 15-30%. In 1997, the land use distribution was primarily managed forest (60%), followed by agriculture (22%), urban (2%), and wetlands (15%).

Katz et al. (1999) estimated that the average residence times of groundwater discharging from Ichetucknee Blue Hole springs at 27-69 years, and post-1993 water accounts for only 22-35% of discharge water in the Ichetucknee Springs. Therefore, historical land use and anthropogenic activities in the contributing area of the basin may be responsible for the nitrates observed in a larger fraction (65-78%) of water discharged by the springs. Further, increased fertilizer use during the 1990s is likely to increase the nitrate concentrations measured in the spring water in the near future.

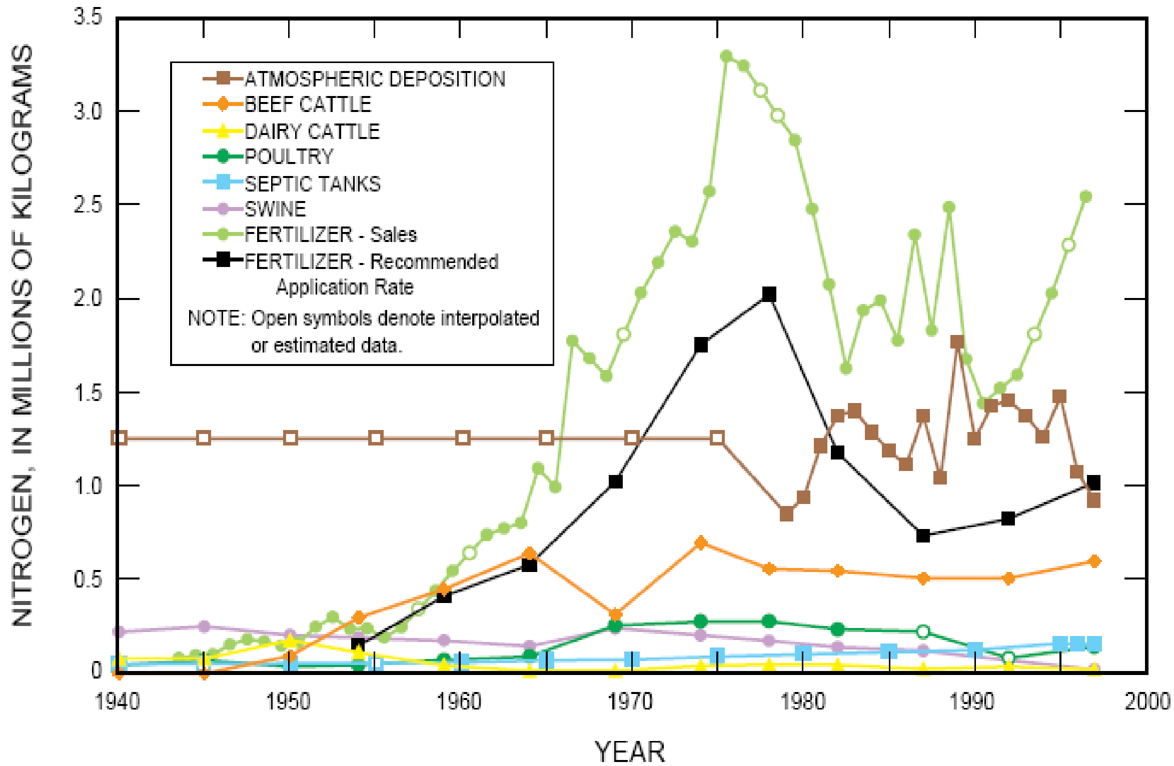


Fig 31. N inputs in Columbia County during 1940 to 2000 (From Katz et al. 1999).

Synthesis of Case Studies

Case studies used here underscore the systemic increase in nitrate concentrations in water discharged from springs. The matrix and conduits of the karst aquifer allow complex ground-water mixing and rapid movement; in areas where the aquifer is unconfined, the impact of nutrient leaching to groundwater will have a direct influence on spring water quality. Seasonal variation in precipitation influences the relative proportion of groundwater and surface water discharged by springs, which has important but mixed effects on water quality. Under baseflow conditions, discharge is primarily composed of deep Floridan aquifer groundwater and therefore, historical land use activities in the springsheds have a major influence on spring water quality. However, during high flow conditions, both historical and current land use activities influence spring water quality. Interestingly, the relationship between flow and nitrate concentrations is a positive association in some springs (e.g. Wekiwa) but negative in others (e.g. Wakulla), underscoring the need for site specific observations. The absence of basic generalizations about the manner in which flow and nitrates co-vary is an important unknown to be addressed.

Nitrate-N concentrations in the Floridan aquifer vary substantially despite the absence of mixing barriers in the porous karst matrix and fractures; substantial variation is observed spatially and temporally. In those studies where spatial surveys of nitrate concentrations in the groundwater have been undertaken (e.g., Silver Springs, Wakulla Springs, Santa Fe River basin), variability in concentrations is often an order of magnitude larger than temporal variability in spring discharge concentrations, suggesting that the aquifer matrix through which water flows to the spring vent are highly anisotropic (i.e. spatially non-uniform with respect to transmissivity). Temporal variability also plays a confounding role in understanding the loading and transport process; for example, the $\delta^{15}N$ value measured in water samples change temporally in response to rainfall events, indicating that the source of nitrates is a dynamic process. In the Wakulla Springs, the $\delta^{15}N$ decreased from 6.8‰ in September 1997 to 5.3‰ in October 2000, which was attributed to increased contribution of nitrates by runoff from inorganic fertilizers after pulses of heavy rain. There is a paucity of isotopic fraction and groundwater age estimation time series; one inference from dynamics of spring systems observed here is that an improved understanding of the vent-discharge mixture can aid in identifying loading dynamics. Of paramount importance for future management of springsheds is improved prediction of how management activities will affect water quality; in the absence of detailed information about the time required for landscape loads to reach the spring vent, ***timelines may be set for meeting load reduction targets that are unrealistic.*** For example, if the age of groundwater emerging from many of the springs is indicative of the age of the nitrates that it carries, then management efforts today may take 20+ years to change output. Preliminary and anecdotal evidence suggests that the travel times of nitrates in the subsurface may be appreciably shorter, but this remains an important unknown.

The various case studies show that nitrate concentrations measured in spring water result from a complex interaction of agriculture, animal and human activities, coupled with hydrogeology - acting over time. The relative contribution of nitrates to spring water from different sources depends on land use activities in the springshed (both historical and current). In Wakulla Springs, for example, nitrate contributions from wastewater treatment facilities are very significant (approximately 55%) while the contribution by agricultural fertilization and animal activities are relatively small. In stark contrast, agricultural and animal activities account for nearly 60% of the N loads in Rainbow Springs, while septic tanks contribute <1% of the total load. In the Woodville Karst Plain, high nitrate-N concentrations (13.8 mg/l) were found at a site near residences with septic-tank systems, suggesting the importance of proximity of high-risk areas to nutrient loading in the spring water. Similarly, high nitrate concentrations in Poe Spring (lower Santa Fe basin) and Lafayette Blue Spring (middle Suwannee River basin) could be related to wastewater disposal systems operated close to the springs. Not all areas of the springshed that have elevated nitrate concentrations will impact the water quality discharged from the springs. For example, sources of nitrates in Wekiwa Springs were primarily from the south and south west of the spring (Toth 1999), suggesting that areas elsewhere in the springshed, even those with high nitrate concentrations, may not substantially contribute to nitrate loads in the spring. Elucidating preferential flow paths in the subsurface that carry water from some areas of the karst matrix but not others to spring vents is a massive challenge, but one that may need to be addressed in order to efficiently plan for development in sensitive areas. One area of research, therefore, is the use of ion profiling of source waters and spring vents to aid in ascribing water emerging in springs to particular parts of the recharge area.

The nitrate in water samples from different springs is comprised of a variety of sources. The minimum, maximum and median values of $\delta^{15}N$ measured in water samples collected from the springs and groundwater are summarized in Table 19. A wide range in $\delta^{15}N$ values is evident, and reflects the diversity of land use activities in the springsheds, and potentially significant temporal variability (either stochastically, or as a function of hydrograph phase). Minimum values in most spring water samples indicates that N was contributed by agricultural fertilization only, while maximum values (e.g., 11.2 and 13.8 mg/l in Rainbow Springs and Wakulla Springs, respectively) indicates that N was contributed primarily from organic sources. Median values for all the springs are in the ambiguous isotopic fraction range, which suggests that spring N loads are derived from a blend of inorganic (agricultural fertilization) and organic sources (septic tanks, animal wastes, etc.). The major sources of nitrates observed in the springs and groundwater are agricultural (crops and pasture fertilization), animal (poultry operations, cattle and horses), and human (sewage, water treatment facility) activities, and atmospheric deposition. Nitrogen loads from different sources into the Wakulla and Rainbow Springs suggest that atmospheric deposition makes a significant contribution to N loads to the springs. It also appears that atmospheric deposition is the only source that significant contributes to N loads in all the springs. To make more informed sense of isotopic ratios observed in spring discharges, a more detailed time-series characterization of multiple springs is needed. Knowledge of, for example, characteristic serial autocorrelation in isotopic fractionation is largely unavailable, which hampers generalization of single observations to whole-spring behavior.

Table 19. Comparison of $\delta^{15}N$ values measured in springs and groundwater basin

Location	N	$\delta^{15}N$ values			Nitrate sources	References
		Min	Max	Median		
Rainbow springshed	19	0.5	7.7	2.4	Inorganic fertilizers	Jones et al. (1996)
Wekiwa springshed	9	3.6	11.2	4.8	Inorganic fertilizers, organic sources	Toth and Fortich (2002)
Woodville Karst Plain	13	1.7	13.8	6.8	Inorganic fertilizers, organic sources	Katz et al. (2004)
Wakulla Springs (subset of the Woodville Plain)	3	5.3	6.1	5.8	Inorganic fertilizers	Katz et al. (2004)
Suwannee Basin springs	26	2.7	10.6	5.4	Inorganic, organic sources	Katz et al. (1999)

In most of the case studies, the impact of urbanization on spring water quality is clearly evident. In particular, when urban areas lie close to spring vents or hydrogeologic conditions favor preferential transport of nutrients from distant urban areas to the vents, the impact of urbanization on water quality can be alarming. For example, in Rainbow Springs, the highest N concentrations were found in areas to the west of the city of Ocala. The impact of the city on elevated nitrate-N concentrations was significant because of a fracture in the aquifer that served as a conduit to transport pollutants rapidly from the city to the springs. A similar scenario appears in Wakulla Springs, where Ames Sink is a known conveyance of water from the urban drainage of the southern part of the City of Tallahassee to the spring vent. Similarly, increases in nitrate concentrations in Silver Springs were related to increases in urban and residential land uses in the springshed.

The lowest groundwater nitrate concentrations were found in areas where the Hawthorn clays overlie the aquifer, and form a protective barrier for entry of nitrates into the groundwater. These findings suggest that hydrogeology is an important factor to influence NO_3-N concentrations measured in the springs and groundwater of a basin. One of the most important assets in water quality protection in the state is the residence time and biological activity of Florida's warm, humid, low-relief landscape. Where the aquifer is unconfined and rainfall can infiltrate to the groundwater with minimal contact with surface reservoirs (wetlands, lakes, organic-rich vadose zone), landscape autopurification is substantially attenuated. These areas need to be primary focal area for future water quality management because of the intrinsic vulnerability of groundwater contamination beneath them. Since all springs exist in areas of the state where the Hawthorn is eroded away, this intrinsic vulnerability translates most directly into risk for declining water quality in spring discharges.

Measured groundwater residence times for water emerging from the springs are on the order of decades; if the nitrates have similar residence times (a speculation that has not been established) nitrates found spring discharge may reflect historical land use and nutrient loadings to the springshed much more than contemporary land use patterns. Given the increasing intensity of land use, this could suggest that spring water quality will continue to decline despite any efforts to mitigate contemporary loading. Data from Ichetucknee Springs suggest that historical land use and anthropogenic activities (peak fertilizer use during the 1970s) in the contributing area of the basin were responsible for elevated nitrate concentrations in the 1990s. Improving our understanding of the residence times of nitrate in groundwater is a central step in setting realistic timelines for water quality improvement with contemporary management.

There is an overall increase in nitrate concentration measured in springs and groundwater over time. However, the increase can be dramatic in areas with high risk land use categories. For example, in the Silver Springs springshed, median nitrate concentrations in groundwater increased from 1.01 to 1.2 mg/l in a decade. This modest increase was paralleled by much more dramatic increases in peak concentration events; that is, the maximum groundwater nitrate concentration increased from 3.6 to 12 mg/l over that same period. This evidence for greater variability may reflect the complex mixing dynamics that occur prior to vent discharge, and may underscore the degree to which site conditions still control aggregate water quality. That is, while the evidence for systematic concentration increases is incontrovertible (Fig. 22), there is also substantial evidence to suggest that natural hydrochemical and biological controls still regulate discharge concentrations to a large extent. Understanding those processes is the essential unknown for springshed management, and the challenge of meeting pollutant load reduction goals.

Conclusion and Recommendations

1. The experience in Florida with nitrogen enrichment is repeated all over the globe, reflecting the dramatic influence which human activities have had on the global N cycle. What sets Florida apart is two-fold: first, the significant role that wetlands play in the landscape in some parts of the state, offering substantial buffering against N loading. Second, the relative rapidity with which nitrate pollution moves from the surface to the subsurface in areas of the state that are hydrogeologically unconfined sets those areas apart as highly vulnerable and in need of protection. Loading of N to springs occurs in areas characterized by the latter condition making the principal challenge of springshed protection the management of sources (e.g., via changing land uses), not the management of sinks. Further, strategically focusing management strategies in areas with high vulnerability to loading is essential.

2. Agricultural activities (crop fertilization, dairy operations, poultry farms) and urban development (fertilization of lawns and golf courses, wastewater effluents, spray fields, septic tanks) are ALL sources of NO_3-N in the springs and groundwater of Florida. While there is evidence of predominance of a particular loading source to a particular spring or river, it is frequently temporally variable and always site specific. Concluding generally that the principal source of N is fertilizer (as inferred from isotopic fingerprinting) is perilous for a specific system without additional confirmatory data. Effective management will require simultaneous attention to all of relevant sources, and characterization of sources and dynamics that are location specific. In particular, a hydrogeologic characterization (both contributing area and flow conveyances) of the springshed is critical so that the areas posing the greatest potential impact on water quality can be targeted while implementing strategies to protect spring water quality.

3. The mean residence time for groundwater discharging from many of the springs is on the order of decades indicating that NO_3-N loading from the land surface could persist in groundwater for several decades before re-emergence into the springs and surface water. In contrast, however, geochemical evidence suggests that water emerging from springs is a complex composite of “old” and “new” groundwater, with strongly

different concentrations of nitrates, as well as other contaminants. Improving our understanding of the temporal dynamics of nitrate loading is critical for setting realistic timelines for management-induced water quality improvements.

4. Nitrate-N concentrations measured in springs and groundwater reflect the hydrogeology and land use activities in the basin, but mixing dynamics between deep groundwater, shallow groundwater, and surface water make the relationships to land use complex. Deep groundwater contributions to spring and river discharge changes with season (baseflow vs. high flow conditions), which has important implications for NO_3-N loading. A program to elucidate mixing dynamics among the various source water end-members (e.g., via ion profiling, isotopic tracers, conservative tracer studies) is an important area of future monitoring.

5. The role of landscape features like wetlands, lagoons, and riparian areas on nitrate attenuation is well established for basins dominated by flows at the surface or near-subsurface. While the capacity of these landscape features to reduce nitrate loading to aquatic systems should be maximized by a combination of their protection, restoration, and enhancement, they are unlikely to be effective in areas where the aquifer matrix is unconfined, which represent the most vulnerable sites. In particular, in areas where aquifer water does not come into contact with organic matter prior to discharge in a spring, sink enhancement measures are unlikely to yield high benefits.

6. Given our principal conclusion regarding the need to address N enrichment at the source, policies and practices that limit N loading are of paramount importance. Knowledge of subsurface conveyances is a first-order challenge in delineating areas of high vulnerability to N loading and transport, particularly given the strongly non-uniform characteristics of the aquifer matrix. By extension, strategies that depend on land management (e.g., altered fertilization schedules) are less likely to yield strong results than strategies that regulate land use, or provide incentives for land use change. Surface flow data suggest that using lands in highly vulnerable areas (e.g., those delineated by the Florida Geological Survey's Floridan Aquifer Vulnerability Assessment – FAVA) for forestry or low intensity pasture will minimize N pollution risks. Few studies have systematically studied vertical N loading rates from different

land uses, so quantitative loading rates in regions where the aquifer is unconfined remain a key uncertainty.

7. The role of urbanization in degrading water quality is evident, but may not be fully realized in spring systems. The combined effects of intensive fertilization on urban lawns and golf courses, and disposal of sewage (wastewater treatment plants, septic tanks) are essential to regulate, particularly where current discharges are made to areas that are hydrogeologically sensitive. For example, WWTFs and spray fields should be constructed in areas where confining layers limit the rate at which surface water is delivered to the Floridan aquifer, and landscapes are better suited for autopurification of nitrate loads. Because rapid drainage is a key criterion for the selection of sprayfield sites, renewed consideration of wetland treatment systems, which have demonstrated N removal capacity, is an important policy priority.

8. The problem of N enrichment in Florida's springs is vast – the principal sources are diffuse, arriving from the lands used for dwellings and food/fiber production. Links between surface activities and subsurface water quality are profoundly variable; in some areas, where the environment has high natural auto-purification potential, that link is weak. In others, where water at the surface rapidly becomes water in the Floridan aquifer, that link is large and important. Ironically, it is the areas most at risk for groundwater pollution that have been the focus of much of the State's agricultural and urban development. Reversing this trend in a strategic and judicious way is the principal challenge facing Florida's springs.

Cited References

Aber, J. D. 1992. Nitrogen cycling and N saturation in temperate ecosystem. Trends in Ecology and Evolution 7: 220-224.

Ågren, I. G., and E. Bosatta. 1988. Nitrogen saturation of terrestrial ecosystems. Environmental Pollution 54: 185-197.

Albert, M.A. 2002. Monitoring and Modeling the Fate and Transport of Nitrate in the Vadose Zone Beneath a Suwannee River Basin Vegetable Farm. University of Florida, Thesis.

Alley, W. M. 1993. Establishing a conceptual framework. In W. M. Alley (ed) Regional ground-water quality, pp 23-62. Van Nostrand Reinhold Library of Congress 92-36483, New York, NY.

Anderson, D.M., Glibert, P.M. and Burkholder, J.M. 2002. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. Estuaries 25:704-726.

Andrews, W. J. 1994. Nitrate in ground water and spring water near four dairy farms in north Florida, 1990-93: U. S. Geological Survey Water-Resources Investigations Report 94-4162, 63p.

Asbury, C. E. and E. T. Oaksford. 1997. A comparison of drainage basin nutrient inputs with instream nutrient loads for seven rivers in Georgia and Florida. U. S. Geological Survey Water-Resources Investigations Report 97-4006. 7 pp.

Barrios, K. 2006. St. Marks River and Wakulla River Springs Inventory Leon and Wakulla Counties, FL. Water Resources Special Report 06-03. Northwest Florida Water Management District, Havana, FL.

Beaulac, M. N., and K. H. Reckow. 1982. An examination of land use-nutrient export relationships. Water Resources Bulletin 18:1013-1022.

Berndt, M. P., D. T. Oaksford, and G. L. Mohan. 1998. Groundwater. In E. A. Fernald and E. D. Purdum (eds) Water resources atlas of Florida. Florida State University, Tallahassee, FL.

Binkley, D. , G. G. Ice, J. Kaye, and C. A. Williams. 2004. Nitrogen and phosphorus concentrations in forest streams of the United States. Journal of the American Water Resources Association 40(5):1277-1291.

Bohlke, J. K. and J. M. Denver. 1995. Combined use of ground- water dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal Plain, Maryland. Water Resources Research 31(9): 2319-2339.

Bormann, F.H. and Likens, G.E. 1979. Pattern and Process in a Forested Ecosystem. Springer-Verlag, New York.

Bowden, W. D. 1987. The biogeochemistry of N in freshwater wetlands. Biogeochemistry 4: 313-348.

Boyer, D. G., and G. C. Pasquarell. 1995. Nitrate concentrations in karst springs in an extensively grazed area. Water Resources Bulletin 31(4) Paper No 93165.

Brady, N. C., and R. R. Weil. 1999. The nature and properties of soils. Prentice-Hall, Inc. Upper Saddle River, NJ.

Burns, D. A., and M. L. Nguyen. 2002. Nitrate movement and removal along a shallow groundwater flow path in a riparian wetland within a sheep-grazed pastoral catchment: results of a tracer study. N. J. J. Mar. Freshwater Res. 36: 371-385.

Bush, P. W., and R. H. Johnston. 1988. Ground-water hydraulics, regional flow, and ground-water development of the Floridan aquifer system in Florida and parts of Georgia, South Carolina, and Alabama. U. S. Geological Survey Professional Paper, 1403-C, 80p.

Canter, L. W. 1996. Nitrates in groundwater. CRC Press, Boca Raton, FL.

Carey, B. M. 2002. Effects of land application of manure on ground water at two dairies over the Sumas-Blaine surficial aquifer. Washington, DC, EPA-600/2-284-107; 259 pp.

Castillo, M. M., J. D. Allan, and S. Brunzell. 2000. Nutrient concentrations and discharges in a Midwestern agricultural catchment. Journal of Environmental Quality 29(4): 1142-1151.

Chapin, S. F., P. A. Matson and H. A. Mooney. 2002. Principles of terrestrial ecosystem ecology. Springer Publishers, New York, NY.

Chelette, A., T. R. Pratt, and B. G. Katz. 2002. Nitrate loading as an indicator of nonpoint source pollution in the Lower St. Marks-Wakulla Rivers watershed. Water Resources Special Report 02-1. Northwest Florida Water Management District, Havana, FL.

Cichon, J.R., A.E. Baker. A.R. Wood, and J.D. Arthur. 2005. Wekiva Aquifer Vulnerability Assessment. Florida Geological Survey Report of Investigation #104, Tallahassee, FL

Cloern, J.E. 2001. Review: Our evolving conceptual model of the coastal eutrophication problem. Mar, Ecol. Prog. Ser. 210:223-253

Copeland, R. 2003. Florida Spring Classification System and Spring Glossary. Florida Geological Survey Special Publication No. 52. 18 pp.

Coplen, T. B. 1993. Uses of environmental isotopes. In W. M. Alley (ed) Regional ground-water quality, pp 227-254. Van Nostrand Reinhold Library of Congress 92-36483, New York, NY.

Correll, D. L., T. E. Jordan, and D. E. Weller. 1999. Transport of nitrogen and phosphorus from Rhode River watersheds during storm events. Water Resources Research. 35 (8) 2513–2521.

Crandall, C.A., B.G. Katz and J.J. Hirten. 1999. Hydrochemical evidence for mixing of river water and groundwater during high-flow condition, lower Suwannee River basin, Florida, USA. Hydrogeology Journal 7:454-467

Creed, I. F., L. E. Band, N. W. Foster, I. K. Morrison, J. A. Nicolson, R. S. Semkin and D. S. Jeffries. 1996. Regulation of nitrate-N release from temperate forests: a test of the N flushing hypothesis. Water Resources Research 32: 3337-3354.

Davidsson, T. E., R. Stepanauskas, and L. Leonardson. 1997. Vertical patterns of N transformations during infiltration in two wetland soils. Applied Environmental Microbiology 63: 3648-3656.

Davidsson, T. E., and M. Ståhl. 2000. The influence of organic carbon on N transformations in five wetland soils. Soil Science Society of America J. 64: 1129-1136.

Drew, D. 1999. Introduction. In D. Drew and Heinz Hötzl (eds) Hydrogeology and Human activities. A A Balkema, Rotterdam, Netherlands.

Duff, J.H. and F.J. Triska. 1990. Denitrification in Sediments from the Hyporheic Zone Adjacent to a Small Forested Stream. Canadian Journal of Fisheries and Aquatic Sciences. 47:1140-1147

Edwards, T. M., L. J. Guillette, Jr., K. McCoy, and T. Barbeau. 2004. Final Report. Effects of Nitrate/Nitrite on Two Sentinel Species Associated with Florida's Springs. Technical Report to the Florida Department of Environmental Protection, Tallahassee, FL. 89 pp, appendix.

Elder, J.F., 1985, Nitrogen and phosphorus speciation and flux in a large Florida river wetland system: Water Resources Research, v. 21, no. 5, p. 724-732.

Etcheverry, D., and P. Perrochet. 2000. Direct simulation of groundwater transit-time distributions using the reservoir theory. Hydrogeology Journal 8: 200-208.

FDEP (Florida Department of Environmental Protection) 2001. EcoSummary Wakulla Springs. 1pp. Florida Department of Environmental Protection, Tallahassee, FL.

Fernald, E.A. and E.D. Purdum. 1998. Water Resources Atlas of Florida. Florida State University. Library of Congress Catalog Number 98-072985 ISBN 0-9606708-2-3

Fisher, D. C., and M, Oppenheimer. 1991. Atmospheric N deposition and the Chesapeake Bay estuary. Ambio 23: 102-108.

Follet, J. R., and R. F. Follet. 2001. Utilization and metabolism of N in humans. In R. Follet and J. L. Hatfield (eds) N in the environment: sources, problems and management, pp. 65-92. Elsevier, New York, NY.

Fustec, E., A. Mariotti, X. Grillo, and J. Sajus. 1991. Nitrate removal by denitrification in an alluvial ground water: role of a former channel. Journal of Hydrology 123: 337-354.

Galloway, J. N., F.J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. C. Cleveland, P. A. Green, E. A. Holland, D. M. Karl, A. F. Michaels, J. H. Porter, A. R. Townsend, and C. J. Vörösmarty. 2004. Nitrogen cycles: past, present, and future. Biogeochemistry 70: 153-226.

Gillham, R. W. 1991. Nitrate contamination of ground water in southern Ontario and the evidence for denitrification. In I. Bogardi and R. D. Kuzelka (eds) Nitrate contamination: exposure, consequence and control, NATO ASI Series G: Ecological Sciences 30. Springer-Verlag, Germany.

Gillian, J. W., J. E. Parsons, R. L. Mikkelsen. 1997. Nitrogen dynamics and buffer zones. In N. E. Haycock, T. P. Burt, K. W. T. Goulding and G. Pinay (eds) Buffer zones: their processes and potential in water protection. Quest Environmental, Harpenden Herts, UK.

Gold, A. J., P. M. Groffman, K. Addy, D. Q. Kellog, M. Stolt, and A. E. Rosenblatt. 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. Journal of the American Water Resources Association 37(4)1457-1464.

Graves, G. A., Y. Wan, and D. L. Fike. 2004. Water quality characteristics of storm water from major land uses in south Florida. . Journal of the American Water Resources Association 40(6) 1405-1419.

Greenwood, D.J. 1962. Nitrification and nitrate dissimilation in Soil. Part 2: Effect of Oxygen Concentration. Plant and Soil 17:365-378

Groffman, P. M. and J. M. Tiedge. 1989. Denitrification in northern temperate forest soils: spatial and temporal patterns at the landscape and regional scales. Soil Biology and Biochemistry 21(5) 613-620.

Groffman, P. M., A. J. Gold, and R. C. Simmons. 1992. Nitrate dynamics in riparian forests: Microbial studies. J. Environmental Quality 21: 666-671.

Groffman, P. M. 1994. Denitrification in freshwater wetlands. Current Topics in Wetland Biogeochemistry. Vol. 1, pp. 15-35.

Guillette, L. J., Jr. and T. M. Edwards. 2005. Is nitrate an ecologically relevant endocrine disruptor in vertebrates? Integrative and Comparative Biology 45(1): 19-27.

Hallberg, G. R., and D. R. Keeney. 1993. Nitrate. In W. M. Alley (ed) Regional ground-water quality, pp. 297-322. Van Nostrand Reinhold Library of Congress 92-36483, New York, NY.

Hallberg, G. R. 1989. Nitrate in ground water in the United States. In R. F. Follet (ed.) N management and groundwater protection. pp. 35-74. Elsevier, Amsterdam, The Netherlands.

Ham, L. K., and H. H. Hatzell. 1996. Analysis of nutrients in the surface waters of the Georgia-Florida Coastal Plain study unit, 1970-91.: U. S. Geological Survey Water Resources Investigations Report 96-4037, 67 p.

Hanson, G. C., P. M. Groffman, and A. J. Gold. 1994. Symptoms of N saturation in a riparian wetland. Ecological Applications 4(4): 750-756.

Harper, H. H., Storm water chemistry and water quality. http://www.stormwaterauthority.org/assets/47chemistry.pdf

Harmel, D., S. Potter, P. Casebolt, K. Reckhow, C. Green, R. Haney. 2006. Compilation of measured nutrient load data for agricultural land uses in the United States. Journal of the American Water Resources Association 42(5) 1163-1178

Harter, T., H. Davis, M. Mathews and R. Meyer. 2002. Shallow ground water quality on dairy farms with irrigated forage crops. Journal of Contaminant Hydrology 55: 287-315.

Haycock, N. E., and G. Pinay. 1993. 1993.Groundwater NO_3 dynamics in grass and poplar vegetated riparian buffer strips during winter. J. Environmental Quality 22: 273-278.

Heathwaite, A. L. 1993. Nitrogen cycling in surface waters and lakes. In T. P. Burt, A. L. Heathwaite, and S. T. Trudgill (eds) Nitrate: processes, patterns and management, pp. 99-140. John Wiley and Sons, New York, NY.

Heaton, T. H. E. 1986. Isotopic studies of N pollution in the hydrosphere and atmosphere: a review. Chemical Geology 59: 87-102.

Hill, A.R. 1996. Nitrate removal in stream riparian zones. Journal of Environmental Quality 25: 743-755.

Hill, A. R., K. J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparian zone: interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51: 193-223.

Holmes, R.N., J.B. Jones, S.G. Fisher and N.B. Grimm. 1996. Denitrification in a nitrogen limited stream ecosystem. Biogeochemistry 33:125-146

Hornbeck, J.W., Martin, C.W., Pierce, R.S., Bormann, F.H., Likens, G.E. and Eaton, J.S. 1986. Clearcutting northern hardwoods: Effects on hydrologic and nutrient ion budgets. Forest Sci. 32:667-686.

Hornsby, H. D. 1994. The Use of δ15N to Identify Non-point Sources of Nitrate-Nitrogen beneath Different Land Uses. M.S. Thesis. University of Florida, Gainesville, FL.

Hornsby, D., and R. Mattson. 1997. Surface water quality and biological monitoring network annual report – 1996, 200p. Suwannee River Water Management District, Live Oak, FL.

Hornsby, D., and R. Ceryak. 1998. Springs of the Suwannee River basin in Florida. Suwannee River Water Management District, WR 99-02, Live Oak, FL.

Hornsby, D., R. Mattson, and T. Mirti. 2002. Surface water quality and biological annual report 2001. Suwannee River Water Management District, WR-01-02-04, Live Oak, FL.

Hornsby, D., R. Mattson, and T. Mirti. 2003. Surface water quality and biological annual report 2002. Suwannee River Water Management District, WR 02/03-03, Live Oak, FL.

Hornsby, D., R. Mattson, and T. Mirti. 2004. Surface water quality and biological annual report 2003. Suwannee River Water Management District, WR 03/04-02, Live Oak, FL.

Hornsby, D., R. Mattson, and T. Mirti. 2005. Surface water quality and biological annual report 2004. Suwannee River Water Management District, WR 04/05-02, Live Oak, FL.

Howarth, R. W., G. Billen, D. Swaney, A. Townsend, N. Jarowski, K. Lajtha, J. A. Downing, R. Elmgren, N. Caraco, T. Jordan, F. Berendse, J. Freney, V. Kudeyarov, P. Murdoch, and Z. Z-Liang. 1996. Regional N budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35: 75-139.

Hubbard, R. K. and J. M. Sheridan. 1994. Nitrates in groundwater in the southeastern USA. In D. C. Adriano, A. K. Iskandar, and I. P. Murarka (ed.) Contamination of groundwaters. Science Reviews, Northwood, UK.

Hudak, P. F. 2000. Regional trends in nitrate content of Texas ground water. Journal of Hydrology 228: 37-47.

Huntington, T. G., Ryan, D. F. and Hamburg, S. P. 1988. Estimating soil nitrogen and carbon pools in a northern hardwood forest ecosystem. Soil Sci. Soc. Am. J. 52: 1162-1167.

Inamdar S. P., S. Mostaghimi, P.W. McClellan, and K.M. Brannan. 2001. BMP impacts on sediment and nutrient yields from an agricultural watershed in the Coastal Plain region. Trans. ASAE 44(5):1191-1200.

James, W. F., Ruiz, C. E., and Barko, J. W. 2004. Nutrient loading characteristics for two sub-watersheds exhibiting differing agricultural land-use practices. SMART Technical Notes Collection, ERDC/TN SMART-04-8, U.S. Army Engineer Research and Development Center, Vickburg, MS.

Jansson, M., R. Anderson, H. Berggren and L. Leonardson. 1994. Wetlands and Lakes and Nitrogen Traps. Ambio 23:320-325

Jansson, S. L., and J. Persson. 1982. Mineralization and immobilization of soil N. In F. J. Stevenson (ed.) N in Agricultural Soils. American Society of Agronomy, Special Publication, 22: 229-252.

Johnson, D. W. 1992. Nitrogen retention in forest soils. Journal of Environmental Quality 21(1): 1-12.

Johnson, K.S. and F. J. Quinlan. 1995. Regional mapping of karst terrains to avoid potential environmental problems. Cave and karst Science 21(2): 37-39.

Johnston, C. A. 1991. Sediment and nutrient retention by freshwater wetlands: effects on surface water quality. Critical Reviews in Environmental 21: 491-565.

Jones, G. W., S. B. Upchurch, and K. M. Champion. 1996. Origin of nitrate in ground water discharging from rainbow springs, Marion County, Florida. Ambient Ground-Water Quality Monitoring Program, Southwest Florida Water Management District, Brooksville FL.

Johnes, P., and T. Burt. 1993. Nitrate in surface waters. In T. Burt, A. Heathwaite, and S. Trudgill (eds) Nitrate. Processes, Patterns and Management. 269-317. Wiley, Chichester

Johnston, C. A. 1991. Sediment and nutrient retention by freshwater wetlands: Effects on surface water quality. CRC Crit. Rev. Environ. Contam. 21: 491-565.

Jordan, T. E, D. L. Correll, and D. E. Weller. 1993. Nutrient interception by a riparian forest receiving inputs from cropland. Journal of Environmental Quality 22: 467-473.

Jordan, T. E., D. L. Correll, and D. E. Weller. 1997a. Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. Journal of Environmental Quality 26: 836-848.

Jordan, T. E., D. L. Correll, and D. E. Weller, 1997b. Nonpoint source discharges of nutrient from piedmont watersheds of Chesapeake Bay. J. Am Water Resources Association 33: 631-643.

Kadlec, R and R. Knight. 1996. Treatment Wetlands. CRC Press, Boca Raton, FL USA

Katz, B. G. 1992. Hydrochemistry of the Upper Floridan aquifer in Florida. U. S. Geological Survey Water Resources Investigations Report 91-4196, 37p.

Katz, B. G., R. S. DeHan, J. J. Hirten, and J. S. Catches. 1997. Interactions between ground water and surface water in the Suwannee River Basin, Florida. Journal of the American Water Resources Association 33(6): 1237-1254.

Katz, B. G., H. D. Hornsby, J. F. Bohlke, and M. F. Mokray. 1999. Sources and chronology of nitrate contamination in spring water, Suwannee River Basin, Florida. U. S. Geological Survey Water-Resources Investigations Report 99-4252, Tallahassee, FL.

Katz, B. G., J. S. Catches, T. D. Bullen, and R. L .Michel. 2001. Changes in the isotopic and chemical composition of ground water resulting from a recharge pulse from a sinking stream. Journal of Hydrology 211: 178-207.

Katz, B.G., J. K. Böhlke, and H. D. Hornsby. 2001. Timescales for nitrate contamination of spring waters, northern Florida, USA. Chemical Geology 179: 167-186.

Katz, B.G. 2004. Sources of nitrate contamination and age of water in large karstic spring of Florida. Environmental Geology 46: 689-706.

Katz, B.G., A. R. Chelette, and T. R. Pratt. 2004. Use of chemical and isotopic tracers to assess nitrate contamination and ground-water age, Woodville Karst Plain, USA. Journal of Hydrology 289: 36-61.

Keeney, D. R. 1986. Sources of nitrate to ground water. Critical Reviews in Environmental Control 16 (3): 257-304.

Kellman, L., and C. Hillaire-Marcel. 1998. Nitrate cycling in streams: using natural abundances of NO3- -δ15N to measure in-site denitrification. Biogeochemistry 43: 273-292.

Kellogg, D. Q., A. J. Gold, P. M. Groffman, K. Addy, M. H. Stolt, and G. Balzejewski. 2005. Journal of Environmental Quality 34: 524-533.

Kendall, C., and R. Aravena. 2000. Nitrate isotopes in groundwater systems. In P. G. Cook and A. L. Herczeg (eds) Environmental tracers in subsurface hydrology, pp. 261-297. Kluwer Academic Publsher, Boston, MA.

Knowles, R. 1982. Denitrification. Microbiology Review 46: 43-70.

Korhnak, L. V. 2006. Unpublished data from the Florida IMPAC watershed studies.

Korom, S. F. 1992. Natural denitrification in the saturated zone: a review. Water Resources research 26(6): 1657-1668.

Kuphal, T. 2005. Quantification of Domestic Wastewater Discharge and Associated Nitrate Loading in Marion County, Florida. Marion County Planning Department, Marion County FL

Lamsal, S., S. Grunwald, G. L. Bruland, C. M. Bliss, and N. B. Comerford. 2006. Regional hybrid geospatial modeling of soil nitrate-N in the Santa Fe River Watershed. Geoderma 135:233-247

Lawrence, R., and R. K. Hubbard. 2001. Denitrification from a swine lagoon overland flow treatment system at a pasture-riparian zone interface. Journal of Environmental Quality 30: 617-624.

Lewis, W. M., J. M. Melack, W. H. McDonnel, M. McClain, and J. E. Richey. 1999. Nitrogen yields from undisturbed watersheds in the Americas. Biogeochemistry 46: 149-162.

Likens, G. E., Bormann, F. H., Pierce, R.S., Eaton, J.S. and Johnson, N. M. 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York, 146 pp.

Line, D. E., White, N. M., Osmond, D. L., Jennings, G. D., and Mojonnier, C. B. 2002. Pollutant export from various land uses in the Upper Neuse River Basin. Water Environment Research 74(1):100-108.

Lopez-Zamora, I., C. Bliss, E.J. Jokela, N.B. Comerford, S. Grunwald, E. Barnard and G.M. Vasquez. In press. Spatial relationships between nitrogen status and pitch canker disease in slash pine planted adjacent to a poultry operation. Environmental Pollution

Lowrance, R. R. 1992. Groundwater nitrate and denitrification in a coastal plan riparian forest. Journal of Environmental Quality 21: 401-405.

Lowrance, R. R., G. R. Vellidis, and R. K. Hubbard. 1995. Denitrification in a restored riparian forested wetland. J. Environmental Quality 24: 808-815.

Lowrance, R. R., S. Dabney, and R. Schultz. 2002. Improving water and soil quality with conservation buffers. J. Soil Water Conservation 57: 36-43.

Madison, R. J., and J. O. Brunett. 1985. Overview of the occurrence of nitrate in ground water in the United States. In National Water Summary 1984 – Hydrologic events, selected water-quality trends, and ground-water resources: U. S. Geological Survey Water-Supply Paper 2275, p. 93-105.

Marti, E., J. Aumatell, L. Godè, M. Poch, and F. Sabater. 2004. Nutrient retention efficiency in streams receiving inputs from wastewater treatment plans. Journal of Environmental Quality 33: 285-293.

Martin, J.B. and R.W. Dean. 2001. Exchange of water between conduits and matrix in the Floridan aquifer. Chemical Geology 179:145-165

Martin, J.B. and E.J. Screaton. 2001. Exchange of Matrix and Conduit Water with Examples from the Floridan Aquifer. In Eve L. Kuniansky (ed.), U.S. Geological Survey Karst Interest Group Proceedings, Water-Resources Investigations Report 01-4011, p. 38-44

Mattson, R.A., E.F. Lowe and C.L. Lippincott. 2006. Potential Nitrate Toxicity to Aquatic Animals in the Wekiva River and Rock Springs Run and Associated Nitrate Concentration Targets. SJRWMD Report, Palatka, FL.

Maxxon, G. L., J. M. Lloyd, T. M.Scott, S. B. Upchurch, and R. Copeland. 1992. Florida's ground-water quality monitoring network program: background hydrogeochemistry, Florida Geological Survey Special Publication no. 34, 364p.

McConnell, R. G., E. G. Araj, D. T. Jones. 1999. Developing nonpoint source water levels of service for Hillsborough County, Florida. Proceedings of the Sixth Biennial Stormwater Research and Watershed Management conference. Southwest Florida Water Management District, 2379 Broad Street, Brooksville, Florida, 34609-6899

McKinnie, F.W., W.D. Grapha, J.W. Jones and D.A. Graetz. 2003. Modeling and Monitoring the Water and Nitrate Transport and Potato Growth at a Vegetable Farm in the Suwannee River Basin, Fl. ASAE Annual Meeting #032127, Las Vegas, NV

McMahon, P. B. and J. K. Böhlke. 1996. Denitrification and mixing in a stream – aquifer system: effects on nitrate loading to surface water. Journal of Hydrology 186: 105-128.

McNeal, B.L., C.D. Stanley, W.D. Graham, P.R. Gilreath, D. Downey and J.F Creighton. 1995. Nutrient-loss trends for vegetable and citrus fields in west-central Florida – 1. Nitrate. Journal of Environmental Quality 24:95-100

Miller, D.N., Smith, R.L., and Böhlke, J.K., 1999, Nitrification in a shallow, nitrogen-contaminated aquifer, Cape Cod, Massachusetts, in Morganwalp, D.W., and Buxton, H.T., eds., U.S.

Geological Survey Toxic Substances Hydrology Program--Proceedings of the Technical Meeting, Charleston, S.C., March 8-12, 1999: U.S. Geological Survey Water-Resources Investigations Report 99-4018, p. 329-336.

Miller, J.A. 1990. Groundwater Atlas of the United States: Alabama, Florida, Georgia and South Carolina. USGS Publication HA 730-G.

Mirti, T., and L. Mantini. 2006. Surface water quality and biological annual report 2005. Suwannee River Water Management District, WR 05/06-02, Live Oak, FL.

Mitsch, W.J, and J.G. Gosselink. 1993. Wetlands. Van Nostrand Reinhold, New York, NY USA

Mitsch, W.J., J.W. Day Jr., J.W. Gillian, P.M. Groffman, D.L. Hey, G.W. Randall and N. Wang. 2001. Reducing Nitrogen Loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to Counter a Persistent Ecological Problem. BioScience 51:373-388

Morris, L.A. 1981. Redistribution and mobilization of nutrients as a result of harvest and site preparation of a pine flatwoods forest . PhD. Dissertation, University of Florida, Gainesville FL

Nolan, B.T., K.J. Hitt and B.C Ruddy. 1998. Probability of nitrate contamination of recently recharged ground waters in the conterminous United States. Environmental Science and Technology 36:2138-2145

Nolan, B.T. 1999. Nitrate behavior in the ground waters of the Southeastern USA. Journal of Environmental Quality 28:1518-1527

Nelson, W. M., A. J. Gold, and R. M. Groffman. 1995. Spatial and temporal variation in groundwater nitrate removal in a riparian forest. Journal of Environmental Quality 24: 691-699.

Obreza, T. 2004. Florida Springs Land Use Information Tool. UF IFAS Extension CIR 1448

Odum, H.T. 1957. Trophic structure and productivity of Silver Springs, Florida. Ecol. Monogr. 27, 55–112.

Otis, R. J., D. L. Anderson, and R. A. Apfel. 1993. Onsite sewage disposal system research in Florida: Report prepared for the Florida Department of Health and Rehabilitative Services, Contract No. LP-596, Ayres and Associates, Tampa, FL, 57pp.

Panno, S. V., K. C. Hackley, H. H. Hwang, and W. R. Kelly. 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. Chemical Geology 179: 113-128.

Peterson et al. 2001. Control of Nitrogen Export from watersheds by headwater streams, Science, 292.

Phelps, G. G. 1994. Hydrogeology, water quality, and potential for contamination of the Upper Floridan aquifer in the Silver Springs ground-water basin, central Marion County, Florida. U. S. Geological Survey Water Resources Investigations Report 92-4159, 69p.

Phelps, G. G. 2004. Chemistry of ground water in the Silver Springs basin, Florida, with an emphasis on Nitrate. U. S. Geological Society Scientific Investigations Report 2004-5144, 54p.

Piersynski, G. M., J. T. Sims, and G. G. Vance. 1994. Soils and environmental quality. CRC Press, Boca Raton, FL.

Pittman, J. R., H. H. Hatzell, and E. T. Oaksford. 1997. Spring contributions to water quality and nitrate loads in the Suwannee River during Baseflow in July 1995. U. S. Geological Survey Water Resources Investigation Report 97-4152.

Postma, D., and C. Boesen. 1991. Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modeling. Water Resources Research 27(8): 2027-2045.

Power, J. F. 1994. Understanding the nutrient cycling process. Journal of Soil and Water Conservation 49: (2): 16-23.

Rabalais, N.N., R.E. Turner, D. Justi´c, Q. Dortch, W.J. Wiseman Jr. and B.K. Sen Gupta. 1996. Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. Estuaries 19:386–407.

Rabalais, N. 2002. Nitrogen in aquatic ecosystems. Ambio 31:102-112

Randall G.W., D.R. Huggins, M.P. Russelle, D.J. Fuchs, W.W. Nelson, and J.L. Anderson. 1997. Nitrate losses through subsurface tile drainage in CRP, alfalfa and row crop systems. Journal of Environmental Quality 26: 1240–1247.

Reay, W.G. 2004. Septic Tank Impacts on Ground Water Quality and Nearshore Sediment Nutrient Flux. Ground Water 42:1079-1089

Recous, S., J. M. Machet, B. Mary. 1988. The fate of 15N urea and ammonium nitrate applied to a winter wheat crop. II. Plant uptake and N efficiency. Plant Soil 112: 215-224.

Reckhow, K. H., Beaulac, M. N., and Simpson, J. T. 1980. Modeling phosphorus loading and lake response under uncertainty: A manual and compilation of export coefficients, U.S. EPA Report No. EPA-440/5-80-011, Office of Water Regulations, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.

Robertson, W. D., and J. A. Chery. 1995. In situ denitrification of septic-system nitrate using reactive porous media barriers: field trials. Ground Water 33: 99-111.

Robertson, W. D., D. W. Blowes, C. J. Ptacek, and J. A. Cherry. 2000. Long-term performance of in situ reactive barriers for nitrate remediation. Ground water 38(5): 689-695.

Rutherford, J. C., and M. L. Nguyen. 2004. Nitrate removal in riparian wetlands: interactions between surface flow and soils. Journal of Environmental Quality 33: 1133-1143.Royal Society. 1983. The N cycle of the United Kingdom. The Royal Society, London.

Schilling, K. and Y-K. Zhang. 2004. Baseflow contribution to nitrate-N export from a large, agricultural watershed, USA. Journal of Hydrology, 295, 305-316.

Schipper, L. A., and Vojvodic-Vukovic, M. 2001. Five years of nitrate removal, denitrification and carbon dynamics in a denitrification wall. Water Research 35: 3473-3477.

Schipper, L. A., G. F. Barkle, J. C. Hadfield, M Vojvodic-Vukovic, and G. P. Burgesss. 2004. Hydraulic constraints on the performance of a groundwater denitrification wall for nitrate removal from shallow groundwater. Journal of Contaminant Hydrology 69: 263-279.

Schipper, L. A., G. F. Barkle, and J. Vojvodic-Vukovic. 2005. Maximum rates of nitrate removal in a denitrification wall. Journal of Environmental Quality 34: 1270-1276.

Seitzinger, S.P. 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnology and Oceanography 33:702-724

Seitzinger, S.P., R.V. Styles, E.W. Boyer, R.B. Alexander, G. Billien, R.W. Howarth, B. Mayer and N. Van Breemen. Nitrogen retention in rivers: model development and application to watersheds in the northeastern USA. Biogeochemistry 57:199-237

Simmons, R. C., A. J. Gold, and P. M. Groffman. 1992. Nitrate dynamics in riparian forests: groundwater studies. Journal of Environmental Quality 21: 659-665.

Smith, R.L., J.K. Bohlke, S.P. Garabedian, K.M. Revesz and T. Yoshinari. 2004. Assessing denitrification in groundwater using natural gradient tracer tests with ^{15}N: In situ measurement of a sequential multi-step reaction. Water Resources Research v40, W07101, doi:10.1029/2003WR002919, 2004

Smith, S. J. 1987. Soluble organic N losses associated with recovery of mineralized N. Soil Science Society of America J. 51: 1191-1194.

Smith, V.H., D.G. Tilman and J.C. Nikola. 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine and terrestrial ecosystems. Environmental Pollution 100:179-196.

Snoeyink, V.L. and D. Jenkins. 1980. Water Chemistry. John Wiley and Sons, New York NY.

Stark, J.M. and S.C. Hart. 1997. High rates of nitrification and nitrate turnover in undisturbed coniferous forests. Nature 285:61-64

Spalding, R. F. and M. E. Exner. 1993. Occurrences of nitrate in groundwater: a review. Journal of Environmental Quality 22: 392-402.

Stainton, R., and M. Stone. 2003. Nitrate transport in shallow groundwater at the stream-riparian interface in an urbanizing catchment. Journal of Environmental Planning and Management 46(4): 475-498.

Steinhart, G.S., G.E. Likens and P.M. Groffman. 1998. Denitrification in stream sediments in fiver northeastern (USA) streams. Proc. Int. Assoc. Theor. Appl. Limnol 27:1331-1336.

Stockdale, E.C. 1991. Freshwater Wetlands, Urban Stormwater and Non-Point Source Pollution: A Literature Review and Annotated Bibliography. Washington State Dept. of Ecology. Olympia WA USA

Stoddard, J.L. 1994. Long-term changes in watershed retention of N: Its causes and aquatic consequences. p. 223-284. In L.A. Baker (ed.) Environmental chemistry of lakes and reservoirs. American Chemical Society, Washington, DC.

Strong, W.A. 2004. Temporal water chemistry trends within individual springs within a population of Florida springs. MS Thesis, University of Florida, Gainesville FL

Swancar, A., and C. B. Hutchinson. 1992. Chemical and isotopic composition and potential for contamination of the upper floridan aquifer, West-Central Florida, 1985-89. USGS Open-File Report 92-47.

Swank, W. T. 1988. Stream chemistry responses to disturbance. In Swank, W.T. and Crossley D.A., Jr (Eds): Forest Hydrology and Ecology at Coweeta. Ecological Studies, Vol. 66. Springer-Verlag, New York, pp. 339-357.

Taraba, J .L., J. S. Dinger, L. V. A. Sendlein, and G. K. Felton, 1997. Land use impacts on water quality in small karst agricultural watersheds. In Proceedings, Karst-Water Environment Symposium, Virginia Polytechnic Institute and State University, October 30-31, Roanoke, Virginia, p. 99-109.

Tesoriero A.J., T.B. Spruill, H. E. Mew, K.M. Farrell, and S.L. Harden. 2005. Nitrogen transport and transformations in a coastal plain watershed: Influence of geomorphology on flow paths and residence times, WRR 41, W92008 doi 10.1029/2003WR002953.

Tilman, D. 1987. Secondary succession and the pattern of plant dominance along experimental nitrogen gradients. Ecological Monographs 57:189-214.

Toth, D. J. 1999. Water quality and isotope concentrations from selected springs in the St. Johns River Water Management District. Technical Publication SJ99-2, St. Johns River Water Management District, Palatka, FL.

Toth, D. J., and C. Fortich. 2002. Nitrate concentrations in the Wekiva groundwater basin with emphasis on Wekiwa Springs. Technical Publication SJ2002-2, St. Johns River Water Management District, Palatka, FL.

Udawatta, R. , G. Henderson, D. Hammer, J. Jones. 1998. Riparian corridor condition and hydrologically sensitive area management to improve water quality. In Riparian Review. Missouri Department of Conservation, Fish and Wildlife Research Center, 1110 S. College Avenue, Columbia, MO 65201.

U.S. Environmental Protection Agency. 1983. Results of the Nationwide Urban Runoff Program: Volume I – final report," U.S. Environmental Protection Agency, PB84-185552, Washington, DC.

Upchurch, S.B., K.M. Champion, J.C. Schneider, D. Hornsby and R. Ceryak. 2004. Identifying Water Quality Domains near Ichetucknee Springs, Columbia County, Florida. In B. Katz and E. Raabe (Eds). Suwannee River Basin and Estuary Integrated Science Workshop: Sept. 2004, Cedar Key FL USGS Open File Report 2004-1332

Van Breemen, N., E. W. Boyer, C. L. Goodale, N. A. Jaworski, K. Paustian, S. Seitzinger, L. K. Lajtha, B. Mayer, D. Van Dam, R. W. Howarth, K. J. Nadelhoffer, and G. Billen. 2002. Where did all the N go? Fate of N inputs to large watershed in the northeastern USA. Biogeochemistry 57/58: 267-293.

Van Herpe, Y., and P. A. Troch. 2000. Spatial and temporal variations in surface water nitrate concentrations in a mixed land use catchment under humid temperate climatic conditions. Hydrological Processes 14: 2439-2455.

Vanni, M. J., W. H. Renwick, J. L. Headworth, J. D. Auch, and M. H. Schaus. 2001. Dissolved and particulate nutrient flux from three adjacent agricultural watersheds: A five-year study. Biogeochemistry, 54 (1)85-114.

Velthof, G. L., O. Oenema, R. Postma, and M .L. Beusichem. 1997. Effects of type and amount of applied fertilizer on nitrous oxide fluxes from intensively managed grassland. Nutrient Cycling Agroecosystems 46: 257-267.

Vinten, A. J. A., and K. A. Smith. 1993. Nitrogen Cycling in agricultural soils. In T. P. Burt, A. L. Heathwaite, and S. T. Trudgill (eds) Nitrate: processes, patterns and management. John Wiley and Sons, New York, NY.

Vitousek, P. M. 1977. The regulation of Element Concentrations in Mountain Stream in the Northeastern United States. Ecological Monographs 47:65-87.

Vitousek, P.M., J. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schindler, W.H. Schlesinger, and G.D. Tilman. 1997. Human alteration of the global nitrogen cycle: causes and consequences. Ecological Applications 7: 737–750.

Vitousek, P.M. and Matson, P.A. 1985. Disturbance, nitrogen availability and nitrogen losses: an experimental study in an intensively managed loblolly pine plantation. Ecology 66: 1360-1376.

Vought, L. B. M., G. Pinay, A. Fuglslang, and C. Ruffioni. 1995. Structure and function of buffer strips form a water quality perspective in agricultural landscapes. Landscape and Urban Planning 31: 323-331.

Waide, J. B., Caskey, W.H., Todd, R.L. and Boring, L.R. 1988. Changes in soil nitrogen pools and transformations following forest clearcutting. In Swank, W. T. and Crossley, D.A. Jr (Eds): Forest Hydrology and Ecology at Coweeta, Ecological Studies, Vol. 66, Springer-Verlag, New York, pp. 221-232.

Wassenaar, L. I. 1995. Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes 15N and 18O in NO_3-. Applied Geochemistry 10: 391-405.

Weil, R. R., R. A. Weismiller, and R. S. Turner. 1990. Nitrate contamination of groundwater under irrigated coastal plain soils. J. Environ. Quality 19: 441-448.

Whigham, D.F. and T.E. Jordan. 2003. Isolated wetlands and water quality. Wetlands 23:541-549

Willems, H. P. L., M. D. Rotelli, D. F. Berry, E. P. Smith, R. B. Reneau, and S. Mostaghimi. 1997. Nitrate removal in riparian wetland soils: effects of flow rate, temperate, nitrate concentration and soil depth. Water Research 31(4): 841-849.

Winkler, S., and A. Ceric. 2006. 2004 status and trends in water quality at selected sites in the St. Johns River Water Management District. Technical Publication SJ2006-6. St. Johns River Water Management District, Palatka, FL.

Woodard, K.R., E.C. French, L.A. Sweat, D.A. Graetz, L.E. Sollenberger, B. Macoon, K.M. Portier, B.L. Wade, S.J. Rymph, G.M. Prine, and H.H. Van Horn. 2002. N removal and nitrate leaching for forage systems receiving dairy effluent. J. Environ. Qual. 31, 1980-1992.

Yoshinari, T., R. Hynes, and R. Knowles. 1977. Acetylene inhibition of nitrous oxide reduction and measurement of denitrification and nitrogen fixation in soil. Soil Biol. Biochem. 9:117-183.

CITED WEB SITES

Nutrient Loss Database for US Agricultural Fields.

http://ars.usda.gov/Research/docs.htm?docid=11079

Springs of the St. Johns River Water Management District:

http://www.sjrwmd.com/programs/plan_monitor/gw_assess/springs/

Florida's Springs

http://www.floridasprings.org

Florida DEP Springs Page

http://www.dep.state.fl.us/springs