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NITRATE FLUX FROM GROUND TO SURFACE WATERS ADJACENT TO THE NEUSE RIVER WASTE WATER TREATMENT PLANT

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ABSTRACT

Biosolids have been land applied at the Neuse River Waste Water Treatment Plant (NRWWTP) since 1980. The long biosolid application history at this site has resulted in a build up of nitrate in the ground water beneath the Waste Application Fields (WAFs). The results of this study demonstrate that ground water nitrate concentrations are spatially heterogeneous under the biosolid WAFs. Large differences in nitrate concentrations can occur across a single field. Nitrate concentrations in groundwater are highest in shallow saprolite wells less than 75 feet deep. Nitrate levels decrease, but are still high and above 10 mg/l in bedrock wells at depths up to 180 feet. Biosolids that are land applied and leached enrich the underlying ground waters in ^{15}N and chloride. The nitrogen and oxygen isotopic composition of nitrate in the biosolid WAF groundwater indicates that 18% of the monitoring wells are impacted by fertilizer N, 57% of the wells are impacted by biosolid N, 22% of the wells are affected by denitrification, and one well is impacted by Atmospherically Deposited N (A.D.N.). Wells that have extensive denitrification are located in hydric or partially hydric soils with high concentrations of TOC. The association of hydric soils with denitrification suggests that geochemical processes play an important role in the spatial heterogeneity of nitrate in groundwater underlying biosolid WAFs. The nitrate/chloride ratios range from 1 to 3.5 in ground waters under the WAFs where denitrification has not affected nitrate concentrations. High nitrate/chloride ratios and enriched ^{15}N - nitrate are geochemical characteristics that can identify ground waters impacted by biosolid N.

The flux of water and nitrate from the biosolid WAFs into the adjacent reach of the Neuse River was measured using two RiverNet monitoring stations. Stations were placed above and below the 6.7 km reach of the river adjacent to the treatment plant. Water and nitrate flux into and out of the reach was monitored for a 24-month period. The net daily contribution of surface / ground water and nitrate to the reach was calculated from the sum of the flux into the reach at the upper RiverNet station plus the plant discharge minus the flux out of the reach at the lower RiverNet station. The difference between the flux into the reach and what is added from the plant to the flux out of the reach is termed the non-point source gain or loss (NPS gain). The NPS gain could come from groundwater and/or surface drainage additions to the reach. On an annual basis, daily integrated NPS nitrate gains were ~70,000 kg in year 1 and ~27,900 kg in year 2. This represents an average over the two year period of ~12% of the total nitrate flux out of the reach and 43% of the nitrate discharged from the treatment plant into the reach. NPS water gains in the reach over the two year period were ~6% of the water flux out of the reach and ~110% of the water discharged from the treatment plant into the reach. The NPS nitrate gains in the reach were event driven, occurring over 1 to 3 day periods. For a given event, NPS nitrate gains in the reach could be up to 2.5 times the magnitude the flux of nitrate that enters the reach from the upper basin. Preliminary data from river nitrate mapping suggests that a major portion of the NPS nitrate flux enters the river along the northern edge of the plant, where nitrate concentrations in surface drainages are the highest. The relative importance of surface drainages and ground water flux to NPS discharge and nitrate gains in the study reach could not be determined from these data, and should be the focus of future research.

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SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

Land application of biosolids produced from waste water treatment in areas of rapidly growing urban populations is a cost effective reuse of nitrogen and phosphorus, as well as an effective disposal method of the sediment and sludge produced during the treatment process. Land application of biosolids may increase significantly in the future as treatment plants expand and other disposal practices such as landfills, incineration, and ocean dumping become too expensive or are banned. Sustainable biosolid management programs require attention to N management, because soil N accumulation affects crop N requirements and the leaching of N from surface soils has important environmental impacts. It is now recognized that groundwater makes up a significant source of water to streams and rivers in almost all catchments. Groundwater storage time and geochemical reactions such as denitrification in the subsurface hydrogeologic environments through which ground waters migrate control nitrate concentrations in receiving streams (Kendall 1998, Aravena and Kendall 2000). Previous studies on the land application of biosolids were generally limited to less than five years, while it can take several decades for recharged groundwater to discharge into streams. This study is unique because biosolids have been land applied at the NRWWTP (Neuse River Waste Water Treatment Plant) near Clayton N.C. since 1980. The amount of Plant Available Nitrogen (PAN) applied to each field and ground water chemistry has been monitored since the initiation of land application. Nitrate concentrations in groundwater under the biosolid WAFs are highly variable ranging from 0.1 mg/l to 180 mg/l. Accumulation of biosolid N in groundwater can be traced with heavy nitrogen isotope ratios in nitrate ($\square^{15}$N) and high nitrate/chloride ionic ratios. Denitrification in ground and surface waters can be detected by nitrogen and oxygen ($\square^{18}$O) isotopic ratios in nitrate. These isotopic indicators suggest that biosolid N has impacted 57% of the monitoring wells at the NRWWTP, and most of the surface waters that drain off the site with elevated nitrate concentrations. Fertilizer N has impacted 18% of the monitoring wells, while nitrate has been significantly attenuated by denitrification in 23% of the wells at the NRWWTP. One well has been affected by atmospheric deposition. The wells that are affected by denitrification are associated with hydric and partially hydric soils. Hydric soils have the right geochemical conditions for denitrification, but are not continuously distributed in the WAFs. The location of hydric soils may explain the heterogeneous distribution of nitrate under biosolid application fields and offsite migration patterns.

The flux of water and nitrate in the Neuse River was quantified at stations located above and below the plant and compared to daily plant discharge for two years. Water gained by the reach approximately equaled water added to the reach from the NRWWTP over two years. Together these water inputs make up about 6% of the water exported from the reach. Nitrate contributed to the reach from non-point sources such as groundwater and streams (NPS flux) was about 43% of the nitrated discharged in plant effluent. NPS nitrate gained in the reach and nitrate discharged from the treatment facility together make up about 38% of the nitrate exported from the reach. The NPS (Non-Point Source) nitrate flux shows large increases (NPS gains) in the reach episodically over 1 to 3 day periods. Preliminary data from river nutrient mapping suggest that NPS nitrate enters the reach along the northern portion of the plant, where WAF biosolid applications have been the heaviest. Surface waters draining from these

northern fields have nitrate concentrations > 50 mg/l. Preliminary data from the riparian buffers indicate that nitrate does not migrate across the riparian areas in shallow groundwater flow paths. Nitrate flux in deep groundwater flow paths has not been measured and should be the focus of future studies.

The total NPS flux in the reach was distinctly different between the two years. NPS nitrate gains in the reach during 2003-04 were over twice the NPS nitrate gains measured in 2004-2005. Precipitation only decreased by only 25% during the second year. The highest NPS gains were measured in the Spring of 2003 when river stage was high. However, biosolid application ceased at the NRWWTP in September 2002 and have not been applied for over three years. NPS nitrate gains in the river may be decreasing because of inter-annual hydrographic variability or because biosolids nitrogen is transported in shallow flow paths that have received less nitrate in recharge since biosolid application stopped in 2003. While nitrate concentrations have not changed significantly in the surface drainages, the flux of water and nitrate in the small streams during storm events remains unknown. The relative importance of surface or ground water nitrate inputs to the Neuse River NPS nitrate flux cannot be determined from these data, and should be the subject of future investigations. Continued monitoring over the next year will determine if the decreasing nitrate gains in the reach observed over the last two years is the result of inter-annual hydrological variability, or because biosolids applications were stopped two years ago. If nitrogen flux in surface water drainages is the most important source of NPS nitrogen in the reach, sustainable biosolid application to the existing fields may be possible by enhancing natural nitrate attenuation in the creeks draining the site. The riparian buffers next to the surface drainages could be enlarged, and wetlands can be constructed at the bottom of the drainages to reduce the nitrate flux into the river from the WAFs.

INTRODUCTION: LAND APPLICATION OF BIOSOLIDS

Land application of biosolids is a common practice in many countries, and is a cost effective reuse of material produced at sewage treatment facilities in areas of rapidly growing urban populations (Weggler et al., 2004). Biosolids are a significant source of nitrogen (N), phosphorus (P), and trace elements. These nutrients can increase production of a wide variety of crops when applied at appropriate rates (Serna and Pomarez, 1992; Korboulewsky et al., 2002; Weggler-Beaton et al., 2003). Addition of biosolids to degraded soils is a cost effective alternative to inorganic fertilizers (Fresquez et al, 1990; Martinez et al., 2003). Land application of biosolids may increase significantly in the future as other disposal practices such as landfills, incineration, and ocean dumping become too expensive or are banned (Pierzynski 1994). Repeated application of biosolids at the same site can reduce the costs of locating and permitting new application sites (Cogger et al., 2001). However, nitrogen, phosphorous, and trace elements can buildup in soils and in ground waters with repeated biosolid applications. The accumulation and export of nutrients from waste application fields (WAF) must be considered for sustainable biosolid management. N management is important because N soil accumulation from previous biosolid applications can have a significant effect on N requirements of succeeding crops (Sullivan et al, 1997). Biosolids organic N content is commonly larger than inorganic N forms and must be mineralized before becoming PAN (Plant Available Nitrogen, Glimour et al., 2003). The solubility of DIN (Dissolved Inorganic Nitrogen) suggests that biosolid N is likely to be exported from waste application fields into underlying ground waters. These ground waters will eventually move into adjacent surface water drainages on time scales specific to the hydrogeology at each site. Accumulation of excess P is a concern usually with animal manures (Sharpley et al, 1997). Because municipal biosolids are produced using lime or metal salts, the potential for biosolids P runoff can vary with the wastewater treatment process. Municipal biosolids produced with iron have the lowest increase in soil extractable P and runoff dissolved reactive P (Penn and Simms, 2002). Biosolids also contain heavy metals such as Cd that can have adverse effects when entering the food chain in elevated amounts (Weggler et al., 2004). Soil organic matter content, soil pH, oxidation / reduction status, and clay type are considered to be major factors in determining the bioavailability of trace metals in soils (Sommers et al., 1987). Increased Cl concentrations have been shown to increase Cd concentrations and bioavailability to plants (Weggler et al., 2004). Most biosolid studies have observed soil chemistry changes over short periods of (1-7 years; Cogger et al., 2001; Meyer et al., 2001; Penn and Simms 2002; Grey and Henry 2002; Korboulewsky et al., 2002; Weggler et al., 2004). Longer studies of biosolid applications are rare, but are important to evaluate sustainable biosolid management practices.

The links between biosolid application rates, groundwater quality, and surface water contamination are not well known. Easton and Petrovic (2004) found that the type of fertilizer applied to turf grass was related to N & P run off. Municipal biosolids, swine and dairy compost applied to turf grass fields resulted in greater P run off, whearas urea and controlled release (sulfur coated) urea resulted in greater N loss on a percentage applied basis. Martinez et al., (2003) found that land applied biosolid and composted municipal solid wastes reduced sediment yield in run-off compared to control plots, but

increased PO_4-P and NO_3-N in runoff and resulted in higher soil NH_4-N concentrations. In a forested watershed, Grey and Henry (2002) found that biosolid application changed the nitrate-N / discharge relationship after 1.5 years, and that increased discharge resulted in increased nitrate concentrations after this period of time. In these forested watersheds P loss was in the particulate form. After 7 years of biosolid application in Washington, Cogger et al (2001) found that soil nitrate increased at the higher application rates. Anthropogenic changes in groundwater recharge chemistry commonly occur in agricultural areas over a period of decades (Böhlke 2002). Groundwater discharge rates to surface streams occur on a much longer time scale than encompassed by most biosolid application studies. To develop sustainable biosolid management programs, ground and surface water quality studies need to be done at a site where biosolids have been applied for periods of time that approaches groundwater discharge rates.

STUDY SITE LOCATION, BIOSOLID PRODUCTION AND APPLICATION

The City of Raleigh Public Utilities Division (CORPUD) has operated the Neuse River Waste Water Treatment Plant (NRWWTP) in southeastern Wake County NC since 1976 (Figure 1). This facility treats wastewater from the City of Raleigh and the towns of Knightdale, Wendell, Garner and Rolesville. The facility collects an average of 38 million gallons per day (MGD) of wastewater from 1616 miles of pipeline fed by gravity flow that is assisted with 74 pump stations. The plant processes wastewater for 107,000 metered customers and serves a population of approximately 315,000 people. The NRWWTP facility consists of a tertiary treatment system with final UV radiation to eliminate bacteria. This effluent is discharged to the Neuse River via an underground pipe on the eastern side of the plant south of field #22 (Figure 2). The NRWWTP is permitted to discharge up to 60 MGD of effluent into the Neuse River (DENR 1998), but averaged about 45 MGD from March 2003 to March 2005 (CORPUD, unpublished data). The NC Division of Water Quality required a 30% reduction in nitrogen discharged to the Neuse River Estuary by January 1, 2003. To meet this requirement, the NRWWTP reduced effluent N discharge to the Neuse by 49% compared to 1995 levels by upgrading treatment facilities at the plant.

Biosolids are produced at the NRWWTP as part of the normal treatment operations. Microorganisms are cultured within aeration basins to convert lighter organic solids and soluble material to solid residue for removal. This is referred to as the "Active Sludge Process". The solid material that is produced settles out in the secondary clarifiers. A portion of this bio-sludge is recycled back into the
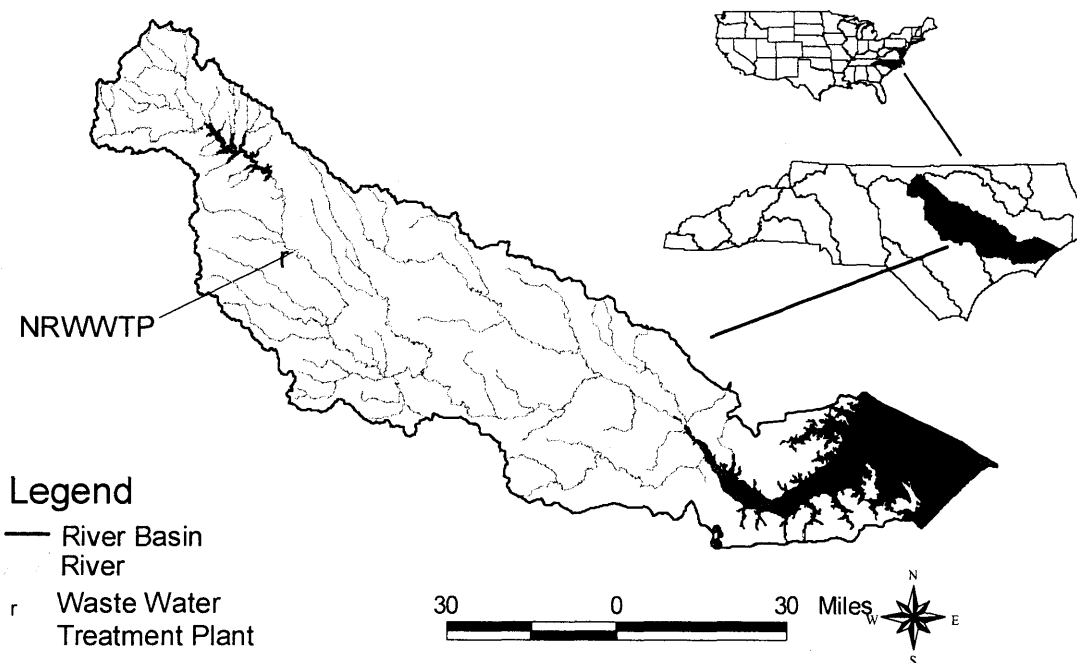
Figure 1. Location of study site, the Neuse River Wastewater Treatment Plant (NRWWTP), in the upper Neuse River Basin.

aeration basins to maintain active microorganism populations, and the rest are moved to reuse for biosolid production. Two types of biosolids are produced at the plant. Class A biosolids are produced by mixing the dewatered sludge with lime and fly ash. Class A biosolids are marketed under the name of Raleigh Plus and are available to the public. Class B biosolids are produced by dewatering the sludge in a conveyor belt process. Class B biosolids are then land applied on the farmland surrounding the plant to produce crops, which are sold as animal feed (Figure 2).

Farmland, state owned forest, and private residences surround the plant. The northern and eastern boundaries of the plant border a 5.79 km reach of the Neuse River. Biosolids have been land applied since 1980 on 1030 acres of farmland owned or leased by CORPUD. The land application permit allows for 7,000 total dry tons of Class B biosolids to be applied per year on farmlands (Permit #WQ0001730). Fields in the northern portion of the plant have the longest biosolid application history and have received biosolids since the early 1980's (Figure 2). Application was stopped in the 1990's in fields 1-3 when they were used for other purposes by the City Police Department. Fields in the
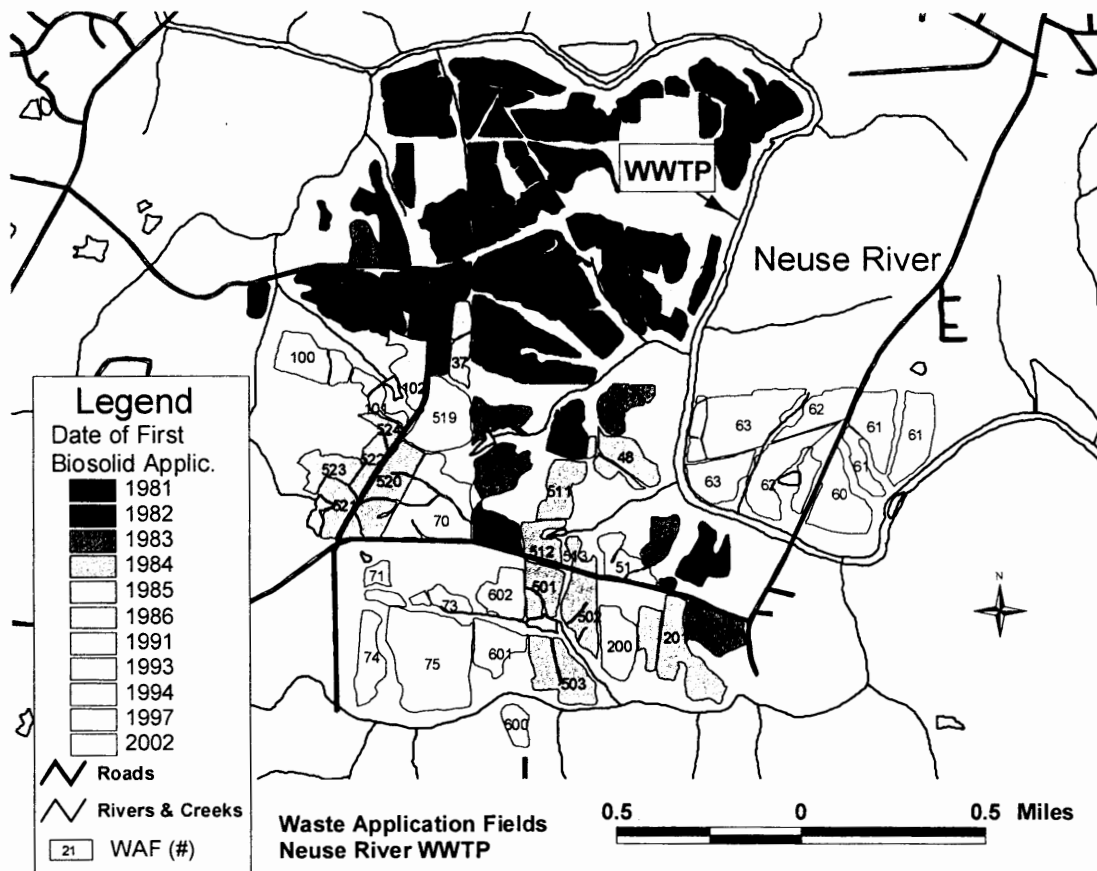
Figure 2. Waste application fields at NRWWTP and the date of first biosolid application. Fields in the northern portion of the plant (1-42) have the longest period of biosolid application. The treatment plant is located in the northeastern portion of the area (WWTP), and effluent from the plant is discharged to the river below Field #22 (arrow)

central and eastern portions of the plant did not receive biosolid application until the mid 1990's (Figure 2).

Land application rates are based on mineralization rates that convert biosolids to PAN. Ammonia, nitrate and organic nitrogen contribute to PAN in municipal biosolids (Glimour et al., 2003). Biosolid organic N is commonly larger than the sum of ammonia and nitrate N, but must be mineralized to become PAN (USEPA 1995). PAN is reduced when biosolids are surface applied because of N loss due to ammonia volatilization and oxidation of ammonia to nitrate followed by leaching or denitrification. Biosolid properties and variations in conditions at the application sites can make predicting total PAN from the decomposition of biosolids a difficult task over an extended period of time. Organic N and decomposition kinetics can vary among different types of biosolids, organic N from the same biosolid incubated in different soils can mineralize at different rates. Changes in temperature or soil moisture can also influence decomposition rates and net N mineralization (Glimour et al., 2003; Ajwa and Tabatabai 1994). Many methods have been proposed to estimate N mineralization rates of biosolids including computer models, C & N contents, plant uptake studies in pots, crude protein content, and biosolid C:N ratio, organic N and total N content (Glimour et al, 2003; Jaynes et al 2003;

Easton and Petrovic 2004). Original errors in the estimation of the PAN at the NRWWTP resulted in biosolid over-application on city owned or leased WAFs (ECS 2002). Biosolid over application occurred primarily during the early 1980's in the northern fields (ECS 2000), and from the mid 1990's to 2001 at fields in all areas of the plant (ENSR, 2002). The City of Raleigh paid a fine of $73,937 to NCDENR for biosolid application permit violations, and temporarily ceased spreading biosolids in 2002 until a Comprehensive Site Assessment (CSA) could be completed.

Biosolid storage at the NRWWTP reached significant levels after the suspension of land application in 2002 resulting in two spills that were contained at the plant site. CORPUD then employed private contractors to move all the stored biosolids to land fills outside of Wake County. All biosolids stored at the plant were removed by Spring 2003. In 2002 CORPUD hired ENSR Consulting and Engineering Inc. to complete a CSA. The CSA report was completed by ENSR in December 2002 (ENSR 2002) with a Supplemental CSA completed in September 2003 (ENRS 2003). The CSA involved soil, surface, and groundwater sampling to determine nitrate concentrations along compliance boundaries, and to characterize groundwater flow in the area surrounding the waste application fields. CORPUD currently has an application pending with NCDENR to resume land application of biosolids at the site.

PREVIOUS GROUNDWATER MONITORING RESULTS

ENSR installed 22 shallow temporary monitoring wells, 13 shallow permanent monitoring wells in the saprolite layer, 1 permanent monitoring well in the partially weathered zone layer, and three deep permanent bedrock wells in 2002 (Figure 3). In addition to these new monitoring wells, 50 monitoring wells had been previously installed at the site over the past 24 years. 33 of these wells are intact and still accessible for sampling (Figure 3). Historical and recent water quality data for a total of 69 monitoring wells at the site are available from CORPUD, NC DENR Groundwater Section, ENSR (2002), and from this report (Figures 3 & 6).

Monitoring wells were sampled on a quarterly basis by CORPUD since the initial biosolid field applications. Water samples were analyzed for nutrients, conductivity, pH, trace metals, and TOC by CORPUD. Monitoring water quality data archived at NCDENR Groundwater Section since 1980 indicates that nitrate has increased only in some of the monitoring wells in the biosolid WAFs (Figure 4). Differences in groundwater nitrate concentrations across one field can approach 100 mg/l. This spatial heterogeneity in groundwater nitrate concentration is perplexing, and is larger than can be accounted for by different hydrogeologic flow paths or groundwater age differences (Böhlke 2002, Böhlke and Denver 1995). Total PAN applied to the fields has varied from 6.92 to 0.23 Mg/ha (6170 – 209 lbs/ac) with the highest total PAN applied in the northern
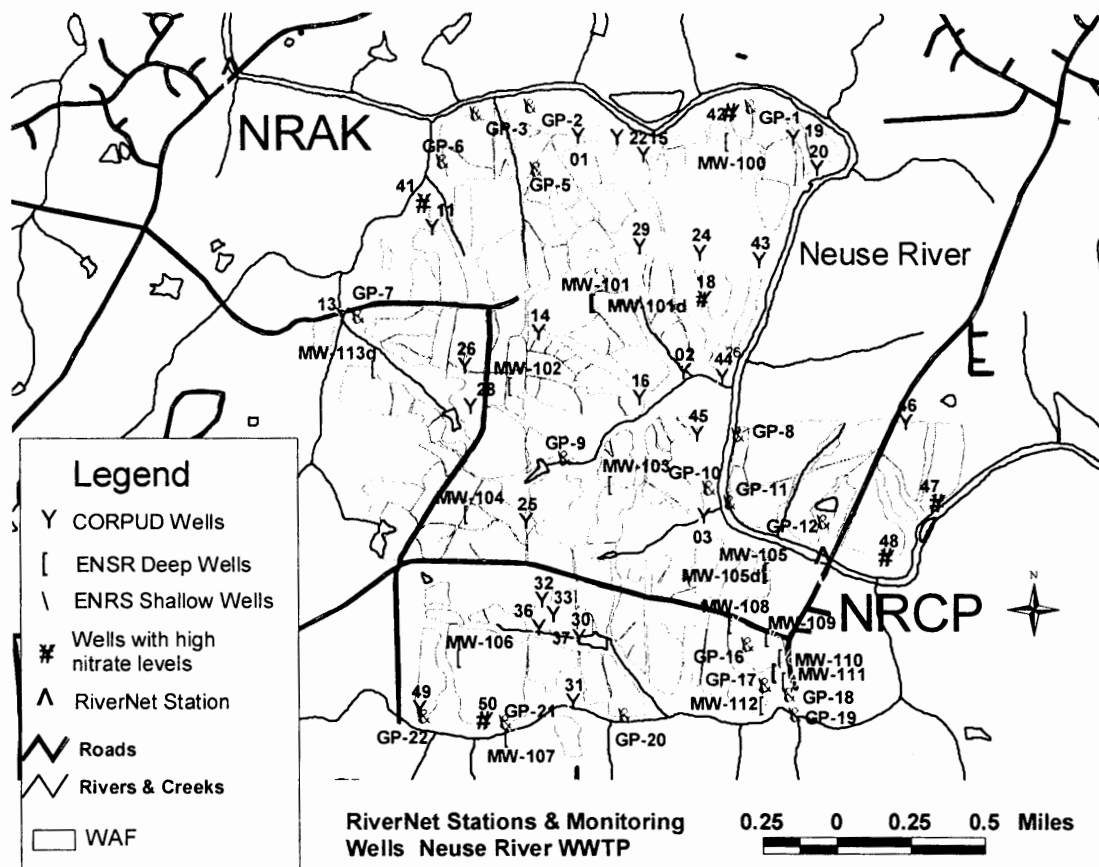
Figure 3. Shallow and deep groundwater monitoring wells at the NRWWTP. The RiverNet monitoring stations are positioned above and below the WAFs. Wells with a solid black circle have had large increases in nitrate concentrations.
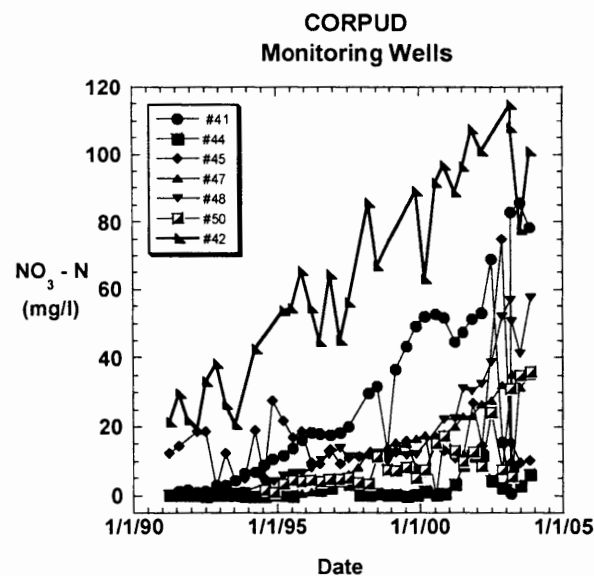
Figure 4. Nitrate concentrations in CORPUD monitoring wells from 1991 to 2004 that show increased nitrate concentrations: data is from NCDENR Aquifer Protection Section. Wells that have shown large increases in nitrate are found in the northern, eastern and southern application fields (see Figure 3).

fields (Figure 5). Wells in which nitrate concentrations have increased significantly are found in the northern, eastern, and southern portions of the WAFs (Figure 3 & 6). A study by Engineering Consulting Services, Ltd. (ECS 2000) concluded that plant available nitrogen (PAN) applications during the 1996-2000 periods exceeded the maximum annual permit of 250 lbs PAN/acre/year in 16 fields mostly in the northern portion of the plant. ENSR (2002) then concluded that PAN limits were exceeded from 1981 to 1985, and from 1990 to 2001 in other fields. Spatial analysis of the amount of nitrogen (lbs PAN) applied per field since 1980 reveals that the northern and central WAFs have had the highest amount of total PAN applied per acre (ENSR, 2002; Figure 5). A total of 1,763 tons of PAN has been applied at the site since land application began in 1980. Welby (2000) conducted a nitrate migration study in Fields 102 and 602 in the west-central and southern portion of the plant. This study suggests that changes in groundwater nitrate concentrations were directly related to continued application rates once 2000 lbs total PAN/acre had been applied to a field. 64 of the 84 fields, or 75% of the WAFs at the NRWWTP had received over 2000 lbs PAN/acre by 2002. Groundwater nitrate concentrations vary from 0.1 mg/l to 160 mg/l under the WAFs (Figure 6). The heterogeneity of groundwater nitrate concentrations does not correlate to total amount of PAN applied to each field or soil type. For example GP 20 and GP 22 at the southern area of the plant have
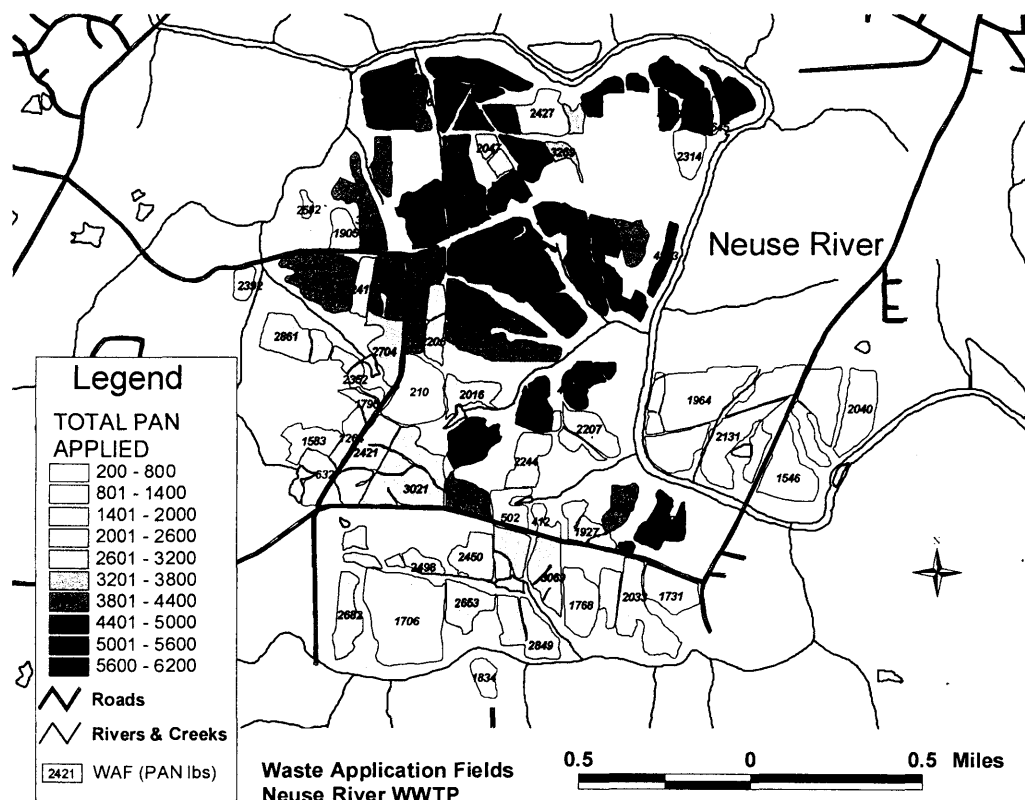
Figure 5. Total amount of Plant Available Nitrogen (PAN) in lbs/ac applied in the NRWWTP Waste Application Fields since biosolid application began in 1980.
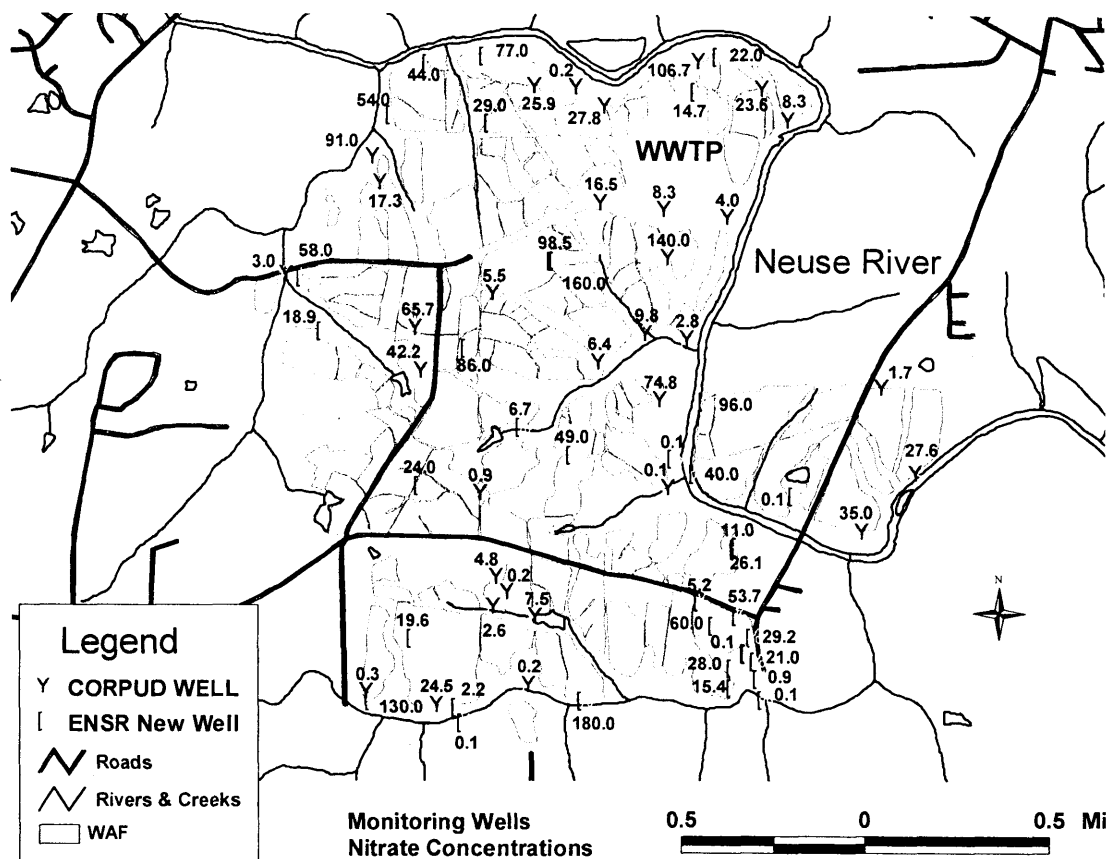
Figure 6. Nitrate concentration in the monitoring wells in the WAFs. The values range from 180 mg/l to 0.1 mg/l.

nitrate concentrations over 100 mg/l. Less than half the Total PAN has been applied to these southern WAFs compared to field #31, which has nitrate concentrations in groundwater of 5.5 mg/l on the western side and 98 - 160 mg/l on the eastern side (Figure 5 & 6). In fields #74 and #75 in the southwest portion of the plant, wells on the southern edge have nitrate concentrations that range from 0.3 mg/l to 130 mg/l. Complex groundwater flow paths can cause variations in nitrate concentrations, and are controlled by local geology and hydrogeology (Böhlke, 2002, Kendall and Aravena 2000, Böhlke and Denver 1995). The following section discusses the geology at the site that may influence groundwater flow paths and nitrate groundwater concentrations.

STUDY SITE GEOLOGY AND SOIL CLASSIFICATION

The NRWWTP site and adjacent Waste Application Fields (WAFs) are situated in the Raleigh Belt and are underlain by the Rolesville Granite (Parker 1979). In this meta-igneous hydro-stratigraphic province of the Eastern Piedmont, the fractured granitic bedrock grades upward into unweathered fractured rock that is covered by a transition zone of highly-fractured partially-weathered rock, a clay-rich saprolite zone, and then a ~ 1 meter soil horizon (Daniel and Dahlen 2002, Daniel and Payne 1990). The Rolesville bedrock is a foliated to massive, megacrystic to equigranular granite cut by intrusive

dioritic dikes. The dikes trend northwest to southeast, and are 100-200 feet across with dike splays 10-20 feet wide (Parker 1979). The local topography consists of rolling hills dissected by v shaped drainages and perennial streams that drain into the Neuse River. Heath (1984) has mapped groundwater discharge zones to the north and south east of the WAFs along the Neuse River. These groundwater discharge zones are areas where streams and seeps discharge water during wet and dry periods. None of the WAFs are in these groundwater discharge zones. The saprolite soils that underlay the waste application fields are well-drained sandy silts to silty sands and loamy sands with porosities of 35 to 55% (Daniel and Dahlen 2002). Red clays and silty sands occur over the intrusive dioritic dikes. The predominate soil types at this site are Appling, Wedowee, Durham, and Altavista, although there are 41 different soil types found in the WAFs (Appendix 1, CGIA, 1983). The saprolite is underlain by the partially weathered zone (PWZ), which is an unconfined aquifer. The PWZ is then underlain by fractured bedrock, which has a porosity of 1-3 % that decreases with depth and closes at ~ 750 ft (Daniel and Dahlen 2002). Shallow groundwater movement in the soil and saprolite is controlled by topography and typically flows from ridges and hilltops down to perennial streams and drainages. The fractured bedrock, PWZ, saprolite, and soil make up a complex flow system. The ridge in the central portion of the plant is incised by surface drainages flowing north and east into the Neuse River. Saprolite is thickest on the ridges and thins in the valleys. Harned & Daniel (1992) and Harned (1989) suggest that the PWZ zone between bedrock and saprolite serves as a primary transmitter of contaminants.

Wells installed at the NRWWTP in 2002 were logged and have four distinct stratigraphic layers (ENRS 2002). The upper soil layer varies from 1-4 feet thick and soil types vary with topography. The saprolite consists of sandy silts and silty sands, which are 30-40 feet thick on the slopes and to 50-60 feet thick on ridge tops. The partially weathered zone has a higher porosity due to the occurrence of parent rock fragments, and is 0 to 10 feet thick below the saprolite and above the fractured bedrock. This geology is not uniform, and complex groundwater flow paths may account for some of the heterogeneity of groundwater nitrate concentrations under these WAFs. The complex hydrogeology would make ground water discharge patterns to the adjacent surface waters difficult to model.

This study evaluates surface and groundwater quality at a site where biosolids have been applied for over 20 years. The purpose of this study is to identify geochemical characteristics of biosolid nitrate that has accumulated in groundwater beneath WAFs. These geochemical properties can then be used to identify nitrogen dynamics and transport of biosolid nitrate off site. Several studies have identified contaminated shallow aquifers underlying active agricultural lands as the dominant source of eutrophication in many watersheds (Howarth et al., 2000, 2002a; Böhlke, 2002). Extensive studies have been completed to understand nitrate contamination and attenuation processes in ground water (Wassenaar, 1995; Böhlke and Denver, 1995; McMahon et al., 1999). Discharge rates of nitrate to streams commonly are not correlated to field application rates. In most watersheds, discharge rates are significantly lower than field application rates (Howarth 2002b, van Breenmen et al., 2002). Riverine nitrogen fluxes typically only accounts for

~25% of the nitrogen input into watersheds (Kendall, 1998; Cane and Clark, 1999; Kendall and Aravena, 2000; van Breenmen et al., 2002). Closing the nitrogen budget by correctly linking field application rates to contaminant loads in surface waters requires an understanding of the dynamics and time scales of contaminant transport through ground water systems and riparian zones that connect ground to surface waters. The NRWWTP is an ideal location to investigate ground to surface water linkages, because biosolids have been applied at the site for a long period of time (24 years), accurate records of the total amount of biosolid PAN applied at the site are available, approximately 70 monitoring wells are located at the site of which about 75% have water quality records that exist for 15 to 25 years, biosolids have a unique nitrogen isotope and major ion / trace element chemistry, and river discharge and nitrate flux have been continuously monitored in the reach adjacent to the site for a 24 month period.

METHODS

WAF monitoring wells and streams were sampled from July 2002 to May 2005. Nitrate concentrations for wells or streams were also taken from CORPUD data or from ENSR (2002), which sampled the wells and streams during the same period of time. Wells were purged of 3-5 volumes of water, then 1 liter samples were collected in acid washed (0.1 M HCl) Nalgene bottles. Samples were filtered with a GWV 63 micron filter and kept at 4°C until processed for nutrient concentrations and isotopic abundances. Continuous monitoring stations were installed in the river attached to bridges above and below the WAFs (Figure 3, NRAK and NRCP). A YSI Sonde equipped with temperature, pressure, pH, conductivity, DO, and turbidity probes along with either a WS Envirotech NAS 2-E nitrate analyzer or a Satlantic ISUS UV nitrate analyzer were placed in an aluminum mesh cage and placed on the river bottom cabled to a bridge pylon. The Sonde and nitrate analyzers were connected to a solar charged battery, Campbell data logger and cell phone modem. The data were transferred to the data logger every 15 minutes and then transmitted to a data server via cell phone once every 24 hours for a 24 month period. Data were checked daily to ensure that the *in situ* instruments were functioning properly. Water samples were collected weekly at each station to check the calibration of both instruments. Temperature, pH, conductivity and DO were measured in the field, and nitrate, dissolved phosphate, ammonia, and turbidity were measured in the lab to check the calibration of the *in situ* instruments. The nitrate concentration of the On Board Standard (OBS) was measured in the lab before and after the NAS-2E was deployed in the river to make sure the calibration did not change during deployment. The OBS was made using sterile procedures to prevent bacterial growth during deployment. Bacterial growth in reagents can be a problem during warm summer months. Freezing of reagents in the winter is not an issue because the instrument is in the water below the river surface. ISUS UV nitrate analyzers were calibrated with three standards prior to deployment and checked after deployment. The mirror was cleaned every two weeks. Weekly river samples were collected at each station and checked against the *in situ* measurements made by both types of instruments. The NAS analyzer made hourly nitrate measurements, whereas the ISUS and Sonde made measurements every 15 minutes for a 24-month period starting March 1, 2003.

River discharge was measured with a SONTEK 3.0 MHz RiverSurveyor Acoustic Doppler Profiler (ADP). The SONTEK ADP was mounted on a 14 ft. aluminum boat equipped with GPS (Trimble Geoexplorer 3 and Beacon on a Belt real time correction) and driven across a straight section of the river multiple times. At least 10 discharge estimates that agreed within 5% were averaged for each river stage as measured with the Sonde pressure transducer at the RiverNet station. 5-8 different river stages were measured, and a logarithmic stage discharge curve was determined for each station (Usry 2005). Stage discharge curves were checked every 3 months to make certain the relationships did not change. The 15-minute pressure readings were then converted to river discharge for each interval. Nitrate fluxes were calculated from the concentration data and calculated water fluxes. Continuous nitrate profiles between the stations were measured during falling discharge periods with a Satlantic ISUS UV nitrate sensor. Position was determined with a Trimble Geoexplorer 3 and BOB that continuously logged the location of the ISUS sensor. The ISUS was calibrated with 3 river water standards that had reagent grade $NaNO_3$ added to increase the NO_3 concentration from 0.3 mg/l to 2 mg/l. Linear corrections were applied to the ISUS measurements when needed. Three 1-second UV pulses were emitted into the river at one-minute intervals, and the average concentration was calculated along with the standard deviation of each one-minute estimate. The boat speed was approximately 6.8 km/hr, so the average distance between measurements was ~100 meters.

In the lab, surface and groundwater samples were filtered through a Gelman AquaPrep 600 cartridge filter (0.45 micron) or a GFF precombusted filter (0.77 micron, heated to 500°C for 4 hours). Nutrient concentrations (NO_3, NH_4, PO_4, Cl) were determined on the filtered samples. Approximately 10 ml of the filtered water were analyzed in an automated flow injection La Chat Quick-Chem 8000 Ion Chromatograph (IC) for chloride (EPA Method 300.0, USEPA 1993), nitrate+ nitrite (EPA Method 353.2, USEPA 1993), phosphate (EPA Method 365.1, USEPA 1993) and ammonium (EPA Method 350.1, USEPA 1993). During each La Chat IC run, an external standard (EPA) and several internal QC standards were run with 10 dilution standards and one spiked river water sample to quantify matrix effects. An additional internal QC standard was run for every 10 samples analyzed. Dissolved Cl, SO_4, Ca, Mg, and Na concentrations were determined in the NCSU Dept. of Soil Sciences Analytical lab by ion chromatography and flame atomic absorption spectrophotometry.

The $\square^{15}N$ of dissolved nitrate or ammonia was analyzed by a modification of the technique of Chang et al., (1999). 1-4 liters of sample, which was enough water to yield 15 $\square$M of nitrogen, were passed through a double ion exchange resin column (1st - cation - 5 ml Biorad AG 50-WX8; 2nd - anion - 2ml Biorad AG 2-X8). The cation column was pre-washed with deionized water. The anion column was pre-washed with 3N HCL, and then repeatedly washed with deionized water to remove all acid residues. Pre-washing the anion column with the same strength acid as the elutant allows 15 $\square$M dissolved samples to be analyzed without an isotopic correction (Chang et al. 1999). Nitrate was eluted from the anion column with 30 ml of 3N HCl. The HCl was neutralized with 15 gm of Ag_2O, the sample was filtered with a Whatman GFF filter, and the filtrate was freeze dried to yield a fine white powder of $AgNO_3$. Half the sample was placed in a tin

boat and combusted in a Carlo Erba NC2500 Elemental Analyzer and isotopically analyzed with a Finnigan Mat Delta+ XLS CF-IRMS to determine δ^{15}N-NO3. The other half of the sample was placed in an Ag boat, and pyrolyzed with a Thermoquest Thermal Conversion Elemental Analyzer (TCEA) and isotopically analyzed with a Finnigan Mat Delta+ XL CF-IRMS to determine δ^{18}O – NO$_3$. The δ^{15}N results were calibrated against NIST 8550, NIST 8548, NIST 8547, and four internal ^{15}N standards. The δ^{18}O results were calibrated against NIST 8542, 8549, NBS 120c, NBS 127, and two internal ^{18}O standards. For ammonia analysis, the order of the resin columns was reversed, the cation resin was air dried at 65°C, and 100-400 ug of resin was placed in a tin boat and combusted in a Carlo Erba NCS 2500 Elemental Analyzer. A carbon trap was placed behind the water trap in the EA to remove the CO_2 peak, and the δ^{15}N-NH$_4$ was determined by CF-IRMS. Statistical analysis of all the river flux, nutrient concentration, and isotopic results were completed using Microsoft Excel spreadsheets.

RESULTS
GROUNDWATERS UNDER WAFs

Previous studies have suggested that groundwater nitrate concentrations are highly variable beneath the biosolid waste application fields at the NRWWTP site (ECS 2000, Welby 2000, ENSR 2002). This study also found highly variable groundwater nitrate concentrations under the biosolid WAFs (Figure 6). The highest nitrate concentrations were found in the northeastern portion of the plant (Wells #41, GP2, GP3, GP6), in the central portion of the plant (Well #18, 45; MW 101, 101D; GP-8), and in the southeastern portion of the plant (GP-20, GP-22). Nitrate concentrations generally decrease with well depth (Figure 7). The highest nitrate concentrations were found in wells with depths less than 50 feet. Most of the monitoring wells at the NRWWTP sample the saprolite zone. One well (113d) samples the PWZ, and three wells (101d, 105d, 111d) plus two older monitoring wells (24, 25) sample the fractured bedrock. In the saprolite, groundwater nitrate concentrations varied from 0.1 mg/l to 180 mg/l, groundwater in the PWZ had nitrate concentrations of 19-21 mg/l, and the deeper fractured rock wells had nitrate concentrations that varied from 0.1 to 100 mg/l. The highest concentrations were found in the shallow saprolite wells located in the north central portion of the plant near fields 28-32. There was no discernable spatial pattern of nitrate concentrations in groundwater. Deeper wells generally have lower nitrate concentrations than shallower wells. Only 6 wells sample ground waters that are not in the saprolite zone, so the deeper ground waters are under sampled (Figure 7). The PWZ groundwater near Field 100 on the western boundary of the plant has a low nitrate concentration of ~20 mg/l. This field has had over 2800 PAN lbs/ac applied since 1985, but PWZ does not appear to be a major conduit for contaminate flow as suggested by Harned and Daniel (1992).
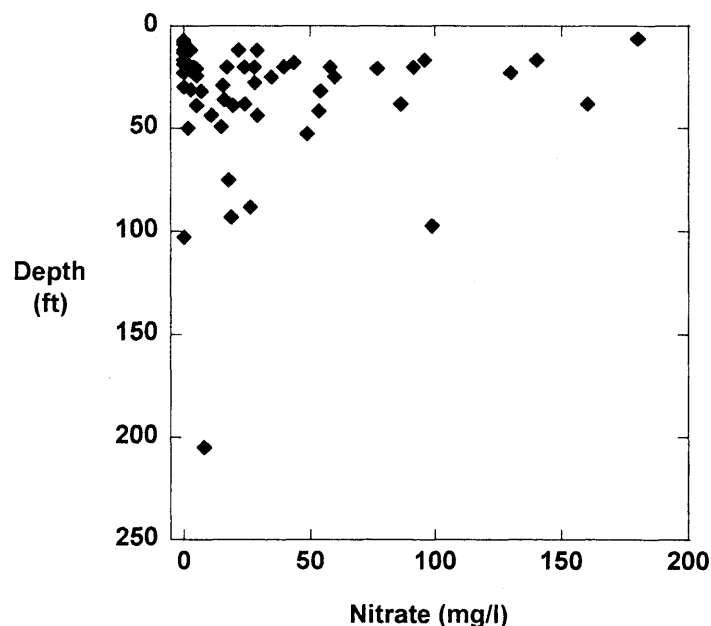
Figure 7. Nitrate concentration versus depth in monitoring wells at the NRWWTP. The highest values occur in wells less than 50 feet deep.

Nitrate concentrations in surface waters draining the WAFs were highest in the northern and east central portions of the plant (Figure 8). Creeks in the northern portion of the plant had nitrate concentrations over 50 mg/l. Creeks in the central portion of the plant had nitrate concentrations above 70 mg/l that attenuate downstream to ~30 mg/l before discharging into the Neuse River. Creeks in the southern portion of the plant had low nitrate concentrations (Figure 8). The highest concentrations in surface drainages were found in the northern portion of the plant in fields that have had the highest total amount of PAN applied over the history of biosolid application (Figures 2 & 5).

The nitrogen isotopic compositions of the biosolids produced at the NRWWTP were dependent upon the formation process and storage conditions. Biosolid A, which is a lime stabilized sludge, had an isotopic composition of +4 to +5 per mil $\square^{15}N$ and a 2-15 N weight % (Figure 9). When not stored under a cover, Biosolid A loses up to 5 weight % N, presumably due to leaching by rainwater. Biosolid B, which is a dewatered sludge, had a $\square^{15}N$ composition of +10 to +12 per mil and a 5-7 weight % N. Without lime stabilization, volatilization of NH_4 increases the $\square^{15}N$ composition and reduces the weight % N of this product. The effluent that is released into the river after treatment in the plant had a $\square$ ^{15}N composition of +35 per mil and an average nitrate concentration of 1.89 ± 0.85 mg/l (Figure 9 & 11a). Microbial digestion and NH_3 volatilization has enriched the effluent from the plant in ^{15}N more than the biosolid composition (Figure 9). Both plant effluent and biosolid $\square$ ^{15}N was distinct from fertilizer ^{15}N, which is near 0 per mil (Kendall 1998, Kendall and Aravena 2000).
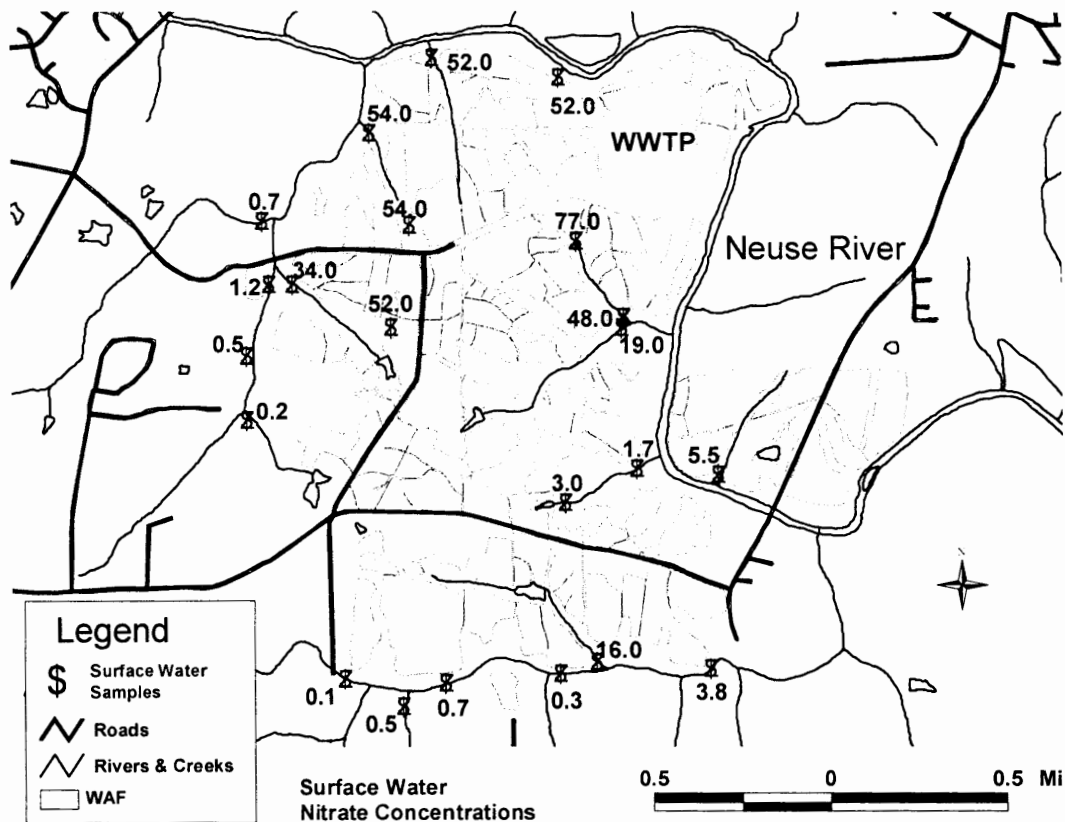
Figure 8. Surface water nitrate concentrations. The highest concentrations were found in the northern portions of the plant where biosolids have been applied for the longest period of period of time.

SURFACE WATER DRAINING WAFS

There are six small drainage basins at the NRWWTP, and four areas that do not have surface drainages (Figure 10). Basins #4 and #6 as well as the East and Bridge areas have had low amount of Total PAN applied during the history of biosolid application at the site (Table 1). These areas also had low surface water nitrate concentrations (Figure 10). Basin #2 and the NW area in the northern
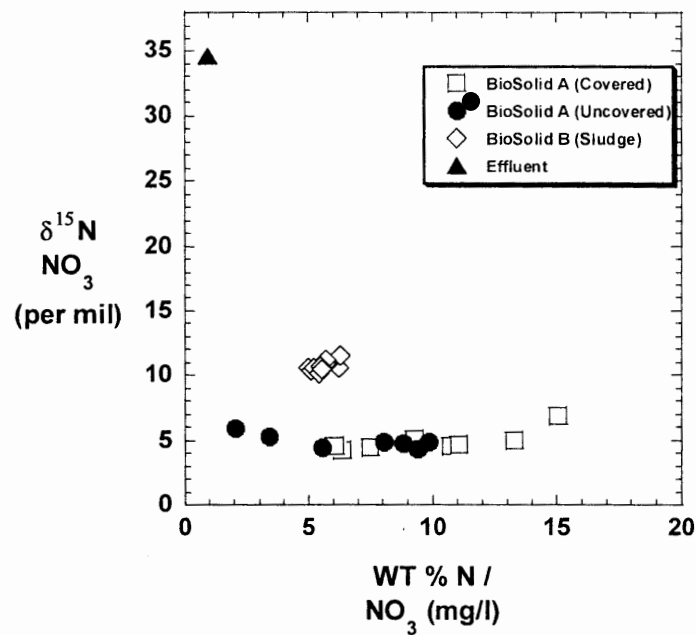
Figure 9. Nitrogen isotopic composition of biosolids produced at the NRWWTP and the ^{15}N composition of nitrogen in the effluent that is released into the Neuse River.
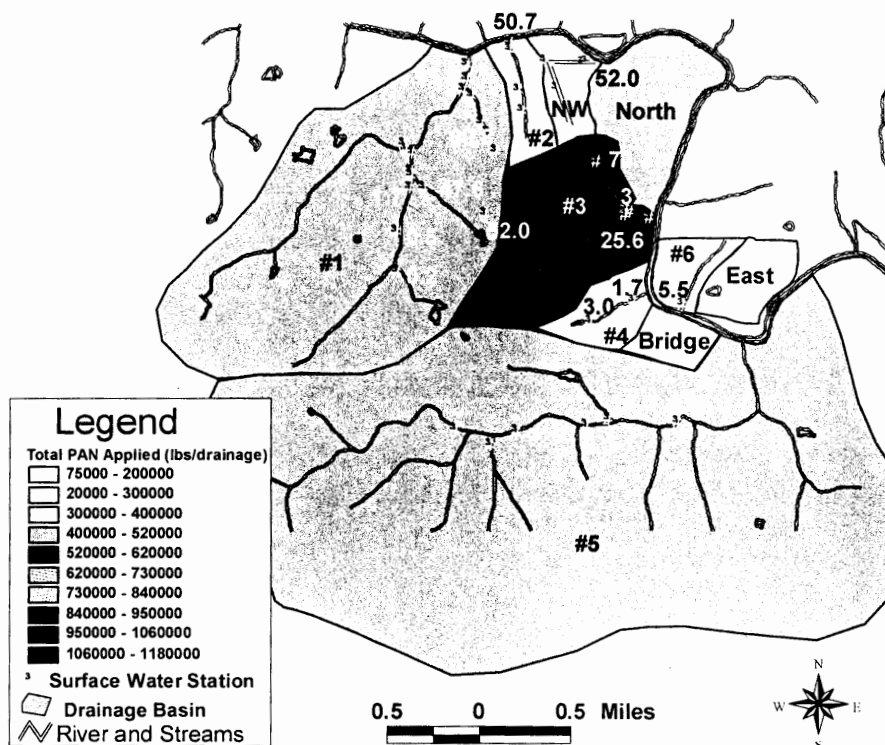
Figure 10. Surface nitrate concentrations in drainage basins with Total PAN applied in each basin. Basins without surface streams are labeled North, NW, Bridge, and East.

TABLE 1. TOTAL AMOUNT OF PAN APPLIED TO DRAINAGE BASINS

Basin	Total PAN Applied (lbs)
1	462890
2	305997
3	1177210
4	84592
5	457178
6	138795
NW	246773
North	422128
East	153706
Bridge	75703
TOTAL (lbs)	**3524970**
TOTAL (tons)	**1762**

portion of the plant have had moderate amounts of Total PAN applied to the fields. Surface drainages in these basins have >50 mg/l nitrate concentrations, most likely because these areas have had biosolids applied since the early 1980s (+20 years). Basins #1 & #5 on the southern and eastern portion of the plant have had a large amount of PAN applied (>400,000 lbs/ac, Table 1). The #5 basin had low nitrate concentrations in surface streams, most likely because biosolid application fields cover a small amount of the drainage area and biosolids have not been applied over a long period of time. Basin #1 has high nitrate concentrations in surface waters that drain the WAFs on the eastern part of the drainage. Basin #3 has had the most Total PAN applied (>1,000,000 lbs/ac, Table 1). Surface water nitrate concentrations in basin #3 varied from 77 mg/l to 33 mg/l. The wetlands and hydric soils in basins #3 and #4 appear to attenuate surface water nitrate concentrations before they flow into the Neuse River (Figure 10).

The isotopic composition of nitrate in ground water under the WAFs varies from +2 to +35 per mil for $\delta^{15}N$, and from +3 to +35 for $\delta^{18}O$ (Figure 11a). Surface water nitrate varied from +8 to +19 per mil for $\delta^{15}N$, and from +1.5 to +10 per mil for $\delta^{18}O$. By plotting the $\delta^{15}N$ and $\delta^{18}O$ of nitrate, the source of nitrate can be identified and the influence of denitrification can be determined (Kendall 1998, Kendall and Aravena 2000). Nitrate derived from fertilizers has relatively low $\delta^{15}N$ compositions, and is isotopically distinct from nitrate derived from wastes which have elevated $\delta^{15}N$ ratios due to ammonia volatilization. Nitrate formed in surface environments from the oxidation of ammonium generally has lower $\delta^{18}O$ ratios than fertilizers. Fertilizer $\delta^{18}O$ ratios are fixed by industrial processes from atmospheric oxygen and have similar $\delta^{18}O$ compositions near +20 per mil (Kendall 1998). Denitrification can shift the ^{15}N composition of nitrate to heavier values (Kendall and Aravena 2000). In this case, the ^{15}N of groundwater nitrate impacted by fertilizer sources and affected by denitrification
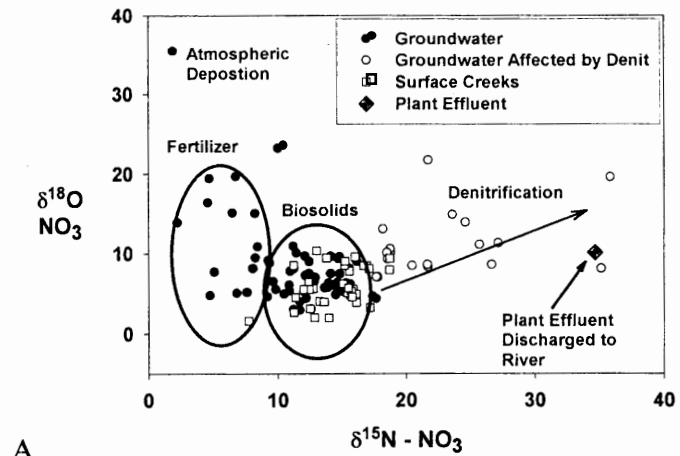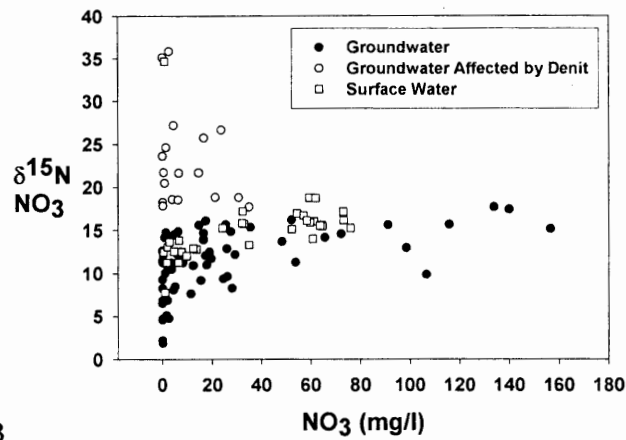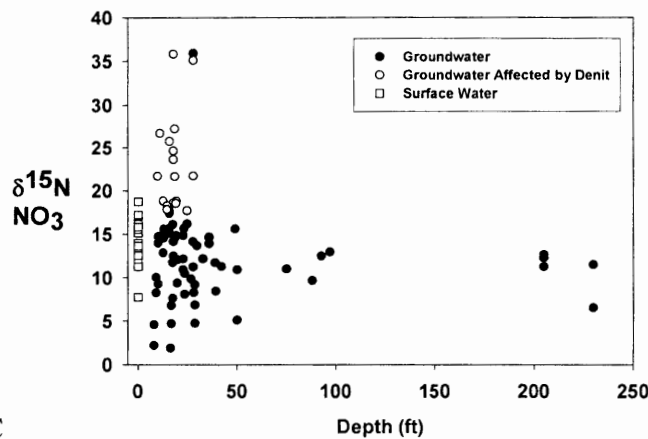
Figure 11. Isotopic composition of nitrate in groundwaters and surface waters at NRWWTP. A. $\delta^{15}N$ nitrate versus nitrate concentration. B. $\delta^{15}N$ nitrate versus well depth. C. $\delta^{15}N$ nitrate versus $\delta^{18}O$ nitrate. The N source and process identification are after Kendall (1998).

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would look like biosolid ^{15}N if only $\square$ ^{15}N was analyzed. With extensive denitrification, $\square$ ^{15}N and $\square$ ^{18}O of the residual nitrate will increase with a characteristic 2:1 slope as concentrations decrease (Kendall 1998, Kendall and Aravena 2000). Using ^{15}N and $\square$ ^{18}O isotopic indicators of denitrification to differentiate between primary and altered groundwater nitrates, 18% of the wells in the WAFs are affected by fertilizer, 57% of the wells are affected by biosolids, 22% of the wells are affected by denitrification, and one well is affected only by atmospheric deposition (Figure 11a). Biosolid nitrate affects most surface waters draining the WAFs. A few surface water samples in the NW basin are affected by denitrification (Figure 11a). The nitrate in ground waters beneath the WAF's varied in concentration from 0 to 180 mg/l while surface waters concentrations varied between 0 to 80 mg/l nitrate. The $\square$ ^{15}N composition in wells with nitrate concentrations above 50 mg/l ranged between +10 to +15 per mil, indicating that biosolids are the primary source of nitrate at these higher concentrations (Figure 11b). Nitrate $\square$ ^{15}N had a wide variation in shallow wells. Elevated nitrate $\square$ ^{15}N in wells shallower than 50 feet were associated with denitrification (Figure 11c). In
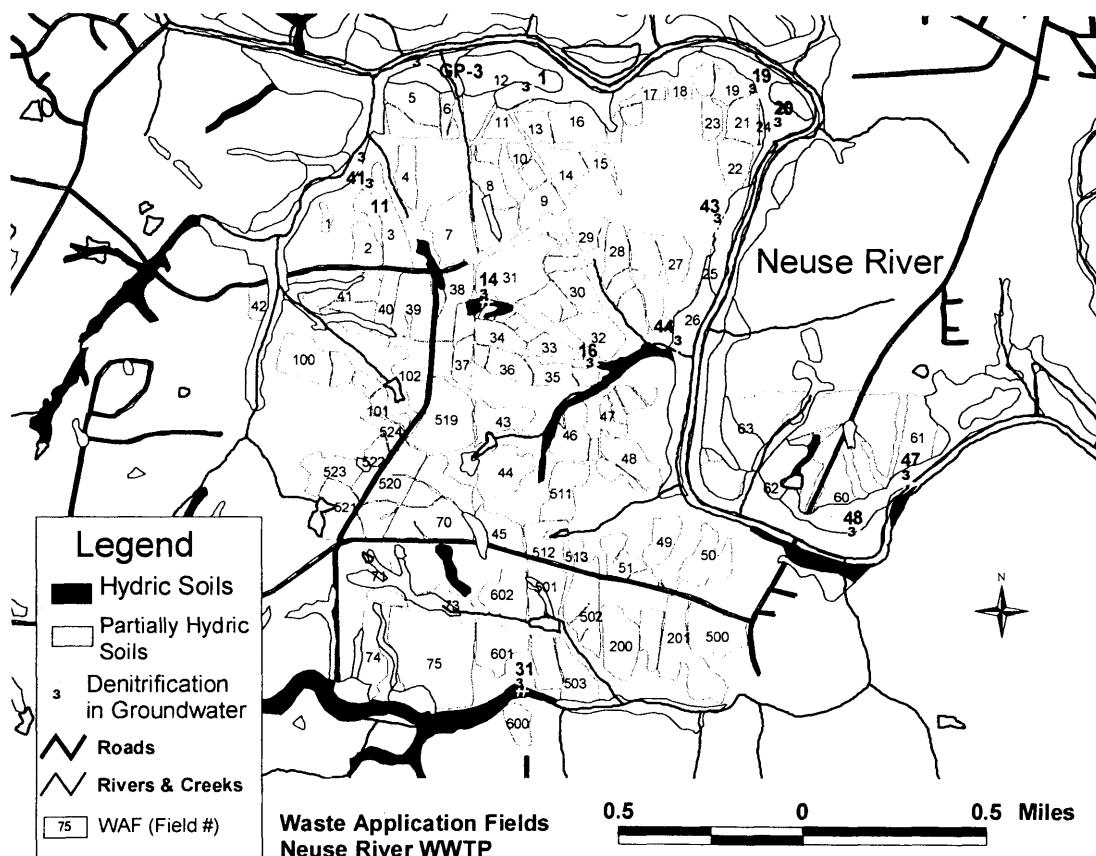
Figure 12. Wells that show isotopic evidence of denitrification are located in hydric and partially hydric soils at the NRWWTP. Wells with extensive denitrification are located in hydric soils.

deeper wells with elevated nitrate concentrations, $\square$ ^{15}N nitrate varied from 10 to 15 per mil indicating that biosolids are the main source of nitrate in these deeper wells as well as the surface drainages (Figure 11c).

The location of the wells that are affected by denitrification can be spatially analyzed using GIS soil data. Wells that were affected by denitrification are located in hydric or partially hydric soils (Figure 12). Hydric soils are wet soils that are anoxic all the time, while partially hydric soils undergo wet and dry periods. High organic carbon content (TOC) and anoxia are required for denitrification (Knowles 1981). Multi-year water quality data from hydric, partially hydric, and non-hydric soils show very different trends (Figure 13). Nitrate and TOC concentrations in groundwater from hydric soils had low nitrate and high TOC contents (Figure 13a). Groundwater in non-hydric soils had high nitrate and low TOC contents (Figure 13c). Groundwater in partially hydric soils had high TOC contents and intermediate nitrate concentrations (Figure 13b). Hydric
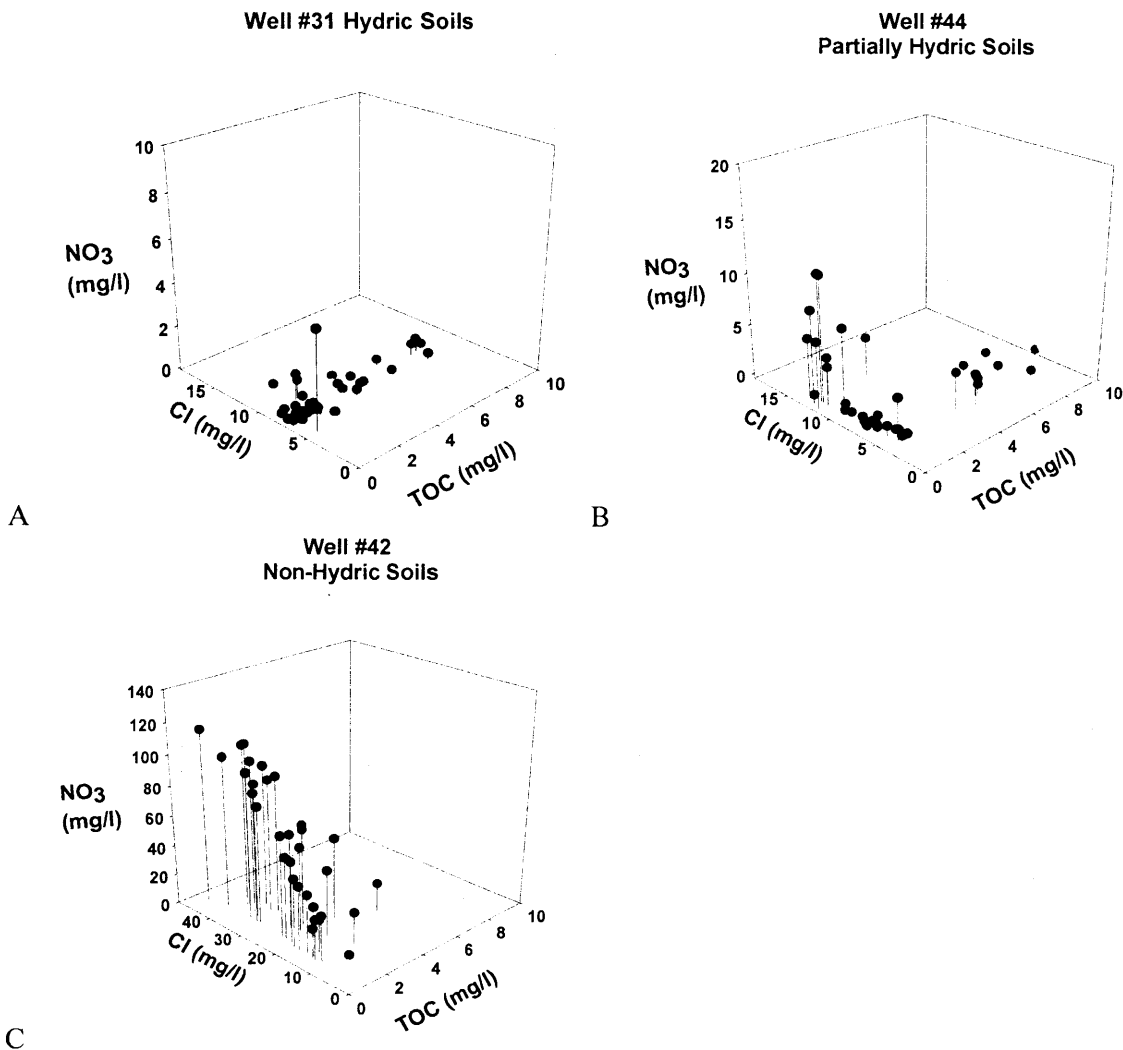
Figure 13. Nitrate, Chloride, and TOC concentrations in quarterly groundwater samples from 1991 to 2004 in hydric soils, partially hydric soils, and non-hydric soils. (For well locations see Figure 14). Note scale changes for nitrate and chloride concentrations.

soils have a discontinuous distribution at this site, while partially hydric soils are located adjacent to the Neuse River, and in the incised drainages in the eastern portion of the plant (Figure 12).

Major Ion Chemistry and Nitrate

Chloride and calcium concentrations increase with increasing nitrate concentrations in the WAF wells (Figure 14). Chloride concentrations are elevated in groundwater affected by urban sewage (Silva *et al* 2002), animal waste Karr *et al* (2001), and biosolids (Weggler 2004). The nitrate to chloride ionic ratio can be reduced by denitrification since nitrate is not a conservative ionic species. WAF wells not affected by denitrification that had nitrate concentrations (above 40 mg/l) have NO_3/Cl ratios above 2 (Figure 15a). WAF wells affected by denitrification had lower nitrate concentrations, higher ^{15}N values, and lower NO_3/Cl ratios (Figure 15a, b). High NO_3/Cl ratios with $\square^{15}N$ ratios that vary from +10 to +15 per mil are indicative of groundwater affected by biosolids, if denitrification is not an important factor.
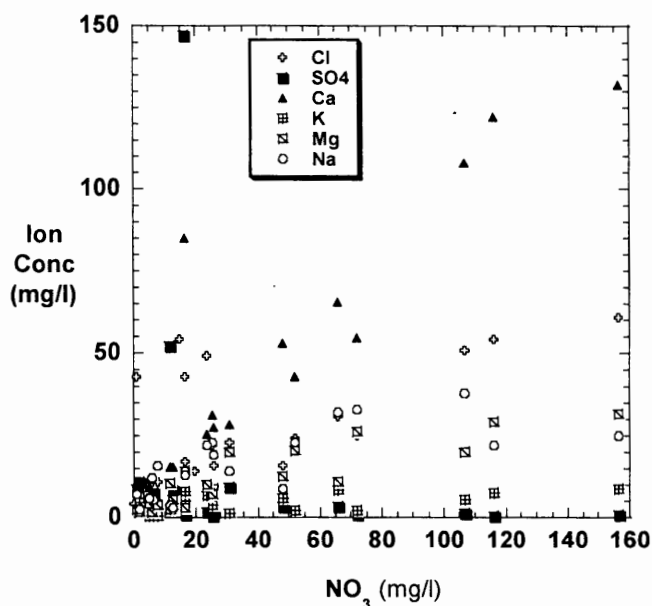
Figure 14. Ion concentration in WAFs wells. Chloride and Ca increase with increasing nitrate concentrations in the WAF wells.

The distribution of hydric soils and denitrification explain the heterogeneity of nitrate concentrations in groundwater under the biosolid WAFs. For example in Field 31 which has had ~4900 lbs/ac total PAN applied over the past 20 years. Well #14 on the western side of the field is in a hydric soil and has a nitrate concentration of 5.5 mg/l (Figures 3, 6 & 8). Wells 101 and 101d on the eastern side of Field 31 are in non-hydric soils and have nitrate concentrations of 98 and
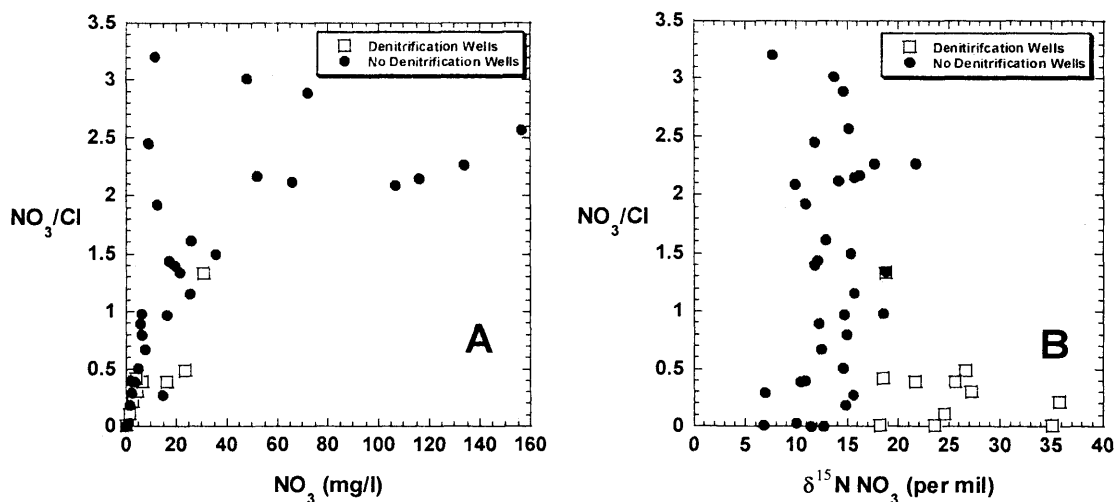
Figure 15. Nitrate concentration and isotopic composition of monitoring wells in biosolid waste application fields. A) Nitrate to chloride ratio versus nitrate concentration in wells with and without denitrification. Wells with increased nitrate concentrations have NO_3/Cl ratios above 2. B) Nitrate to chloride ratio versus ^{15}N in monitoring wells. Wells with denitrification have higher ^{15}N and lower NO_3/Cl ratios.

160 mg/l. Waste application fields are bounded by hydric or partially hydric soils around the perimeter of the entire plant except in the southeastern portion of the plant north and east of fields 49, 50, 500, and 201 and to the west of fields 521 and 523 (Figure 12). Fields 521 and 523 have had 708 and 1773 lbs/ac total PAN applied over the history of biosolid application, so it is unlikely that nitrate would migrate from these fields. Fields 49, 50, 500, and 201 have had 2000 lbs/ac or more Total PAN applied over the history of biosolid application. Nitrate migration in groundwater from these fields is likely, because of the higher amounts of Total PAN applied and because these fields are not bounded by hydric soils. High concentrations of nitrate in surface drainages in the northern portion of the plant and in basin #3 also indicate that biosolid nitrate may migrate into the Neuse River along the northern and eastern boundaries. To investigate nitrate gains in the reach, the nitrate flux entering and leaving the reach was quantified and compared to the daily nitrate flux discharged from the plant.

NEUSE RIVER NITRATE FLUX

The concentration and flux of nitrate in the Neuse River varies on an hourly basis at both the NRAK and NRCP stations (Figure 16). These concentration variations occur during high and low flow conditions. The average nitrate concentration over the reach increased from 0.3 mg/l to 0.5 mg/l during the two years of the study (Table 2). The average nitrate concentration of the effluent from the plant varied little from year to year with averages of 1.7 and 1.9 mg/l nitrate, and 2.8 and 3.0 mg/l total N average concentration (NO_3+NO_2+TKN, CORPUD unpublished data) for year 1 and 2 respectively. The flux of nitrate through the reach can be calculated from the hourly concentration and discharge data with rating curves produced from the River Surveyor ADCP profiles (Acoustic

Doppler Current Profiling System; Usry 2005, Herschy, 1995) according to the following formula:

$$Q = C(h + a)^n$$

where Q is the discharge, h is the depth, C and n are constants derived from a log-log plot of discharge versus depth, and a is a correction factor for the depth of the river at zero flow (Herschy, 1995). The correction factor, a, was determined experimentally from the maximum depth of the channel in relation to the station's

TABLE 2. AVERAGE DAILY CONCENTRATION & FLUX IN THE STUDY REACH

	Upper Station	NRWWTP Pipe	Lower Station
Year 1			
in situ Nitrate (mg/L)	0.33	1.92	0.49
Flux NO_3 (kg/d)	1063	328	1439
Year 2			
in situ Nitrate (mg/L)	0.34	1.71	0.55
Flux NO_3 (kg/d)	609	298	883
Total			
in situ Nitrate (mg/L)	0.34	1.82	0.52
Flux NO_3 (kg/d)	836	313	1161

depth in the river cross-section. Comparison of the *in situ* nitrate measurements with the grab sample concentrations measured in the lab on a La Chat ion chromatograph showed an average difference of -0.01 to 0.05 mg/l with a standard deviation of $\pm$ 0.1 to $\pm$ 0.05 mg/l at the NRCP and the NRAK stations, respectively. The NAS 2E nitrate analyzers had a precision of $\pm$ 0.1 mg/l nitrate, and the La Chat ion chromatograph had a precision of $\pm$ 0.03 mg/l nitrate for replicate analyses during the monitoring period period. This good agreement between the *in situ* and grab sample nitrate measurements indicates little error was introduced into the flux calculations from nitrate concentration data.

The standard error of estimate (S_e) for the depth-discharge relationship is given by:
$$S_e = [\Sigma d^2 / (N-2)]^{0.5}$$

where d is the deviation of an ADCP measurement from the calculated value from the depth-discharge regression and N is the total number of ADCP
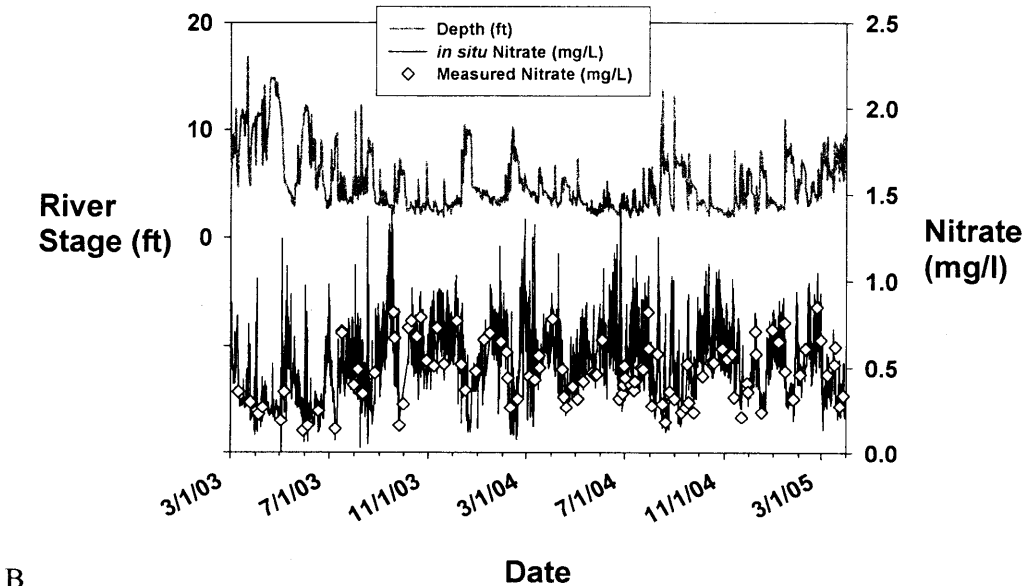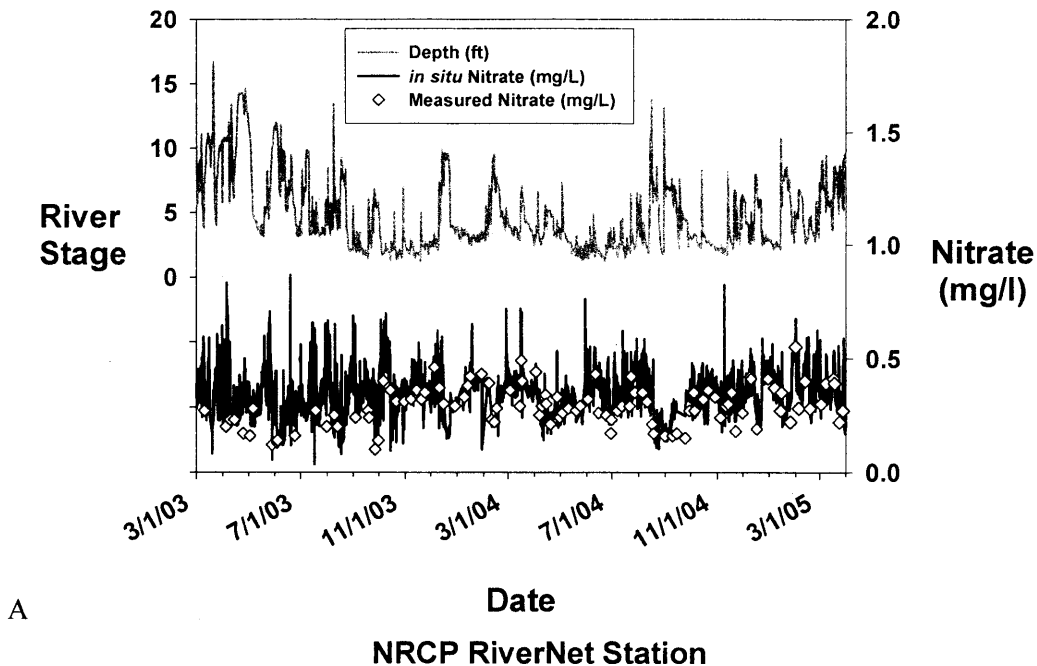
Figure 16. Stage and Nitrate concentration measurements at the upper (A) and lower (B) RiverNet Stations from March 1, 2003 to March 31, 2005. Stage is measured every 15 minutes, nitrate *in situ* measurements are made hourly. Discrete grab samples (measured nitrate) are analyzed with a La Chat ion chromatograph for comparison to the *in situ* measurements. Approximately 70,000 stage measurements, 17,800 *in situ* nitrate measurements, and 220 discrete grab samples were analyzed at each station during the two-year monitoring period.

measurements (Herschy, 1995). Student's t values are needed to correct for small sample sizes (< 20 measurements). Therefore the 95% confidence interval of scatter about the regression is given by, tS_e (Herschy, 1995). Based on sample sizes (N = 10-11

measurements), a Student's t value of 2.2 was chosen for the two sites (Usry 2005). The uncertainty of estimates of discharge from the depth-discharge equation is determined by calculation of the standard error of the mean relation (S_{mr}) for the 95% confidence interval. This gives minimum error at the mean value of the regression and maximum at the upper and lower limits (Herschy, 1995). The mean error of discharge was calculated to be 8% at the two sites, but there is no independent measure to verify this estimate. This is similar to mean errors determined at USGS gauging stations (Herschy, 1995). These estimates of error indicate that most of the uncertainties introduced into the nitrate flux calculations are from the discharge estimates and not from the nitrate concentration data. The average nitrate fluxes in the river are reduced by ~40% during the second year compared to the first year. The plant fluxes did not change significantly over the two year period. The large differences in discharge and nitrate flux suggest hydrological inter-annual variability is important to fluxes of nitrate and water in the upper Neuse Basin. A one-year estimate of fluxes may not be a good estimate of groundwater discharges to surface waters, and multi-year monitoring is required to capture the full range of fluxes at this site.

By comparing the fluxes into and out of the reach, discharge and nitrate gains and losses can be determined. Plant fluxes are reported on a daily basis, so a 24-hour period is the shortest time scale that discharge and nitrate gains can be estimated (Figure 17a). The calculated NPS[*] nitrate flux had large gains and losses in this reach during the two-year period, while the water influx and outflow are more closely matched (Figure 17b). NPS nitrate gains (positive fluxes) occur over a 1-3 day period, while NPS nitrate losses (negative fluxes) occur over a 1-5 day period. On an annual basis over the two-year period these NPS nitrate gains equal ~ 12% of the nitrate flux that is exported from the reach, and is ~ 43% of the nitrate flux that is discharged from the treatment plant (Table 3). There are significant variations in the reach nitrate gains on an annual, monthly, and daily

TABLE 3. NITRATE AND WATER FLUX IN THE STUDY REACH

	Daily Integrated NO3 Gains	% Total NO3 Output (NRCP)	% Total NO3 Output NRWWTP	Daily Integrated Discharge Gains	% Total Q Output (NRCP)
Year 1	70098	13	58	4520132409	9
Year 2	27876	9	26	272321563	1
Total	97974	12	43	4792453972	6

basis (Figures 18a,b; Table 3). The first year NPS nitrate gains in the reach are more than twice the second year NPS nitrate gains. The yearly NPS nitrate gains vary from 26% to 58% of the nitrate discharged from the plant. On a monthly basis, the NPS nitrate gains can vary from 1% to 200% of the monthly

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[*] NPS flux is the Non-point Source flux that is derived from the integrated daily out of the reach minus the daily integrated flux into the reach plus the flux from the Treatment Plant.
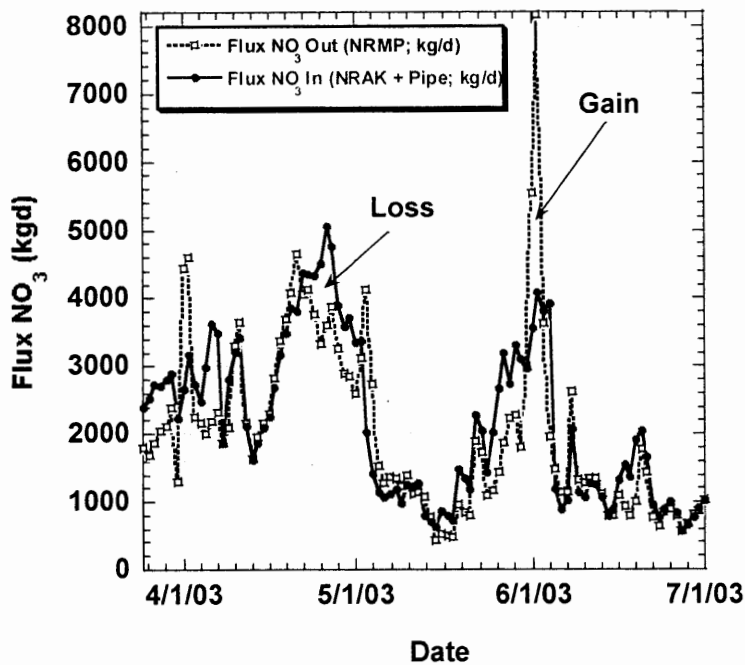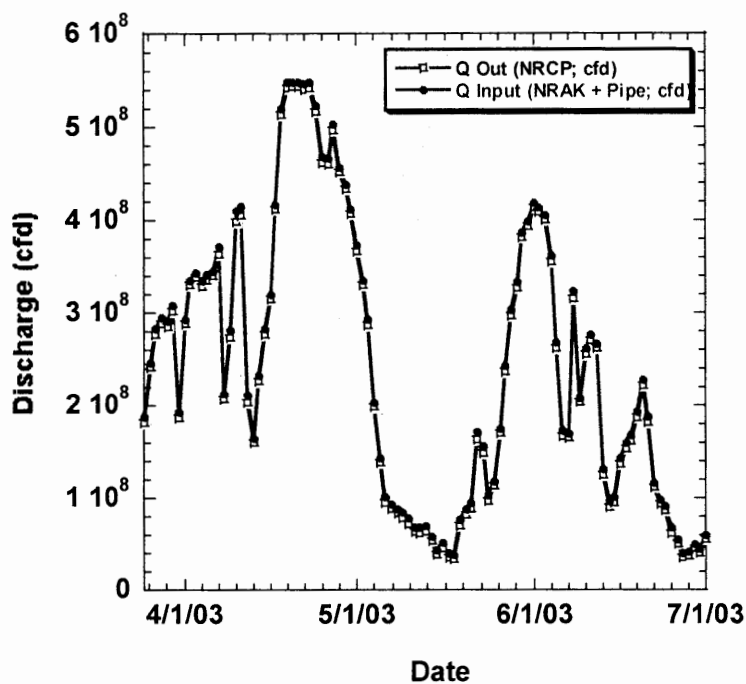
Figure 17. Comparison of the flux from April to June 2003 of nitrogen (A) and water (B) into and out of the river reach adjacent to the NRWWTP. Nitrate shows periods of NPS loss and gain, while water inputs and outflow are more closely matched suggesting that hydrological and biogeochemical process control nitrate flux. NPS gains occur when the output flux exceeds the input fluxes (Upper NRAK station plus Pipe or Plant discharge).

nitrate flux discharged from the plant (Figure 18). The most NPS nitrate was gained in the reach during the Spring of 2003. NPS nitrate gains tend to increase in the winter and decrease in the summer. On a daily basis the NPS nitrate gains do not directly correlate with precipitation or to river stage. The highest NPS nitrate gains are observed during Spring 2003 when river stage was high, but precipitation was low (Figure 18b). After Spring 2004, precipitation events correlate to NPS nitrate gains. River stage at the site is related to precipitation and water discharge levels from Falls Dam, which is approximately 20 miles upstream from the site. The lack of correlation between nitrate gains in the reach and stage or precipitation suggests that the NPS nitrate gains may be related to a complicated series of hydrological variables and interactions between ground water and surface water that are difficult to model without more detailed monitoring data.

The nitrate concentration in the river varies significantly with discharge at both RiverNet stations above and below the plant (Figure 19a, b). Nitrate concentrations increase with decreasing discharge and reach a maximum at low flow of 0.5 mg/l above the plant and 1.2 mg/l below the plant. There is a significant log relationship between discharge and ^{15}N at the lower RiverNet station (NRCP), but not at the upper station. The higher discharge ^{15}N nitrate values at both stations are 4 to 6 per mil, which are characteristic of soil organic nitrogen and fertilizer N. These low $\square^{15}N$ ratios in high flow river nitrate are distinct from the ^{15}N of biosolids and plant effluent. This ^{15}N/discharge relationship indicates that both forms of waste nitrogen have little influence on river nitrate flux during high flow periods (Figure 19c). Low discharge ^{15}N nitrate values do not change at the upper station as discharge decreases. However, at the lower station low flow $\square^{15}N$ river nitrate ratios increase up to +30 per mil. The change in low flow ^{15}N nitrate values between the two stations indicates the relative importance of biosolid and/or effluent nitrate entering the reach during low discharge to the nitrogen flux out of the reach. But does biosolid nitrate enter the Neuse River from the WAFs or just from the effluent discharge pipe? If nitrate concentrations in the reach increase before the discharge pipe, then biosolid nitrate in contaminated groundwater or surface water is entering the reach from the WAFs. If nitrate concentrations in the reach do not change from the upper station to the discharge pipe in the reach, then biosolid nitrate is probably not important to river N flux along the northern portion of the plant.

To determine where nitrate is entering the river, the nitrate concentration was mapped during falling/low discharge stages with an ISUS UV nitrate analyzer. Nitrate concentration measurements were made in the river from NRAK to NRCP stations every minute. At the speed traveled down the river, measurements were approximately 100 meters apart (Figure 20). The nitrate concentration in the reach increases before the effluent pipe on the northern portion of the WAFs, has a sharp increase at the discharge pipe, and a sharp decrease where wetlands drain into the river on the eastern side of the plant (Figure 20). The nitrate
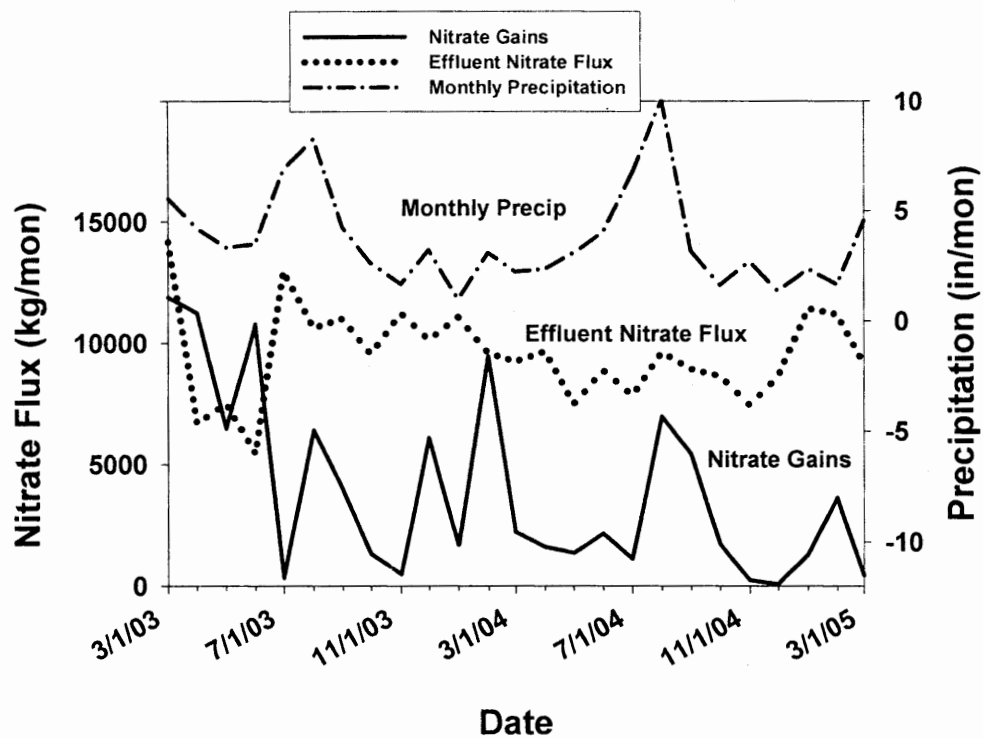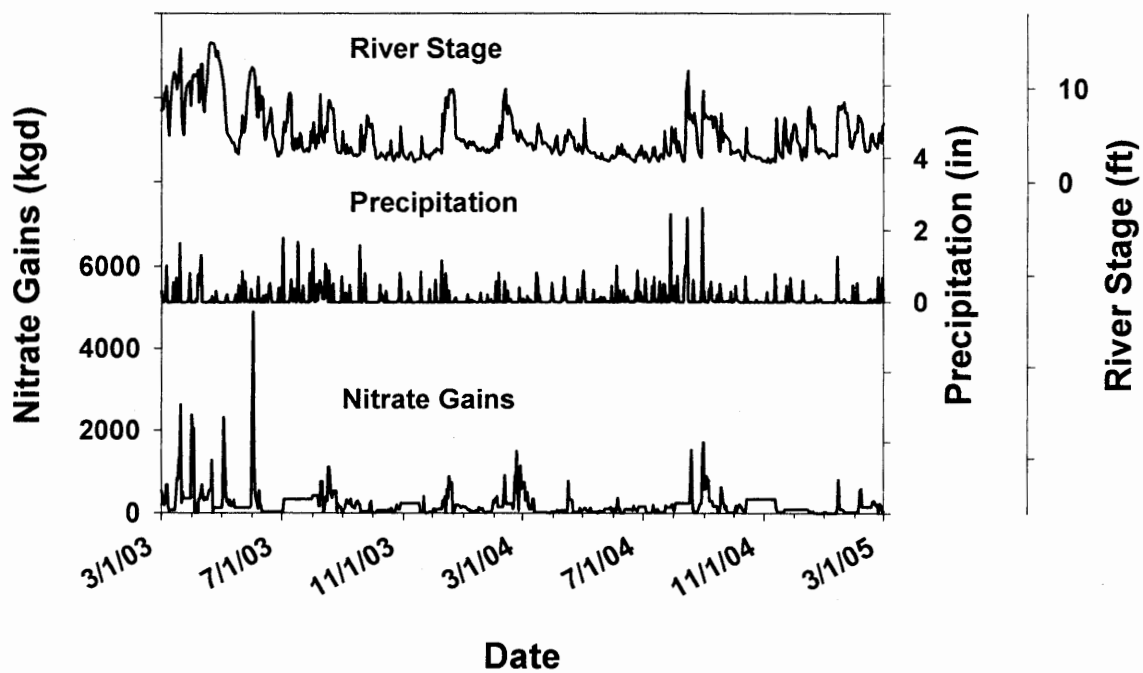
Figure 18. A. Nitrate gains in the reach of the Neuse River adjacent to the NRWWTP averaged on a monthly basis with nitrate flux from the plant, and monthly precipitation; B. daily nitrate gains with precipitation and river stage.

NRAK RiverNet Station

A

NRCP RiverNet Station

B

C
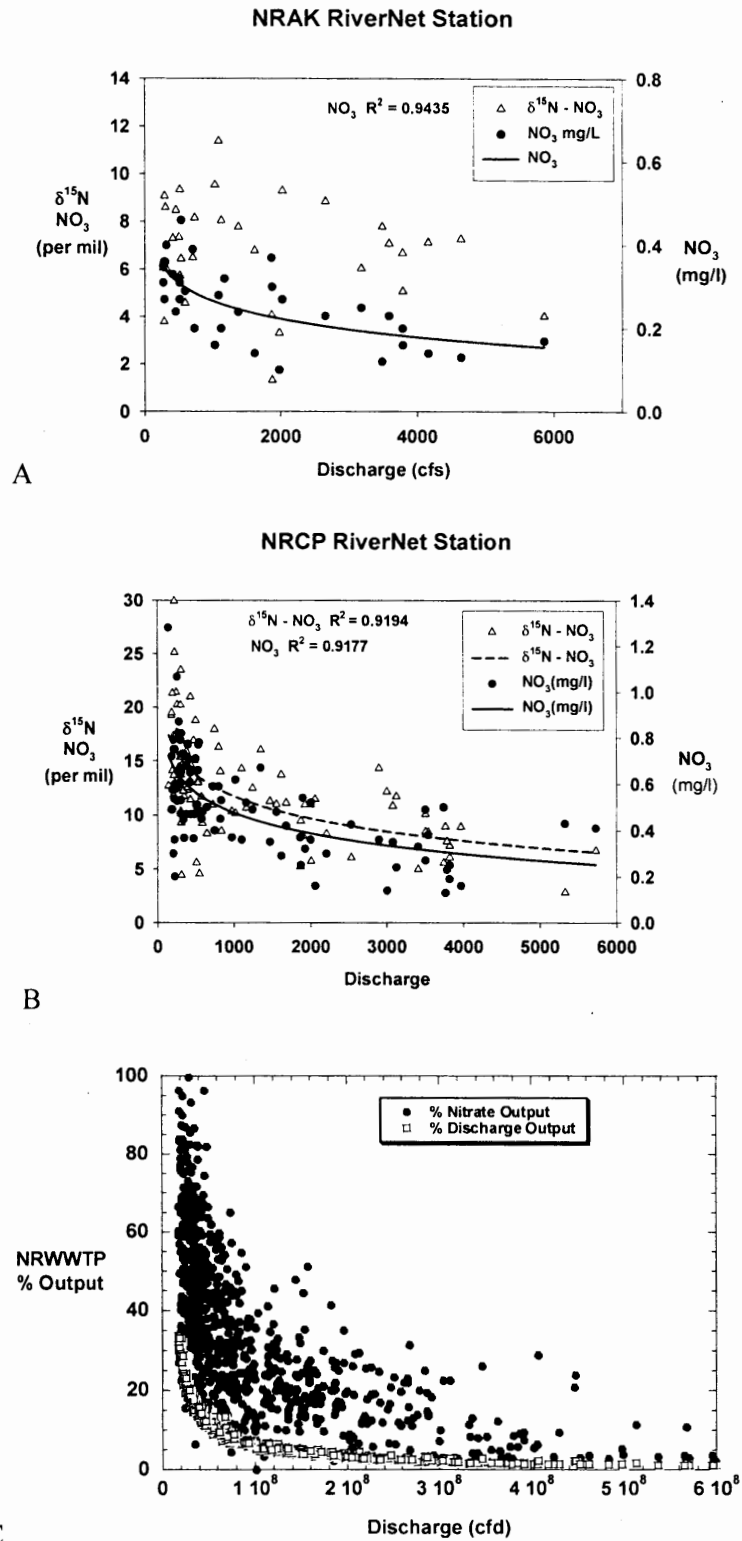
Figure 19. Nitrate concentration and nitrogen isotope relationship with discharge above (A. NRAK) and below (B. NRCP) the waste application fields at the NRWWTP. C. Daily River Discharge vs the % of NRWWTP discharge of Q & N flux out of the reach. At high flow less than 5% of the Q & N flux out of the reach originates from the plant.
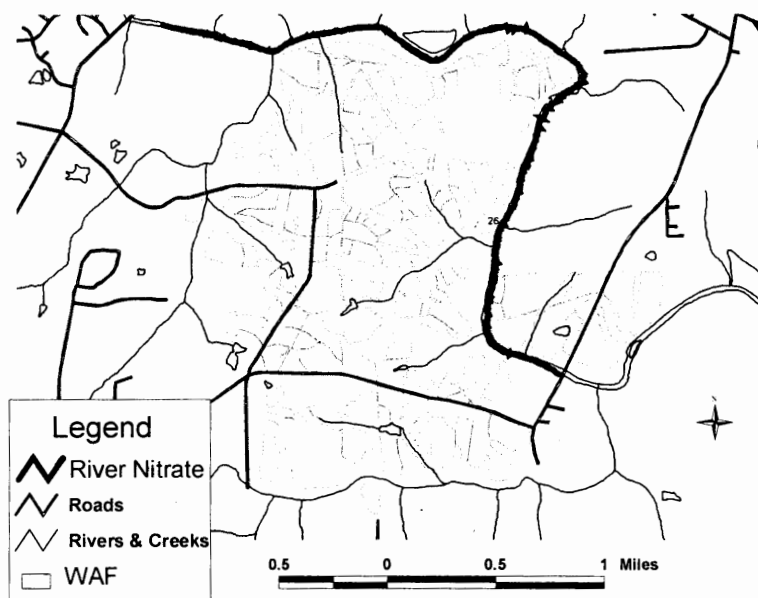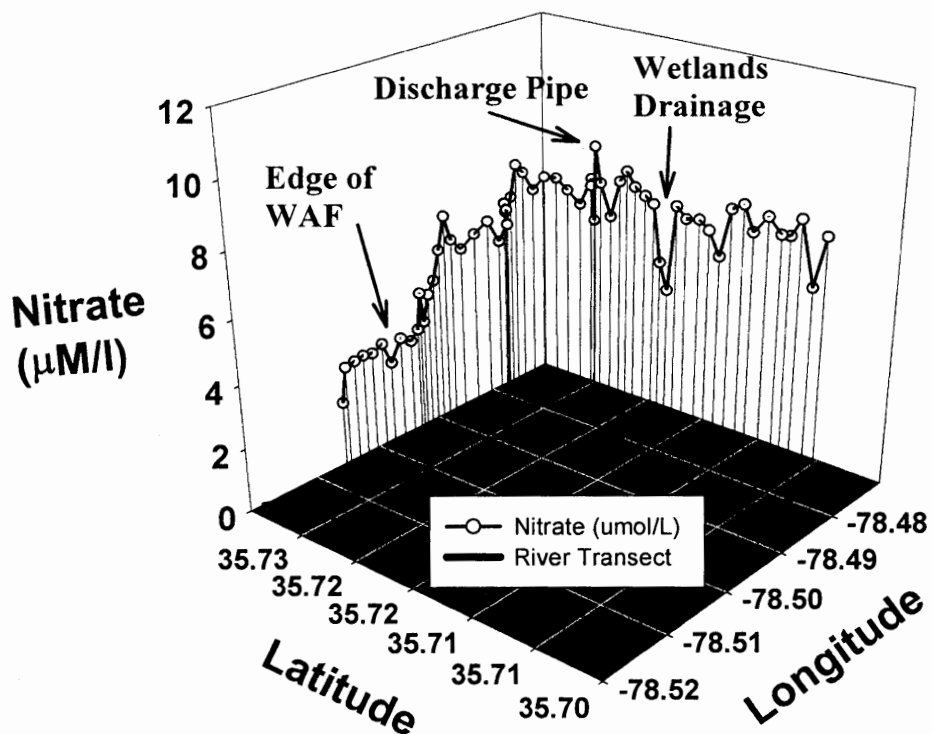
Figure 20. River mapping of nitrate concentration in the reach adjacent to the NRWWTP during falling discharge. The nitrate concentration increases on the northern edge of the plant, has a sharp increase at the discharge pipe, and a decrease where wetlands drain into the river.

concentrations do not change from the wetlands drainage to the bottom of the reach (Figure 20). These data clearly indicate that river nitrate concentrations increase along the northern portion of the plant approximately 1.7 miles before the effluent pipe discharges into the reach. This spatial pattern of low flow nitrate concentrations suggests that biosolid nitrate is entering the Neuse River along the northern portion of the reach, and that the nitrate gains in the reach are most likely controlled by hydrological processes at the site that are unknown and link biosolid nitrate enriched groundwater to surface waters in the Neuse River.

DISCUSSION

Agronomic use of biosolids as a soil fertilizer remains controversial because of environmental concerns despite, widespread adoption of the practice over the past 20 years (Shober et al., 2003). Long-term studies of biosolid amended soils indicate that soil accumulation of organic carbon, total carbon, and ammonia are not significant. However, nitrate, phosphate, calcium and some trace elements do accumulate in biosolid amended soils (Cogger et al., 2001). Potassium can also be lost, which is a concern for K fertility (Cogger et al., 2001). This study indicates that after 22 years of application, municipal biosolid nitrate has migrated from ground waters into surface waters adjacent to the waste application fields underlain by fractured granite. Groundwater that accumulates biosolid nitrate has positive $\square^{15}$N-nitrate and elevated NO_3/Cl ratios. These distinct geochemical characteristics in groundwater not affected by denitrification can be used to trace the environmental impact of biosolid application practices. ^{15}N data from groundwater nitrate at the site indicates that biosolid nitrate has migrated into the deep fractured rock aquifer, as well as the shallow unconfined saprolite aquifer. The nitrate concentration in groundwater under the WAFs varied spatially from 180.0 to 0.01 mg/l nitrate. The application of biosolids in WAFs at this site has varied from 400 to 61700 lbs/ac Total cumulative PAN. The highest concentrations of PAN have been applied for the longest duration in the northern portion of the plant. The differences in amount of PAN and duration of biosolid application do not totally explain the variations of groundwater nitrate concentrations. The distribution of hydric and partially hydric soils does correlate to the nitrate, chloride, and TOC concentrations in the underlying groundwater. The isotopic composition of groundwater nitrate indicates that 18% of the WAF monitoring wells are affected by fertilizer, 57% are affected by biosolids, 22% of the wells are affected by denitrification and one well is affected by A.D.N. (Atmospherically Deposited Nitrogen). Wells that are significantly affected by denitrification as indicated by the trend of ^{15}N and ^{18}O nitrate ratios are located in hydric or partially hydric soils. These hydric or partially hydric soils are located around the perimeter of the plant and discontinuously in the narrow v-shaped drainages that disect the eastern portion of the plant. The variable nitrate concentration in the groundwater at this site is likely the result of differences in application rates, complicated groundwater flow paths, and the presence or absence of significant amounts of denitrification in anoxic or partially anoxic soils.

Hourly river nitrate flux and daily plant discharge data over a 24 month period estimates that 70,098 kg of NPS nitrate migrated into the reach during the first year of monitoring, and 27,876 kg of NPS nitrate was gained in the reach during the second year

(Table 3). These nitrate gains in the reach occur on an episodic basis, typically over a 1 to 3 day period. The NPS nitrate gains are equal to 58% of the plant effluent nitrate discharged during the first year and 26% of the plant effluent nitrate discharged during the second year. Over the two year period the NPS nitrate gains in the reach equal 43% of the amount of nitrate discharged from the treatment plant. These NPS nitrate gains are therefore significant, but difficult to model because the inter-annual differences are large. The NPS water gained in the reach represents 206% of the amount of water discharged by the plant during the first year and 12 % of the water discharged from the plant during the second year, for a total of 108% of the amount of water discharged from the plant over the two-year period. The hydrographic conditions during the two years were different. While precipitation was not significantly greater during the first year (50.74" total rainfall vs 38.39" total rainfall measured at the Clayton Horticultural Station; State Climate Office), discharge was high during the first year most likely because stage height was augmented by water release from Falls Dam. Changes in groundwater levels are not known. During high river stage, the river banks are flooded which promotes bank infiltration. Water exchange between the river bank and groundwater is controlled by the relative elevation differences between groundwater and river stage as well as bank porosity (Figure 18B). Hydric soils are a barrier to nitrate, but not water migration along the northern, and eastern borders of the WAFs (Figure 12). Preliminary data in these riparian areas indicates that shallow field edge wells have nitrate concentrations of ~ 40 mg/l, while shallow river edge wells have consistent nitrate concentrations below 0.1 mg/l (Fountain et al., in prep). The riparian buffer width next to the Neuse River ranges from 100 to 250 feet (GIS analysis of 1999 Wake County digital orthophotographs). Gilliam (1994) and Spruill (2004) suggest that buffers of this width are adequate to attenuate nitrate migration into the river, although Spruill (2004) also emphasizes the role of organic rich hyporheic sediments in the river bottom that contribute to nitrate attenuation. This buffer width also conforms to the BMPs described by Gilliam et al (1997), and should provide effective protection for nitrate migration from the WAFs into the Neuse River at the site. The data and buffer width BMPs suggest that nitrate migration through the riparian buffers adjacent to the Neuse River is not important for nitrate gains in the river. Given the distribution of hydric soils around the biosolid WAFs, biosolid application history, and site topography, biosolid nitrate migration from the WAFs is only likely north and east of fields 49 and 50 and east of fields 201 and 500. If nitrate is not likely to migrate through the riparian buffers at the site, then another mechanism must account for the NPS nitrate gains in the reach.

Nitrate could enter the reach via small streams that are deeply incised and drain the WAFs at the site (Figure 10). Surface water drainages have nitrate concentrations that can vary up to 77 mg/l nitrate. Streams that drain the northern WAFs generally have nitrate concentrations above >50 mg/l. Riparian buffers adjacent to the small surface drainages vary from 0 to over 100 feet in width, less than recommended BMPs (Gilliam et al., 1997). The ^{15}N and ^{18}O composition of nitrate found in these surface drainages suggest that biosolids are the source of the nitrogen in these streams and creeks (Figure 12a). The highest nitrate concentrations in surface drainages are in the northern basins and basin #3 in the central portion of the plant (Figure 10). These WAFs have had the heaviest application rates over the longest duration (Figures 2,5). Nitrate concentrations in the

monitoring wells along the northern edge of the plant vary from 0.2 to 106 mg/l (Figure 6). Wetlands occupy the eastern edge of the plant adjacent to the Neuse River in basins #3 and #4 (Figure 10). Surface water nitrate concentrations are low in basin #4 due to the low amounts of Total PAN applied and the presence of hydric soils. In basin #3, which has had the most amount of PAN applied, surface water nitrate concentrations are attenuated from 77 mg/l to ~30 mg/l in wetlands (Figure 10). River nitrate mapping shows a drop in nitrate concentrations in the Neuse River adjacent to these wetland areas (Figure 20). It is likely that groundwater contaminated with biosolid nitrate enters the river along the northern portion through the surface drainages. These drainages are deeply eroded through the overlying soils and cut into the top of the porous saprolite. This creates shallow groundwater flow paths that would direct recharge concentrated with biosolid N into the surface drainages. These drainages cut across the riparian buffers next to the Neuse River and would not attenuate nitrate in the stream. The episodic discharge of these drainages after a precipitation event linked with shallow groundwater flow paths may explain why nitrate gains are observed in the reach over a 1-3 day period and then cease. Groundwater levels and surface water discharge monitoring are needed to understand the importance of these surface water drainages to NPS nitrate gains in the reach in the future.

Intrusive diabase dikes are found at this site (Parker 1979) and are another potential shallow groundwater flow path from the WAFs. Diabase dikes have been mapped crossing the Neuse River in the northern portion of the plant (Daniel and Payne 1990, ENSR 2002, 2003) where river nutrient mapping documents increases in riverine nitrate concentrations. The hydraulic impact of these dikes on groundwater flow, and links to surface water is not known and could be potentially variable. Increased fractures in the country rock adjacent to the dike along the margins of the dikes caused by the dike intrusion could be a conduit for groundwater into the river. The weathering of the diabase into clays could also reduce porosity and form a hydrologic barrier to water flow. A peak in the river nitrate concentration occurs near the surface drainage in the NW basin, where a large diabase dike crosses the river (Figure 20). More low flow river mapping at finer spatial scales is required to determine if the nitrate concentration increases observed in the river is associated with the surface water drainages or the location of the diabase dikes. Increased transport of groundwater along side of the diabase dikes could link deep groundwater to the Neuse River with short residence times. However, the highest nitrate concentrations are found in groundwater shallower than 50 feet at this site, so the diabase dike effects on groundwater flow would be most important in the saprolite where clay weathering and hydrologic flow restrictions are most likely (Figure 7).

ENSR (2003) estimated that approximately 65,435 kg of nitrogen was discharge from groundwater into the Neuse in 2003 with a steady state groundwater flow model, uniform subsurface flow paths, and a 30% mineralization rate for organic nitrogen. This is within 7% of the 2003-2004 NPS nitrate gains estimated in the reach with hourly river monitoring. Simulated groundwater discharge to the Neuse with this model suggests nitrogen gains from groundwater will peak in the Neuse River at 71,940 kg in 2005. In 2006 the model predicts that nitrogen gains will decrease to 35,720 kg. Monitoring

estimates that NPS nitrate gains dropped in the river during 2004-2005 to 27,876 kg. According to the ENSR model, nitrate discharges should decrease after the 2005 peak flux if biosolid fields are managed so that the maximum nitrate in recharge to groundwater is <6 mg/l. The model estimates that 30 to 40 years is required for nitrate concentrations in groundwater to decrease below 10 mg/l. Actual monitoring of the NPS nitrate gains in the river do not agree with the model nitrate flux predictions. The differences may be because the ENSR model does not take into account the heterogeneous location of denitrification in hydric sediments, the variable rates of biosolid remineralization, and heterogeneous subsurface flow. Shallow groundwater flow paths through the riparian buffers do not appear to carrying most of the biosolid nitrate into the river as suggested by the model. Inter-annual hydrological variability, changes in groundwater levels, and nitrate flux in surface drainages may control nitrate gains in the reach on a yearly basis which are not addressed by the ENSR model.

The ^{15}N nitrate / discharge relationship in the river becomes significant below the WAFs. This is the result of positive ^{15}N nitrate values observed in the river during low flow conditions. Welby (2000) found that the rates of nitrate accumulation in groundwater under WAFs in the western portion of the plant were directly related to application rates when over 2000 lbs/ac Total PAN had been applied to a field. This application threshold has been exceeded all along the northern portion of the plant. However, during high flow conditions the ^{15}N composition of the river does not change significantly. This is the result of dilution of the nitrate entering the river from the waste application fields by nitrate entering the reach from upstream during high flow (Figure 19c). At the highest discharge levels, the nitrate contributed by the treatment plant equals <5% of the nitrate transported out of the reach while the water amounts to less than 2% of the water that leaves the reach. Complicated interactions between high river stage and groundwater levels controlling bank infiltration and exfiltration are important to nitrate migration across riparian buffers. Flooded river banks would enhance the denitrification potential of the partially hydric soils that line the river bank and decrease NPS nitrate transport to the river. The ^{15}N composition of groundwater under the WAFs becomes more positive due to biosolid degradation and leaching to the water table. Groundwater nitrate that migrates off the WAFs to the riparian buffer would become even more isotopically positive as a result of denitrification in sediments adjacent to the river. ^{15}N values of nitrate in river edge wells are ~ 60 per mil (Fountain *et al.*, in prep), but $\square^{15}$N nitrate values that heavy have not been observed at low flow in the river. This isotope data combined with the riparian buffer nitrate concentration data suggests that the shallow groundwater pathways through the riparian buffers is not important to river NPS nitrate flux. Groundwater that is intercepted by deeply incised surface drainages and leaves the WAFs as surface runoff would have shorter residence times and less nitrate attenuation by denitrification than shallow groundwater moving through the riparian buffers.

The relative importance of NPS nitrate groundwater inputs through riparian buffers, or NPS nitrate in surface waters that drain into the Neuse River to the nitrate flux in the river cannot be determined from this data and should be the subject of future investigations. The relative difference in NPS flux through different pathways is

important because artificial wetlands can be constructed to attenuate the surface water nitrate flux to the river. Ground water nitrate flux through riparian buffers is unlikely at this site, but more buffers need to be monitored. Groundwater nitrate moving along basaltic dikes, if present, would be more difficult and costly to remediate. NPS nitrate inputs from surface or groundwater sources contributed approximately 40% compared to the nitrogen discharged as effluent by the plant over the 2003-05 period. Understanding the predominate NPS nitrate flow path to the Neuse River at the site is critical for designing remediation strategies. Surface water discharge and nitrate concentrations need to be monitored and compared to reach NPS nitrate gains to determine the relative important of each flow path. Streams on the eastern side of the plant drain into a wetland and surface water nitrate concentrations decrease by ~ 50% before the water enters the Neuse River. During high stages, river water floods up these drainages creating shallow flooded wetland areas that attenuate nitrate in the surface drainage. Construction of artificial wetlands along the northern edge of the plant and reducing flow in the streams with rock dams may produce the same result observed during the flooded drainages on the eastern side of the plant. Enhancing denitrification and water retention in the surface drainages, widening the narrow buffers adjacent to the stream drainages in the fields, and reducing the surface drainage nitrate flux to the Neuse River by creating artificial wetlands at the base of these drainages would be cost efficient approaches to formulate sustainable biosolid land application practices at the Neuse River Waste Water Treatment facility.

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Legend

∧∨ Rivers & Creeks

Soil Types
- Altavista
- Appling
- Augusta
- Borrow Pit
- Buncombe
- Cecil
- Chewacla
- Colfax
- Congaree
- Creedmore
- Durham
- Enon
- Faceville
- Georgeville
- Goldsboro
- Granville
- Gullied
- Helena
- Herdon
- Lloyd
- Louisburg
- Louisburg-Wedowee
- Lynchburg
- Made land
- Madison
- Mantachie
- Mayodan
- Norfolk
- Orangeburg
- Pinkston
- Plummer Sand
- Gravel Pit
- Quarry
- Rains
- Roanoke
- Swamp
- Vance
- Wagram
- Wahee
- Wake
- Wedowee
- Wedhadkee
- White Store
- Wilkes
- Worsham
- water

0.25   0   0.25   0.5 Miles

N

See Appenedix 1 for listing of
Wake County Soil Types