A GEOCHEMICAL STUDY OF THE EFFECTS OF LAND USE ON NITRATE CONTAMINATION IN THE LONG ISLAND AQUIFER SYSTEM

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Introduction:

Elevated concentrations of nitrate in ground water are an environmental hazard and a public health risk. High concentrations of nitrate interfere with the ability of the blood to transport oxygen which leads to chronic illness in adults and death in young infants. Therefore, the United States and Canada have set drinking water limits of 45 mg/l as nitrate or 10 mg/l as nitrogen (Freeze and Cherry, 1979). Sandy, unconfined, coastal plain aquifers such as the Long Island Aquifer System are particularly susceptible to nitrate contamination from anthropogenic sources. Potential sources of nitrate include: a) agricultural fertilizers, b) turf grass fertilizers c) septic tank effluent or leaking sewer lines, d) landfill leachate e) commercial or industrial wastewater, and f) atmospheric nitrates (primarily industrial pollutants). The objective of this study will be to place constraints on the relative contributions of these various sources to nitrate contamination of the aquifer. A preliminarty study conducted last summer with the assistance of the Suffolk County Department of Health Services indicates that the nitrogen and oxygen isotopic composition of ground water nitrates can be used to place constraints on the sources of nitrate in Long Island ground water.

Evaluating the Isotopic Composition of Ground Water Nitrates:

Numerous researchers have successfully used nitrogen isotopes to characterize nitrate sources (table 1) and also to identify processes such as denitrification that may alter the concentration of nitrate within the aquifer system (Mariotti et al., 1988). Several recent studies have taken advantage of the additional constraint that can be provided by the measurement of the oxygen isotopic composition of the nitrate (figure 1). Due to the large oxygen isotopic contrast between nitrates produced in the atmosphere and those produced by microbial processes in the soil (nitrification), the oxygen isotopes in nitrate are particularly useful for the identification of fertilizer nitrates (Amberger and Schmidt, 1987) and atmospheric nitrates (Durka, et al., 1994). The $\delta^{18}O$ vs $\delta^{15}N$ plot also allows one to evaluate mixing more easily because the two-element plot separates the nitrate sources into distinct fields.

Plots of $\delta^{18}O$ vs $\delta^{15}N$ will be used to place constraints on the sources of nitrate in Long Island ground waters. Since there are regional differences in the isotopic composition of nitrates due to differences in aquifer materials, land use practices, and the isotopic composition of meteoric waters, it will be necessary to determine the end-member nitrogen and oxygen isotopic composition of nitrate sources on Long Island. Ground water samples will be collected from monitoring wells downgradient from particular land use activities. The nitrogen and oxygen isotopic compostion of the nitrate will be determined by stable isotope mass spectrometry at the Environmental Isotope Laboratory, University of Waterloo, Ontario.

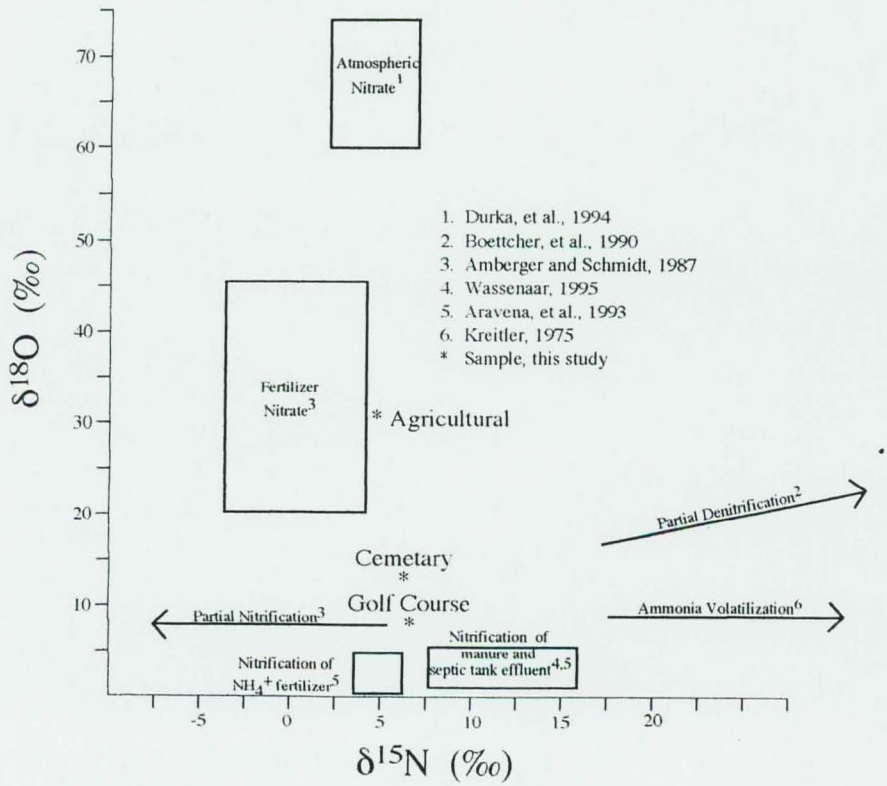
For the preliminary study, several samples were collected with the assistance of the Suffolk County Department of Health Services (SCDHS). The nitrogen and oxygen isotopic compositions of nitrates collected downgradient from an agricultural area, a golf course, and a cemetary are plotted in figure 1. The oxygen isotopic compositions of the cemetary and the golf course nitrates are elevated with respect to nitrates produced by nitrification in other localities. Although this is due at least in part to the heavier isotopic composition of Long Island groundwaters, it may also reflect an atmospheric contribution. Ground water samples will be collected from shallow wells in an undisturbed area, such as the Pine Barrens, to determine the initial isotopic composition of ground water nitrates. Additional samples collected from wells located in residential areas with septic systems and wells downgradient from a landfill will fill in the fields for the remaining sources.

Table 1: Nitrogen Isotopic Composition of Nitrate Sources

Source	$\delta^{15}N$ ‰*	Reference
Suburban Lawns, Long Island, NY	+1.1 to +7.1	Flipse, et al., 1984
Golf Course, Long Island, NY	+3.8 to +14.	Flipse and Bonner, 1985
Potato Farm, Long Island, NY	+3.7 to 12.2	Flipse and Bonner, 1985
Soil Organic Nitrogen	+4 to +9	Heaton, 1986
Non-fertilized cultivated fields, TX	+2 to +8	Kreitler, 1975
Wet Precipitation, U.S.	-7.2 to +2.6	Hoering, 1957
Wet Precipitation, S. Africa	-18 to +7	Heaton, 1986
Wet Precipitation, Germany	+2.6 to +6.3	Durka, et al., 1994
Feedlot, Minnesota	+5.4 to +43.1	Komor and Anderson, 1993
Residential w septic, MN	+1.5 to +11.7	Komor and Anderson, 1993
Manure Fertilization, MN	+12 to +16	Komor and Anderson, 1993
Grassland, France	-6.3 to -4.3	Mariotti, et al., 1988
Sewage, Septic wastes France	+10 to +13.5	Mariotti, et al., 1988
N fertilizer	-4 to +4	Kreitler, 1979
Animal Waste	+10 to +22	Kreitler, 1975
Septic Plume	+8.1 to + 13.9	Aravena, et al., 1993
Poultry Manure Fertilization	+8 to + 16	Wassenaar, 1995

*$\delta^{15}N$ reported relative to atmospheric nitrogen standard

Figure 1: Nitrogen and Oxygen Isotopic Composition of Nitrates



$\delta^{15}N$ reported relative to atmospheric nitrogen standard

$\delta^{18}O$ reported relative to standard mean ocean water

Biogeochemical Constraints on the Stability of Nitrate:

Many reactions within the Long Island Aquifer System including those of the nitrogen cycle (figure 2) are biologically mediated redox reactions. Nitrogen can exist in six different oxidation states. The equilibrium distribution of the various species depends on the pE and the pH of the system (figure 3a), but kinetic factors determine the rate at which equilibrium is approached. Biological organisms catalyze energetically favorable redox reactions and effectively determine the rate of reaction for processes such as nitrification and denitrification. Biogeochemical parameters such as the availability of oxygen and labile organic carbon (Starr and Gilham, 1993) may determine whether or not a reaction proceeds. Other elements that exist in more than one oxidation state also contribute to the redox potential of the aquifer system (figure 3b).

Under aerobic conditions, nitrate is the stable species. In the well-oxygenated environment characteristic of cultivated fields and lawns, ammonium is rapidly converted to nitrate through the process of nitrification (Fig. 2, rxn e). As long as aerobic conditions persist, nitrate will remain the predominant species because denitrification and dissimilatory nitrate reduction take place under anaerobic conditions. Within the Upper Glacial Aquifer, "pristine" Long Island groundwaters contain concentrations of dissolved oxygen that approach equilibrium with respect to atmospheric oxygen (Suffolk County Comprehensive Water Resources Management Plan, 1988). This is probably due to the paucity of organic matter within these upper glacial sediments. Nitrate can be expected to behave conservatively within the Upper Glacial Aquifer due to the prevalence of aerobic conditions.

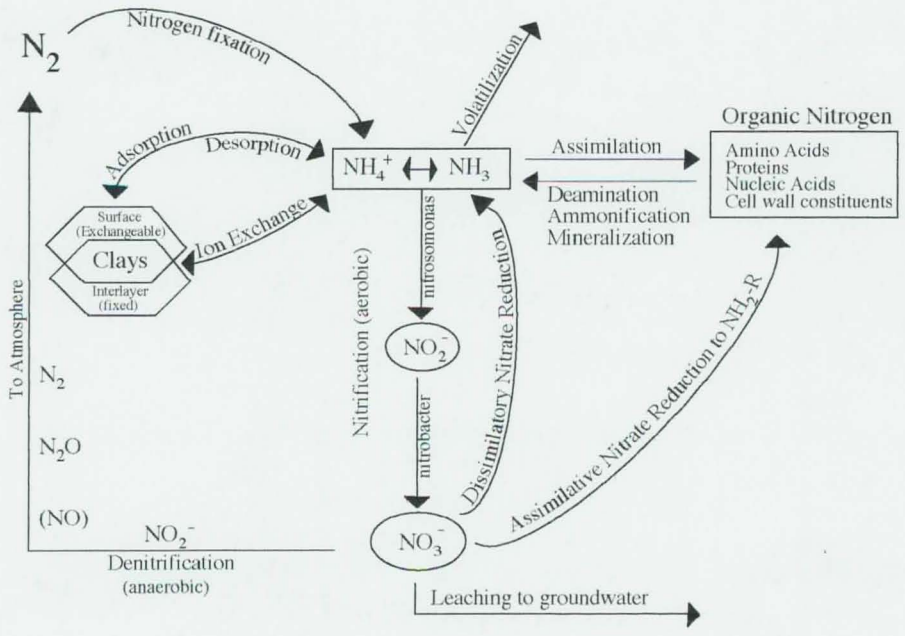
Redox conditions within a contaminant plume differ from those of the surrounding aquifer. Landfill leachate and septic tank effluent contain elevated concentrations of organic carbon and ammonium. Nitrification and aerobic respiration of organic carbon (Fig. 2, rxn c) result in the depletion of oxygen. Under anaerobic conditions, nitrate may be reduced to ammonium through the process of dissimilatory nitrate reduction (Fig. 2, rxn g) or eliminated from the system through the process of denitrification (Fig. 2, rxn f). Ammonium that is adsorbed on the sediments can subsequently be reintroduced into the ground water flow system as nitrate if more oxygenated waters mix with the leachate or pass through the sediments due to pumping activities (Baedecker and Back, 1979).

Denitrification is likely to occur within parts of the Magothy Aquifer. The sediments of the Magothy Formation were deposited in a deltaic environment and contain more organic carbon than those of the Upper Glacial. In older waters, dissolved oxygen has been completely removed through interaction with aquifer materials (Perlmutter and Koch, 1972). Lignite and pyrite, potential electron donors in the reduction of nitrate, are present within parts of the Magothy. Furthermore, in ground water systems, the reduction of nitrate precedes that of iron, manganese, and sulfate (Korom, 1992) and reduction of the latter species has been documented within the Magothy Formation (Vecchioli et al., 1974).

Biogeochemical parameters will be monitored so that I can place constraints on processes that alter the concentration and isotopic composition of ground water nitrates. I will measure temperature, conductivity, dissolved oxygen, pH, alkalinity, and dissolved organic carbon. Temperature, dissolved oxygen, conductivity and pH will be determined in the field using the appropriate meters and probes. Dissolved oxygen concentrations will be verified by Winkler titration. Alkalinity will be determined by titration. The concentrations of redox sensitive species, such as ammonium, iron, and manganese will be determined by spectrophotometry using Hach methods.

In addition, the carbon isotopic composition of dissolved inorganic carbon (DIC) will be measured. Redox processes that consume dissolved organic carbon and produce carbon dioxide lead to the formation of an isotopically light DIC pool (Wassenaar et al., 1991). Conversely, methanogenesis, an important reaction in landfill environments, produces an isotopically heavy residual carbon pool (Baedecker and Back, 1979). Carbon isotopes can be used to distinguish between DIC derived from the dissolution of carbonates and that derived from biological processes in the soil (Pawellek and Veizer, 1994). The isotopic composition of DIC will be determined by stable isotope mass spectrometry at the University of Waterloo. 1 mg of carbon is required for the analysis and the precision is reported to be 0.2‰.

Figure 2: The Nitrogen Cycle in Terrestrial Ecosystems



Reactions of the Nitrogen Cycle*

a) Ammonia Volatilization

$$NH_4^+{}_{(aq,soln)} \Leftrightarrow NH_{3(g,soln)} \Leftrightarrow NH_{3(g,\ soil)} \Leftrightarrow NH_{3(g,atm)}$$

b) Nitrogen Fixation

$$N_2 + 3\ NADPH + 5H^+ + 12\ ATP + 12\ H_20 \Leftrightarrow 2NH_4^+ + 3\ NADP + 12\ ADP + 12P_i$$

c) Respiration

$$C_{106}H_{263}O_{110}N_{16}P + 138O_2 \Leftrightarrow 106\ CO_2 + 16\ NO_3^- + 122H_2O + 18H^+ + \text{trace elements, energy}$$

d) Ammonification

$$NAD + \text{Amino Acid} + H_2O \Leftrightarrow \text{Keto Acid} + NH_3 + NADH$$

$$NH_3 + H_2O + CO_2 \Leftrightarrow NH_4+ + HCO_3^-$$

e) Nitrification

$$NH_4+ + 1.5O_2 \Leftrightarrow NO_2^- + H_2O + 2H^+$$

$$NO_2^- + 0.5O_2 \Leftrightarrow NO_3^-$$

f) Denitrification

$$NO_3^- \Leftrightarrow NO_2^- \Leftrightarrow NO \Leftrightarrow N_2O \Leftrightarrow N_2$$

g) Dissimilatory Nitrate Reduction

$$NO_3^- + 2CH_2O + 2\ H^+ \Leftrightarrow NH_4^+ + 2CO_2 + H_2O$$

h) Combustion

$$N_{2(g)} + O_{2(g)} \Leftrightarrow 2NO_{(g)}$$

$$N_{2(g)} + 2O_{2(g)} \Leftrightarrow 2NO_{2(g)}$$

i) Industrial Fixation (Haber Process)

$$2N_{2(g)} + 3\ H_{2(g)} \overset{P,\ T}{\underset{\text{Catalyst}}{\Leftrightarrow}} 2\ NH_{3(g)}$$

*(Drever, 1988; Lehninger, 1982; Stumm and Morgan, 1996)

Figure 3a: pE vs pH for Nitrogen at T = 12 C

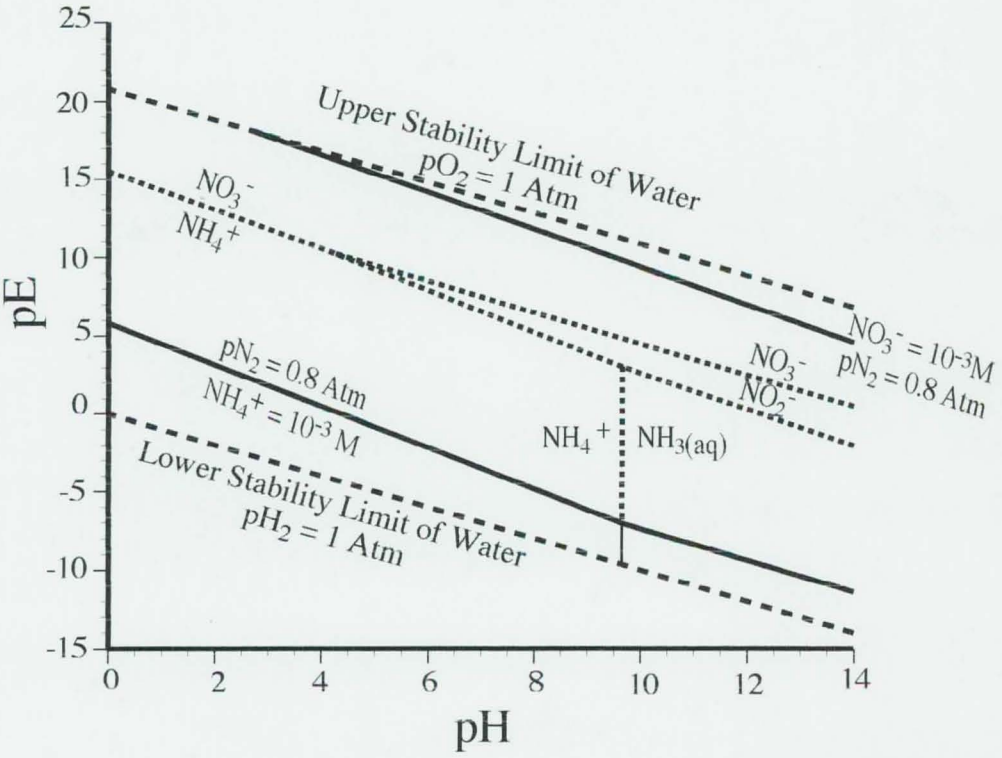
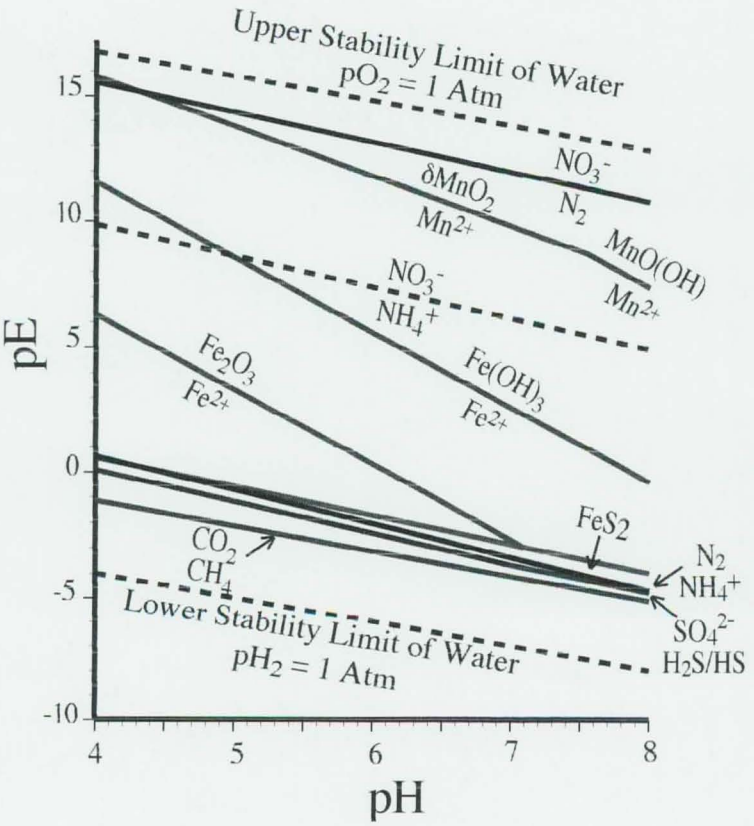


Figure 3b: Important Redox Reactions within the Long Island Aquifer System



Adapted from Drever, 1988
pE vs pH for 25C and 1 atm
Activity of solute at
solid/solution boundaries:
$Fe^{2+} = 10^{-6}$ M
$Mn^{2+} = 10^{-6}$ M
$SO_4^{2-} = 10^{-4}$ M

Major and Trace Element Geochemical Tracers:

The major-ion composition of the various contaminant sources will be characterized to aid in the interpretation of the nitrogen and oxygen isotopic data. Ternary plots of the major cations and the major anions present in ground water (constructed from water quality data in the Land Use Monitoring Study, Suffolk County Comprehensive Water Resources Management Plan, 1988) illustrate that the major ion composition of ground water varies depending on the associated land use activity (figure 4). For example, agricultural waters contain elevated proportions of calcium, magnesium, sulfate, and nitrate while septic plumes are high in bicarbonate, sodium and potassium. The reducing environment associated with septic plumes and landfill leachate also produces elevated concentrations of iron and manganese due to the dissolution of iron and manganese oxide coatings from aquifer materials (figure 3b).

Perturbations due to particular activities will not necessarily persist within the aquifer system. For example, potassium which has been displaced by ammonium may be readsorbed downgradient and iron and manganese oxides may reprecipitate when redox conditions change. Therefore, I will also evaluate whether the isotope ratios of boron, an element which is believed to behave conservatively within the ground water flow system, can be used to place additional constraints on the possible sources of nitrate contamination.

Boron is a conservative tracer in most groundwater environments although fractionation may occur if the flowpath passes through clay layers in which adsorption is an important process (Davidson and Bassett, 1993). Elevated concentrations of boron detected in Long Island ground waters have been correlated with agricultural land use and the degree of residential development (Eckhardt and Stackelberg, 1995), however, the isotopic composition of boron in Long Island ground water has not been measured. Anthropogenic sources of boron include agricultural fertilizers for row crops (Eckhardt and Stackelberg, 1995), municipal wastewater (Buszka et al., 1991), detergents in landfills (Barth et al., 1996), and fly ash leachate from landfills (Davidson and Basset, 1993). Boron isotopes have been successfully employed by other workers to distinguish between ground water contaminated by agricultural activities and sewage (Buszka et al., 1991; Gellenbeck, 1994). The boron isotopic composition of ground water will be measured by negative thermal ionization mass spectrometry building on techniques developed by Hemming and Hanson (1994).

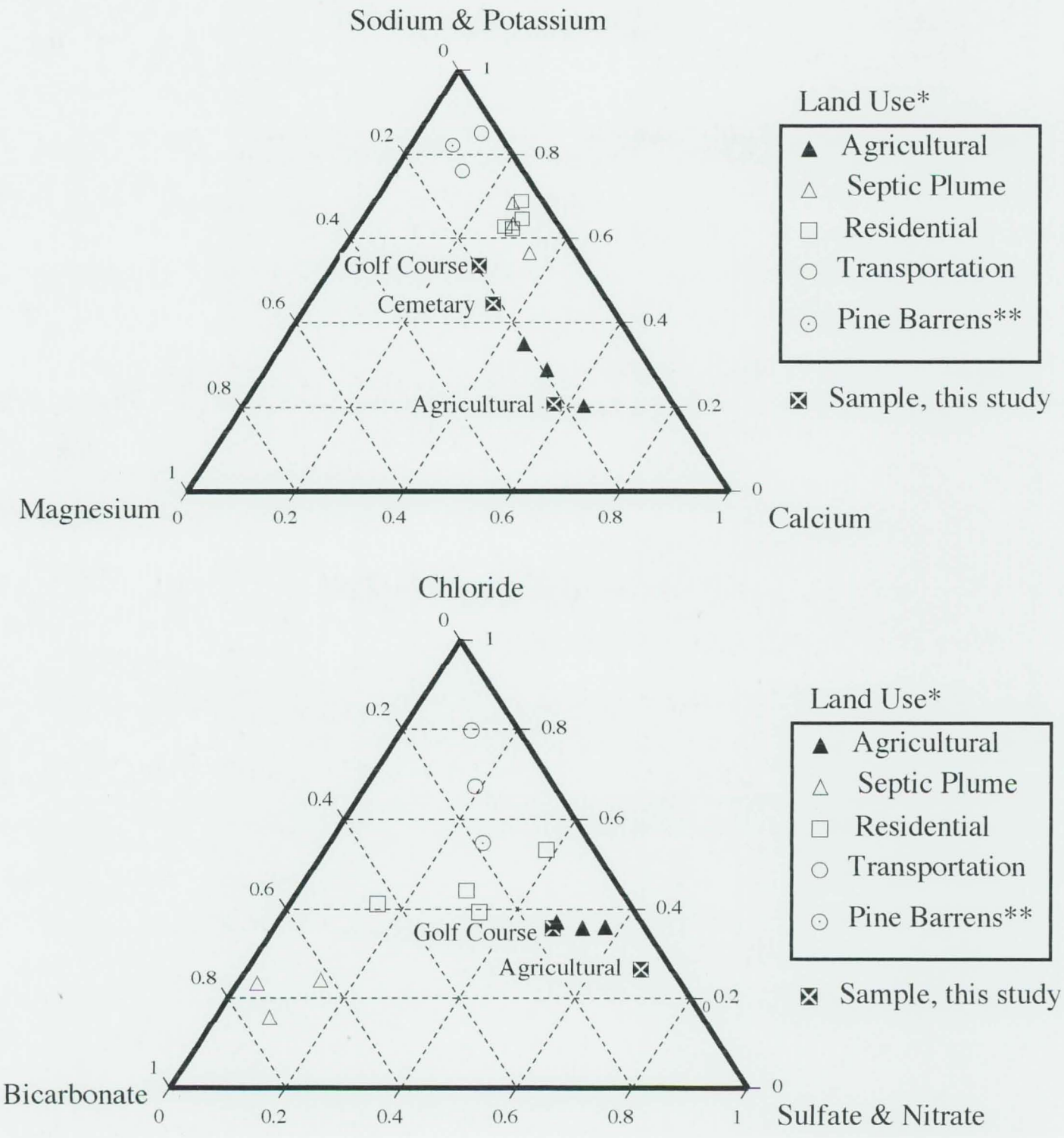
Summary of Approach:

Samples will be collected from shallow monitoring wells downgradient from particular sources in order to determine the nitrogen and oxygen isotopic composition of end-member nitrate sources. Ternary plots of major ion data will be used to verify that the geochemistry of the sample obtained is consistent with that of the intended source. Biogeochemical data will be used to place constraints on reactions that may alter the concentration or isotopic composition of nitrate. Plots of $\delta^{18}O$ vs $\delta^{15}N$ will be constructed to determine the range of nitrogen and oxygen isotopic compositions to be expected for each nitrate source.

Samples will be collected from public supply wells to determine the average concentration and isotopic composition of nitrates within a cross-section of the aquifer. The isotopic composition of these samples will be compared to the isotopic composition of the end-member nitrate sources in order to place constraints on the relative contributions of each nitrate source to nitrate contamination within the aquifer. The carbon isotopic composition of DIC and the boron isotopic composition of ground water will be used to place additional constraints on mixing end-members.

Since supply wells are screened at various depths within the aquifer and are located in varying proximity to point sources of contamination, it is anticipated that there will be some variability in the combination of sources that contribute to the contamination of different sections of the aquifer. Geochemical, hydrological, stratigraphical and land use data will be compiled on a GIS in order to facilitate the relation of nitrate contamination within the aquifer system to land use at the surface. The results of this study will help water supply managers to evaluate actions that could be taken to reduce nitrate contamination of the aquifer.

Figure 4: Major Cations and Anions In Long Island Ground Waters According to Land Use



*Land Use Data and major-ion analyses from Suffolk County Comprehensive Water Resources Management Plan, 1988. **Pine Barrens Data from Schoonen and Brown, 1994

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