

## THE USE OF MAJOR ION CHEMISTRY IN DETERMINING NITRATE SOURCES OF GROUNDWATER IN SUFFOLK COUNTY, LONG ISLAND, NY

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### Abstract

Suffolk County is the eastern most county on Long Island with an area of 2,500 square kilometers and a population of 1.4 million. Groundwater is the only source of potable water for Suffolk County. Nitrate levels have become a concern as a result of the continued eastward urbanization of Long Island since the mid 1900's. In 2003, 2% of 1000 public supply wells had greater than 10 ppm nitrogen as nitrate, 8% had 6 to 10 ppm nitrogen as nitrate and 62% of the wells were rated as susceptible to increased nitrate contamination based on land use, travel time and prevalence. Nitrogen as nitrate above 10 ppm is harmful to infants and is currently the drinking water standard of the Environmental Protection Agency. The major sources of the nitrate in the urbanized areas are most likely turf grass fertilizer and sewage from septic tank/cesspool systems and sewage treatment plants that provide only secondary treatment of the wastewater. Some sewage treatment plants provide tertiary treatment that reduces the nitrate content of the effluent to less than 10 ppm nitrogen as nitrate. Turf grass occupies about 28% of the land. Two-thirds of the houses have septic tank/cesspool systems and a majority of the sewage treatment plants discharge effluent to the groundwater. Previous investigators of the sources of nitrate in groundwater on Long Island have used <sup>15</sup>δN values of nitrate-nitrogen to identify nitrate contamination (Bleifuss et al., 2000; Flipse and Bonner, 1985; Flipse et al., 1984; Kreitler et al., 1978). However, due to overlapping source signatures, nitrogen isotopes alone were not sufficient to characterize the sources of nitrate. More recent studies have shown that major elements that accompany nitrate in the groundwater (Bleifuss et al., 2000; Elhatip et al., 2003; Trauth and Xanthopoulos, 1997) may distinguish sources of nitrate with less ambiguity.

In this study samples of waste water from septic tank/cesspool systems and sewage treatment plants and samples of soil water collected below turf grass that is not fertilized, fertilized with organic fertilizer and fertilized with chemical fertilizer were analyzed for major elements. Major element data for groundwater from Suffolk County Water Authority municipal wells have been characterized as a function of capture zone land use (Source Water Assessment Project, (CDM, 2003). The elements Cl, Na, Mg, Ca, SO<sub>4</sub> and NO<sub>3</sub> show promising results as nitrate tracers. This report will present the data for the groundwater and the waste water and the soil water compared on a ternary diagram of Cl, SO<sub>4</sub> and N-NO<sub>3</sub>. The other elements will not be shown here even though element vs. element plots normalized to Cl show encouraging results. A greater understanding of groundwater migration for Na, Mg and Ca are needed to better understand these plots. Our data show a distinct relationship between land use and source of nitrate contamination such that ground waters sourced in: (1) vacant or open land use plot close to average rain water compositions (2) residential land use plot as a mixture of turf grass cultivation and wastewater and (3) agricultural land use plot with slightly higher concentrations than the turf grass cultivation field. This relationship is further proven by calculating mixing relationships.

## Introduction

Health awareness of nitrate contamination of Long Island groundwater initiated with publications by the United States Geologic Survey (Perlmutter and Koch, 1972; Perlmutter et al., 1964; Ragone et al., 1976) and State of New York Dept. of Health (Flynn et al., 1969; Smith and Baier, 1969) and became a reality in Nassau County when wells were abandoned due to high nitrate concentrations. The Environmental Protection Agency (EPA) has determined drinking water levels that exceed 10 ppm nitrogen as nitrate to be unsafe to humans. This is especially true for infants where blue baby syndrome, or methemoglobinemia, may occur.

Methemoglobinemia is a blood disorder caused when nitrate is converted to nitrite which interacts with the hemoglobin in red blood cells reducing its ability to carry oxygen. Health concerns regarding nitrate in adults are inconclusive (Weyer, 1999).

In 2003 (CDM, 2003) 2% of 1000 wells tested in Suffolk County exceeded the 10ppm nitrate-nitrogen limit and 8% tested between 6 to 10ppm nitrate-nitrogen. When assessing susceptibility of Suffolk County wells for nitrate contamination 62% were rated high susceptibility and 4% very high. Susceptibility takes into account prevalence, or occurrence and concentration, and sensitivity, or mobility, based on land use and travel time.

Nitrogen in its various forms (1) is produced in the soil from decayed organic matter and by fixation by bacteria, (2) enters the soil from the atmosphere as  $N_2$  gas and in rain water, (3) leaches from landfills, (4) is present in storm water runoff, (5) leaks from sewer lines, (6) leaches from cesspools and (7) is applied as fertilizer for management of turf grass and agricultural fields. Once in the soil, micro organisms may convert nitrogen (all forms) to ammonium ( $NH_4$ ) or nitrate ( $NO_3$ ). Nitrate is more water soluble and absorbed on solid particles less readily than  $NH_4$  and is therefore more available to plants.

The most efficient way to prevent nitrate contamination is to determine its source and reduce it there. Previous investigators have used  $^{15}\delta N$  values of nitrate-nitrogen to identify nitrate contamination (Bleifuss et al., 2000; Flipse and Bonner, 1985; Flipse et al., 1984; Kreitler et al., 1978). Due to overlapping source signatures caused by fractionation in the subsurface, nitrogen isotopes alone are not sufficient. Recently studies have shown that major ion chemistry (Bleifuss et al., 2000; Elhatip et al., 2003; Trauth and Xanthopoulos, 1997) may distinguish between sources with less ambiguity. In this study in Suffolk County (Figure 1), which began in the Fall of 2002 we have analyzed for soil and wastewater for  $NO_3$ ,  $SO_4$ ,  $PO_4$ , B, Ca, Mg, Na, K, Cl, F, Br, P and S with the ultimate goal to determine for a given groundwater the relative proportion of the sources of nitrate that are turf grass fertilizer (organic or chemical) and wastewater.

## Description of Study Area

Suffolk County is the easternmost county on Long Island (Figure 1), covering 912 square miles of land. Population in 2001 had reached 1.4 million. Geology on Long Island is dominated by glacial deposits and is described in detail in Fuller, 1914. Underlying the glacial deposits is Cretaceous sediment. Bedrock dips about one degree to the southeast and is generally greater than 600ft below the surface.

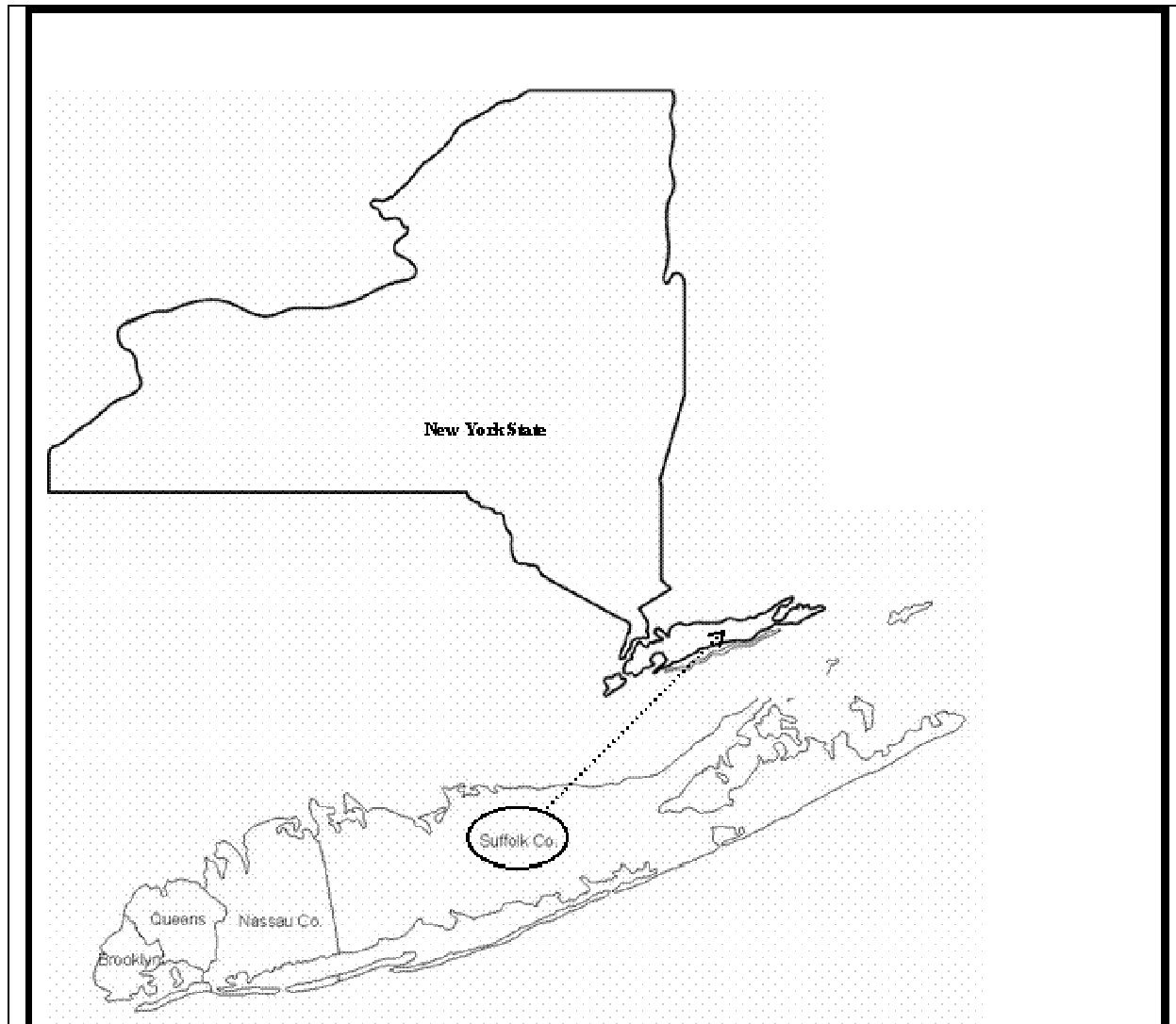
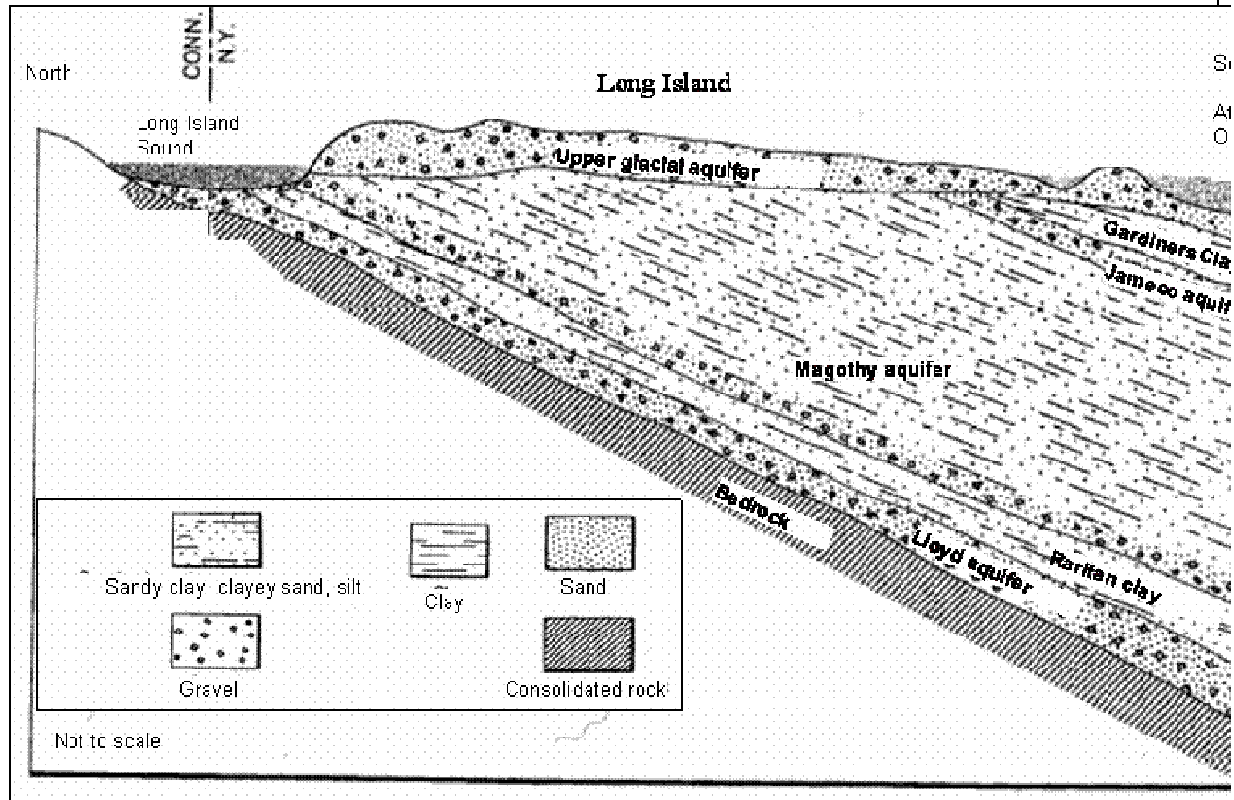


Figure 1 Map showing area of study, Suffolk County, which is located on Long Island in New York State

Glacial deposits and Cretaceous alluvial deposits host Long Island's groundwater in unconsolidated sands, gravel, silts and clay (Figure 2,(Kimmel, 1984)). Fine grained, well drained loams formed on late Wisconsinan loess deposits. Sandy, coarse textured, poorly drained soils formed on glacial outwash. With development in Suffolk Co. much of the original soil series has been converted to cut and fill land. Cut and fill land is land that has been altered for non farm purposes to a degree that the original soil series is unidentifiable. Long Island receives on average of 48 inches of rain annually ([www.worldclimate.com/](http://www.worldclimate.com/)). Each day 1,126 million gallons of water are recharged from this precipitation. The majority of water served to Suffolk County Water Authority customers comes from the Magothy Aquifer. This water is up to 1,000 years old in its deepest layers underlying the south shore ([www.scwa.com](http://www.scwa.com)).

**Figure 2**

Hydrogeology of Long Island (Kimmel 1984)



### *Nitrogen Sources*

Major sources of nitrate-nitrogen in Suffolk Co. are turf grass fertilizers and wastewater via septic tank/cesspool systems and discharge from sewage treatment plants (Flipse et al., 1984; Kimmel, 1984). Farming was extensive on Long Island but as urbanization spread eastward from New York City, much land is now used for residential purposes. Turf grass occupies about 28% of land use in Suffolk County, as golf courses, parks, residential and commercial lawns. Suffolk County Water Authority estimates 21 million gallons/day, or 30% of the water pumped (Personal Communication, Michael Stevenson Suffolk County Water Authority, August 2003) is used for the sole purpose of lawn irrigation.

A large proportion of the homes in Suffolk Co. dispose of wastewater through septic tank/cesspool systems. A typical US home yields 44.5 gallons of sewage/day/person (Bennett et al., 1974). The 2000 census bureau reported 522,323 housing units in Suffolk County. Public Health (1969) monitored 4 septic systems in Suffolk County and reported effluent values from 775-3130 gallons/week. These values show that homes in Suffolk Co. discharge more than typical US homes. Using the average, 1690 gal/week or 241gal/day and if all the homes reported in 2000 operated on septic tank/cesspool systems the total discharge is 126 million gallons/day (MGD). Since 2/3 of the housing units operate on septic tank/cesspool systems this number is

closer to 84 MGD. Public and private sewage treatment plants in Suffolk Co. yield 70 MGD (Heath and Cohen, 1966 and personal calculation). One hundred and seventy sewage treatment plants are in operation in Suffolk County. They range in size, treatment and disposal method. All plants perform secondary treatment of waste and some denitrify waste before disposal. A majority of these plants dispose their effluent to the groundwater while less than 15% discharge to surface waters including Long Island Sound. Sewage treatment plants generally serve a limited clientele such as a housing community, a shopping mall, a college, a nursing home or a small community (Personal Communication, Chris Biemiller Suffolk County Public Works, 2003).

### Methods

To evaluate the chemical signature of various lawn maintenance procedures lysimeters (soil water samplers) have been installed in maintained lawns at eight locations; to depths up to 150cm, throughout Suffolk County on Suffolk County Water Authority property. Two of these locations are undergoing chemical turf grass treatment while the other six are treated organically. Chemical sites are treated by either Scotts® brand fertilizers or LESCO® brand. Treatment of Scotts® brand fertilizers began in 2000 by Schuchman, 2001 on new sod. The other sites are on more established lawns. Treatment using LESCO® brand fertilizers commenced in 2003 with a granular grade fertilizer. Organic treatment, started in spring of 2002, is maintained by a contract landscaper utilizing athletic turf mix composed of compost, lime and a granular fertilizer Pro-Grow manufactured by North County Organics. Fertilizer regimes are representative of typical applications on Long Island. Soil water samples from lysimeters were acquired monthly totaling 92 samples; 17 samples influenced by chemical fertilization, 6 influenced by no fertilization and 69 influenced by organic fertilization.

Twelve wastewater samples from cesspools or septic tanks and 21 sewage treatment plant samples were acquired through Suffolk County Department of Public Works. Cesspool samples are from either residential or industrial sources, while a sewage treatment plant serves a community which may include both residential and industrial. Wastewater samples were prepared by centrifuging at 20 RPM for an hour to separate the solids from liquid. If necessary the liquid was decanted and centrifuged again. The liquid was then filtered with Millipore AP15 glass fiber filter.

All samples were collected in polypropylene plastic bottles. Samples were stored at 4°C until analyzed. Polypropylene plastic bottles for cation samples were acid rinsed and the samples were preserved with a few drops of HCl. These samples were analyzed at Cornell University Nutrient and Elemental Analysis Laboratory. Cation concentrations were determined using an ICP-OES (inductively coupled plasma optical emission spectroscopy) and anion concentrations were determined using an IC (ion chromatograph).

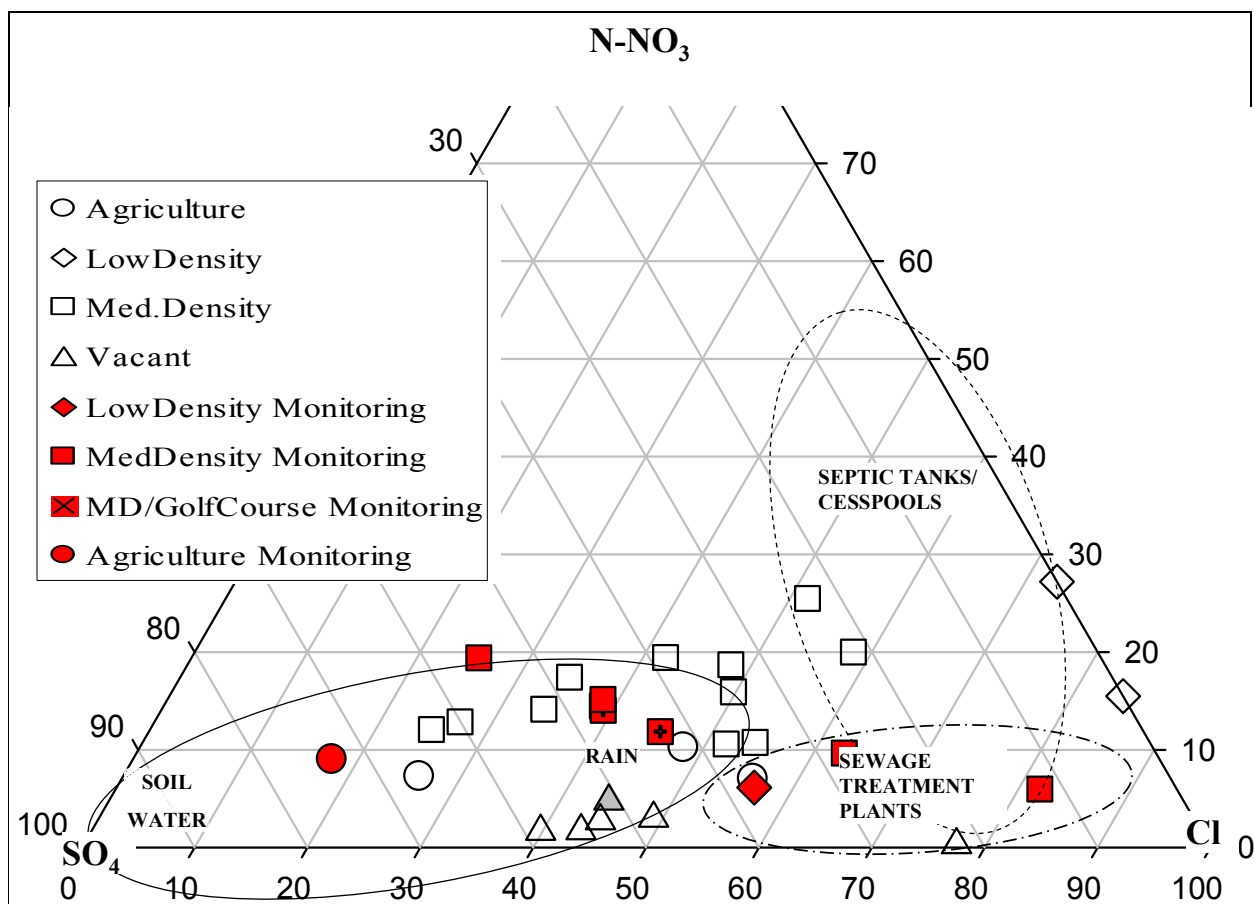
One hundred and twenty five samples were analyzed for major and minor ion concentrations, 13 elements were most promising for tracer work. These are NO<sub>3</sub>, SO<sub>4</sub>, PO<sub>4</sub>, B, Ca, Mg, Na, K, Cl, F, Br, P and S. Note that N-NO<sub>3</sub> data for septic tank/cesspool systems and sewage treatment plants are values of effluent. Most of the nitrogen at this stage is ammonium or organic nitrogen. Once the effluent is discharged from the cesspool or sewage treatment plant

essentially all of the nitrogen will be converted to  $\text{NO}_3$  because Long Island's shallow aquifers are dominantly oxidizing. The detection limits for the IC are for Cl, F and  $\text{SO}_4$  are 0.1ppm, for  $\text{NO}_3$  and Br is 0.2ppm and for  $\text{PO}_4$  is 0.5ppm. The precision determined from anonymous standards and duplicate samples for Cl, F, Br, and  $\text{SO}_4$  are  $\pm 10\%$  and for  $\text{PO}_4$  and  $\text{NO}_3$  are  $\pm 20\%$ . The uncertainty based on replicate analyses is high for phosphate due to low concentrations and also high for nitrate possibly due to conversion of organic nitrogen to nitrate by micro organisms from time of sampling to analysis. B, Ca, Mg, Na, K, P and S were analyzed on the ICP-OES. The detection limits are for B 0.0005 ppm, Ca 0.002ppm, K 0.13ppm, Mg 0.0001ppm, Na 0.05ppm, P 0.001ppm and S 0.003ppm. The precision determined from standards and anonymous duplicate samples are for B, S, Na, and Ca  $\pm 10\%$ , for Mg  $\pm 5\%$ , for K  $\pm 15\%$  (possibly high due to temperature sensitivity of the analysis) and for phosphorous  $\pm 20\%$  (high due to low concentrations).

## Results

The most useful geochemical tracers are conservative elements, that is those that do not adsorb onto soil surfaces, or degrade with time due to biological or physical processes. Chloride, bromide and nitrate are the most conservative of the analyzed elements because of their negative charge and because they do not react in the Long Island aquifer. Bromide concentrations, although useful in other studies, (Davis et al., 1998; Fabrykamartin et al., 1991; Iqbal and Krothe, 1997) were most often below the ion chromatograph (IC) detection limit of 0.2ppm. Boron is suited for use as a conservative tracer because of its high solubility in aqueous solution, presence in nearly all water, and the lack of effects by evaporation or volatilization, by oxidation-reduction reactions, or by mineral precipitation or dissolution in all but extremely saline water. Element vs. element plots with boron and phosphorous showed promising differences in the source fields but concentrations in groundwater samples were below the detection limit of 0.1ppm (Suffolk County Water Authority analysis). The cations Ca, Mg, Na and K will tend to adsorb to the negatively charged soil particles but with accurate adsorption modeling such as (Voegelin et al., 2000) and a understanding of plant uptake, concentrations in groundwater can be predicted.

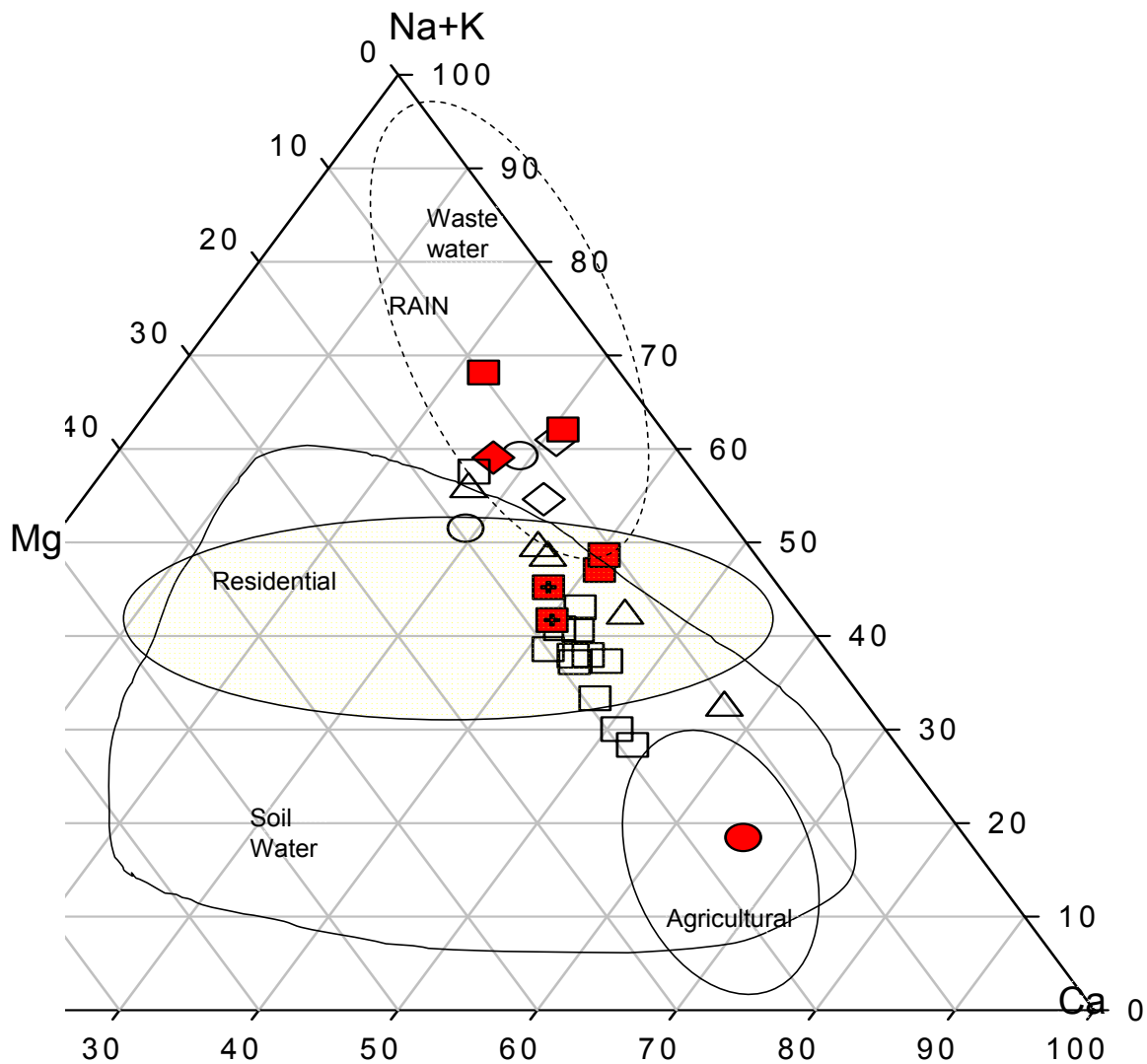
Chemical analyses of groundwater from twenty two Suffolk County Water Authority public supply wells and eight monitoring wells from [Bleifuss \(2000\)](#) represent a range of land use. The data for the groundwater and the waste water and the soil water are compared in Figure 3. In this figure the solid blue field represents soil water from turf grass cultivation sources, influenced by no fertilization, by chemical turf grass fertilization and by organic turf grass fertilization. Although there is some difference in the concentrations of the soil waters their fields overlap and so all soil water data is plotted as one field. The dashed red field represents wastewater sources with no denitrification, from both residential septic tank/cesspool systems. Rain water is an average value compiled from the literature for Suffolk County. The yellow field is for sewage treatment plants that denitrify their waste water.



The groundwater data is plotted as a function of primary land use. Land use was determined from modeling capture zones (CMD, 2003) for Suffolk County Water Authority supply wells. Primary land use is defined as the type of land use that covers the largest percentage of the capture zone. For agricultural land use this is greater than 54%, for high density residential (greater than 10 dwelling units per acre) and medium density residential land use (2-10 dwelling units per acre) this is greater than 28%, for low density residential land use (one or less dwelling units per acre) this is greater than 20% and for vacant or open space land use this is greater than 56%. For low density residential land use groundwater samples the secondary land use was always medium density residential land use. Land use for monitoring wells was determined by [Bleifuss \(2000\)](#) from Regional Planning Board Land Use maps. Although this method is less precise than modeling it is appropriate for shallow wells.

Figure 3 suggest that there is a distinct relationship between land use and source of nitrate contamination such that groundwater sourced in: (1) vacant or open land use plot close to

average rain water compositions, (2) residential land use plot as a mixture of turf grass cultivation and wastewater and (3) agricultural land use plot with slightly higher concentrations than the turf grass cultivation field. Agricultural land use groundwater samples plot in the turf grass cultivation and wastewater source field.



**Figure 4. Ternary diagram for major cations.** Wastewater and soil water fields are from this study. Residential and agricultural fields are compiled in Bleifuss, 2000 from groundwater data of previous researchers. Refer to legend for symbols of groundwater wells.

Caution is needed when using cations as geochemical tracers because of ion exchange with the sediments. [Bleifuss 2000](#) compiled major ion data from previous studies of groundwater in Northport. This data is shown in Figure 4 as well as the sources analyzed in this study of wastewater and soil water data. The groundwater from municipal supply wells and monitoring wells were then compared to the source fields. [Bleifuss 2000](#) distinguished between



groundwaters sources in a residential land use and an agricultural land use. Data from this study are for soil water and wastewater sources, both of which are associated with residential land use, which is why the residential field from [Bleifuss 2000](#) plots as a mix of these two sources. The agricultural field plots within the soil water field consistent with both sources utilizing fertilizers, but the groundwater wells from SCWA influenced by agricultural land use do not fall with in the field. This may be since the monitoring well, which plots in the agricultural field, is shallower than the supply wells of SCWA.

Although Figure 4 shows a relationship between land use and source field it is important to note that addition of Na and K may misrepresent the fields since Na and K may travel at different rates in the aquifer. Also, average rain water falls within the wastewater field and vacant land use waters do not plot next to rain water.

### Discussion

Two sources of nitrate, turf grass cultivation and wastewater effluent, contributing to Suffolk County groundwater were examined for differences in major ion chemistry. A small percentage of public supply wells from Suffolk County Water Authority data and monitoring wells from [Bleifuss \(2000\)](#) were chosen to examine the use of major ion chemistry for determining nitrate sources. The results suggest that the primary source of nitrates in these wells plot as a function of land use.

### Acknowledgments:

We thank Suffolk County Water Authority (SCWA) for funding this project and their concern regarding keeping Suffolk County groundwater clean. We thank Chris Biemiller at Suffolk County Public Works for acquiring cesspool/septic and sewage treatment plant samples. We also thank Ed Truskol at SCWA for use of their Source Water Assessment Project (SWAP) data and providing chemical analysis.

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