I. CHAPTER 1

Using major elements to determine sources of nitrate in groundwater

i. Introduction

Nitrate and urban contamination affects many aquifers, for example, in Turkey (Elhatip et al., 2003), the UK (Barrett et al., 1999), many parts of the United States (Kolpin et al., 2002; Lerner, 2002; Thomas, 2000; Williams et al., 1998) and Germany (Trauth and Xanthopoulos, 1997). The most cost efficient way to prevent nitrate contamination is to determine its source and reduce it there. Previous investigators of the sources of nitrate in groundwater on Long Island have used $\delta^{15}N$ values of nitrate-nitrogen to identify nitrate contamination (Bleifuss et al., 2000; Flipse and Bonner, 1985; Flipse et al., 1984; Kreitler et al., 1978). 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 soil water collected below turfgrass that is fertilized with natural organic fertilizer, traditional chemical fertilizer and not fertilized and samples of wastewater from septic tank/cesspool systems and public sewage treatment plants were analyzed for major elements. Major element data for groundwater from Suffolk County Water Authority municipal wells (CDM, 2003) and monitoring wells from Bleifuss et al. (2000) have been characterized as a function of land use. The data for the groundwater were compared to the wastewater and the soil water. Binary plots of the elements Na, Mg, Ca, SO_4 and N-NO_3 when normalized to Cl concentrations proved most successful as nitrate tracers along with binary and ternary diagrams of Cl, SO_4 and N-NO_3. Normalizing the data to a conservative element[1] such as Cl reduces the effects of mixing and dilution providing a more precise evaluation of nitrate sources. Estimates of mixing proportions from each source were calculated using a mass balance and water budget approach.

Nitrate sources: chemical concentrations and origin

Researchers commonly contribute elevated levels of major ions in groundwater influenced by residential areas to be from wastewaters but few have analyzed wastewater or other urban sources. Some of these studies include (1) Renyolds (1994) who noted elevated concentrations of Cl, NO_3, Na, Ca and K in urban groundwater (2) Wayland et al. (2003) noted elevated levels of Na, K and Cl in urban areas compared to agricultural areas (3) Bleifuss et al. (2000) found elevated levels of Na and Cl in residential land use groundwater (4) Trauth and Xanthopoulos (1997) found elevated SO_4, K and B below urban areas and (5) Thomas (2000) found elevated levels of Cl, Na and Ca in shallow groundwater of urban areas.

Data presented in this study show elevated concentrations in Ca, Mg and SO_4 in soil water influenced by turfgrass maintenance compared to wastewater samples and that wastewater is enriched in K, Na, Cl, N-NO_3 and PO_4 compared to water influenced by turfgrass maintenance. The following paragraphs discuss previous work to explain some of these differences.

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[1] A conservative element is an element in groundwater that travels at the same rate as the groundwater flows. That is, the element is not retarded.

Concentrations of elements in rain water are influenced by the source of the storm. This can be either marine or continental in origin. The total observed loadings due to all storm events for Long Island is highest for SO_4 followed by NO_3, Cl and Na (Proios and Schoonen, 1994). Rain water chemistry is strongly influenced by the oceans and acid deposition (Schoonen and Brown, 1994). Combustion of coal and other fossil fuels increase sulfur and nitrogen inputs to the atmosphere which in turn increases the acidity of rain. Acid rain, a recent event, is the probable cause for high loadings of SO_4 and NO_3 in Long Island rain. Trends since 1955 show an increase in the acidity of pH in rain and increases in the global emissions of sulfur and nitrogen (Mackenzie, 1998). The high levels of SO_4 in water influenced by turfgrass maintenance, however, are mostly derived from fertilizers. Sulfur content in Scotts Turf Builder fertilizer are 8-11% sulfur. Sulfur is also present in a Lesco brand and natural organic fertilizers at lower percentages. The Lesco brand fertilizer is sulfur coated urea form, a slow release nitrogen source. The sulfur in the natural organic fertilizer is natural potassium sulfate. Elevated levels of Ca and Mg in water collected below turfgrass sites are likely from the application of lime to increase soil pH.

K, Na, Cl, N-NO_3 and PO_4 in wastewater come from a variety of household items used in the kitchen, bathroom and laundry and are present in human waste. According to Medcalf and Eddy (2003) typical fluid contributions from a house to a septic system are 26.7% from toilets, 21.8% from clothes washing, 16% from showers, 15.7% from faucets, 13.7% from leakage, 1.7% from baths, 1.4% from dishwashing and 2.2% from other sources. An average Long Island cesspool discharges 240 gallons (900 liters) per day (Flynn et al., 1969).

Eleven rural households in Wisconsin were monitored in 1976 to determine source specific wastewater use and quality (Siegrist et al., 1976). Water usage has changed from 1976 to 2003 but the relative proportions reported by Siegrist et al. (1976) agree with those of Medcalf and Eddy (2003). Siegrist et al. (1976) found that most of the total nitrogen in wastewater is from nonfecal toilet flushes, making up 43.5% and fecal toilet flushes were 24.6% of the nitrogen in wastewater analyzed in his study. All toilet flushes make up 13.8% of total phosphate concentrations. Siegrist et al. (1976) reported 2.64g N/person/day and 0.28g PO_4/person/day in nonfecal toilet flushed and 1.5g N/person/day and 0.27g PO_4/person/day for fecal flushed.

The Swedish Environment Protection Agency (Beckerus et al., 1998) determined that in 1992 in Sweden the concentrations in urine are 11g N/person/day and 1g PO_4/person/day and that feces have 1.5g N/person/day and 0.5g PO_4/person/day. Another Swedish study analyzed nutrient and heavy metal concentrations in urine for the purpose of agricultural reuse from a source separating sewage system (Jonsson et al., 1997). They found that urine had 4g N/L and 0.35g P/L. Jonsson et al. (1997) acknowledged that these values are lower than those of the Swedish Environment Protection Agency and attributed this to the higher proportion of vegetarians and children in their study. Some recent studies report that up to 80% of nitrogen and around 50% of phosphate in wastewaters is from urine (Gajurel et al., 2001; Jonsson, 2001; Larsen et al., 2001; Wilsenach and van Loosdrecht, 2003). These percentages are higher than Siegrist et al. (1978) and Jonsson et al. (1997). The differences could be due to geographical differences or to differences in food consumption patterns. The nitrogen balance of a mature human body is zero, so that the nitrogen intake is equal to the excretion. A high consumption of meat and other protein-rich products will result in a higher nitrogen concentrations in urine (Vijst and Groot-Marcus, 1999).

Chloride excretions in urine and fecal matter are approximately 6g per day per person (Medcalf and Eddy, 2003) Daily nutritional intake for the average person is 5000mg Na (http://www.feinberg.northwestern.edu/ nutrition/fact-sheets.html). Jonsson et al. (1997) reports an average value for urine of 1.2g Na/L and 1g K/L. Researchers have reported around 50% (Gaillardet et al., 2001; Gajurel et al., 2001; Jonsson, 2001) and up to 90% (Larsen et al., 2001) of the potassium in wastewater is from urine and fecal matter. There are acceptable ranges of most elements in urine for healthy adults (Lindberg, 2004). These values range from 0.7-8.75g Cl/person/day, 0.345-5.75g Ng/person/day and 0.975-4.68g K/person/day.

The second largest contribution of water to the septic system is from clothes washing. In addition to the water used in the laundry load contributions will also come from the dirt on the clothing and from the washing soaps (Ligman et al., 1974). Laundry soaps vary in components and concentrations but according to Beckerus et al. (1998) they are made up of surfactants, pH stabilizers, softeners/builders, bleaches, brighteners, protective colloids, preservatives, enzymes, perfume, fillers, defoamer, corrosion inhibitors, coloring agents and color stabilizers. Among these phosphates are used as softeners/builders. Phosphates coming from detergents make up from 15% (Beckerus et al., 1998) to 54% (Siegrist et al., 1976) of the concentrations in wastewater. Total nitrogen contributions from clothes washers were 12% (Siegrist et al., 1976) of the total nitrogen in wastewaters. Siegrist et al. (1976) reports 0.73g N/person/day coming from clothes washers and 2.15g PO_4/person/day. Sodium compounds are used as corrosive inhibitors, fillers, softener/builders and pH stabilizers (Beckerus et al., 1998) in detergents. Potassium and sodium salts are used to replace surfactants in detergents (Beckerus et al., 1998).

Siegrist et al. (1976) reported that automatic dish washer and kitchen sink usage accounted for 31.2% (1.24g PO_4/person/day), and bath/shower for 0.9% (0.036g PO_4/person/day) of the total phosphate concentrations in wastewater and that automatic dish washer and kitchen sink usage were 15% (0.91g N/person/day) and bath/shower was 5% (0.31g N/person/day) for total nitrogen concentrations. Sodium laurel phosphate is a common cleaning agent that is used in shampoos, soaps and toothpaste. Chlorine is common in household cleaning products (Source: WebElements http://www.webelements.com/) due to its bleaching and disinfection properties.

Table 2 Sources of elements in wastewater

Source		**Na**	**K**	**Cl**	**N**	**PO_4**
Urine	g/person/day	0.35-5.8[1,5*,6]	0.98-4.7[3,6]	0.7-8.8[4*,6]	2.64-11[1,2,3]	0.28-3.5 [1,2,3]
Feces	g/person/day	\	\	\	1.5[1,2]	0.27-0.5 [1,2]
Dishwater and Kitchen Sink	g/person/day	\	\	\	0.91[1]	1.24[1]
Shower and bath	g/person/day	\	\	\	0.31[1]	0.036[1]
Laundry	g/person/day	\	\	\	0.73[1]	2.15[1]
Total	g/person/day	**0.35-5.8**	**0.98-4.7**	**0.7-8.8**	**6.09-14.45**	**3.98-7.42**

[1]*Siegrist et al. et al, 1976* [2]*Beckerus et al, 1998* [3]*Jonsson et al, 1997* [4]*Medcalf and Eddy, 2003* [5]*http://www.feinberg.northwestern.edu/ nutrition/fact-sheets.html* [6]*Lindberg, 2003*
**includes both urine and feces*

Budgets for K, Na, Cl, NO_3 and PO_4 in wastewater are not balanced here but a general understanding is presented of their sources in wastewater (Table 2). It is clear that a complete and up to date, study is needed to understand the source of chemicals in wastewater. There is a problem of finding studies that are specific to the United States and since culture influences eating habits and household products a geographically specific study is important.

Although concentrations of Ca, Mg and SO_4 are lower in wastewater than in water collected below turfgrass sites they are still higher than average groundwater levels. Daily nutritional requirement are 2500mg Ca and 350 mg Mg (http://www.feinberg.northwestern.edu/nutrition/fact-sheets.html). Lindberg (2004) reports average values of calcium in urine to be 100-300mg/person/day. Jonsson et al. (1997) reported in urine concentrations of 18mg Ca/L, 11.1mg Mg/L and 331mg S/L. Calcium is found in household products such as in toothpastes and used as a disinfectant and magnesium is present in pharmaceuticals (Source:WebElements http://www.webelements.com/). Sulfate in wastewater is derived from detergents, disinfectants, pharmaceutical products and is used in cleaning cesspools (Bleifuss et al., 2000).

ii. Methods

To evaluate the chemical signature of various lawn maintenance procedures lysimeters (soil water samplers) have been installed to depths up to 150cm in maintained lawns at eight locations on Suffolk County Water Authority property and on the Stony Brook University campus. Refer to Figure 3 for locations. One site which is not fertilized is used as a control (Stony Brook); two locations are undergoing traditional chemical turfgrass treatment (Stony Brook and Oakdale) while the other five are treated with natural organic fertilizer (East Hampton, Hauppauge, Huntington, Coram and Oakdale). Traditional chemical sites are treated by either Scotts® brand or LESCO® brand fertilizers. Treatment with Scotts® brand fertilizer began in 2000 (Schuchman, 2001) on new sod. The other sites are on more established lawns.

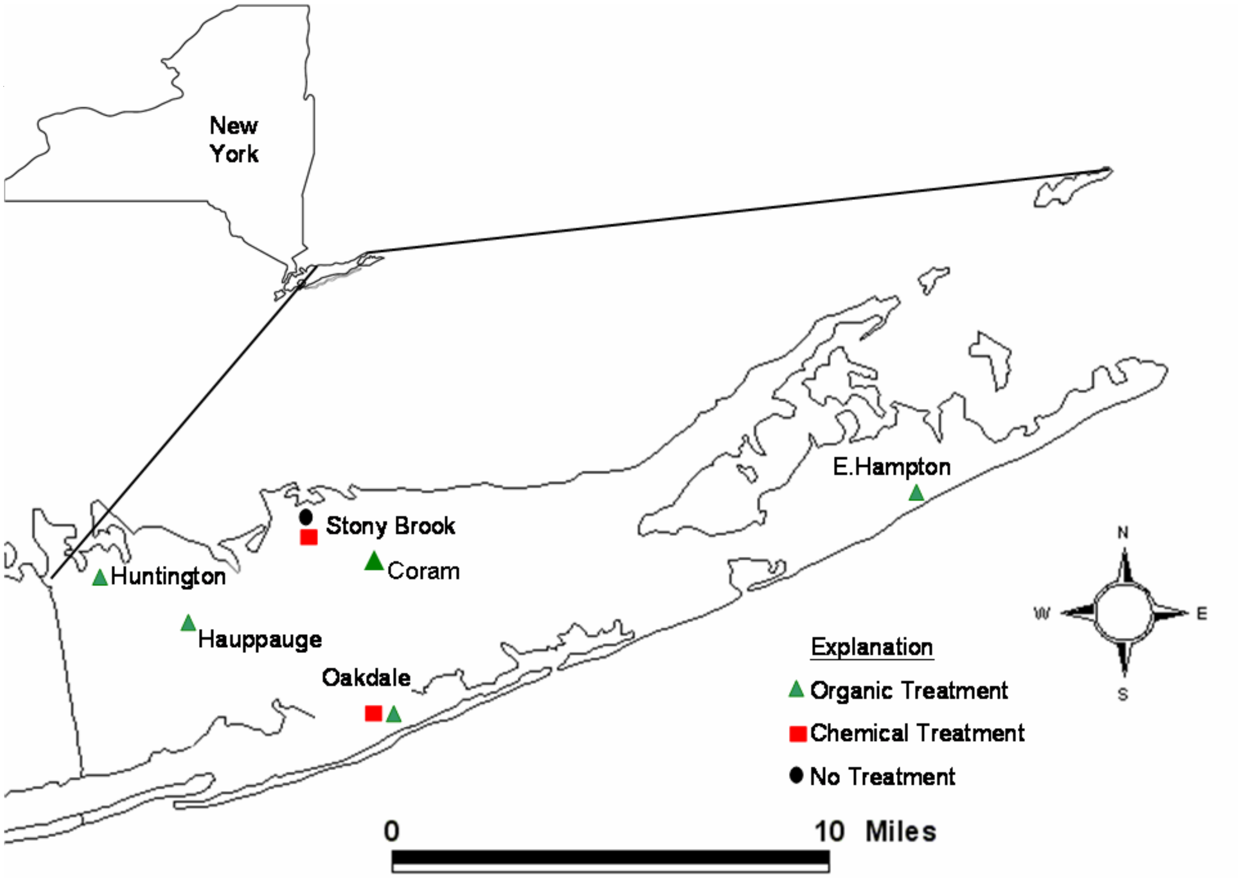


Figure 3 Locations of turfgrass sites in Suffolk County, Long Island, New York

prepared by centrifuging in an International Equipment Corporation (IEC) Model CS floor mounted centrifuge at 2000 RPM for an hour to separate the solids from the 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. Polypropylene plastic bottles for cation samples were acid rinsed and the samples were preserved with a few drops of HCl. Samples were stored at 4ºC until analyzed. The samples were analyzed at Cornell University Nutrient and Elemental Analysis Laboratory. Cation concentrations were determined using an inductively coupled plasma optical emission spectroscopy (ICP-OES). Anion concentrations were determined using an ion chromatograph (IC).

The detection limits using IC for Cl, Fl and SO_4 are 0.1 ppm, for NO_3 and Br 0.2ppm and for PO_4 0.5ppm. The precision and accuracy based on anonymous standards and duplicate analyses for Cl, F, Br, and SO_4 is 10% and for PO_4 is 20% and NO_3 is 15%. The uncertainty associated with the precision is high for phosphate due to low phosphate concentrations.

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 and accuracy determined from standards and anonymous duplicate samples for B, S, Na, and Ca are 10%, for Mg 5%, for K 15% and for phosphorous 20% (high due to low concentrations).

Average rain water composition was compiled from the literature for Suffolk County (Proios and Schoonen, 1994; Schoonen and Brown, 1994).

iii. Results

One hundred and three samples were analyzed for major and minor ion concentrations, from which 13 elements were found to be most promising for tracer work (Table 3). These are NO_3, SO_4, PO_4, B, Ca, Mg, Na, K, Cl, F, Br, P and S. My analysis of nitrate sources in residential areas show elevated concentrations in Ca, Mg and SO_4 in soil water influenced by turfgrass maintenance compared to wastewater samples. Wastewater samples were enriched in K, Na, Cl, N-NO_3 and PO_4 compared to water influenced by turfgrass maintenance. Concentrations in rain water for major elements are lower than wastewater and soil water collected below turfgrass sites.

Ca and Mg are enriched in soil water collected below turfgrass plots due to the addition of lime to maintain a neutral pH and SO_4 is from the fertilizers used.

Assuming the average cesspool in Long Island discharges 240 gallons (900 L) per day (Flynn, 1969), that three people occupy a home, using data from Table 2 and the concentrations of wastewater found in this study we can calculate contributions of the elements to a cesspool. Urine and feces would contribute 28% (13.6 ppm) of the nitrogen in wastewaters using raw concentrations from Siegrist et al. (1976) while data from Beckerus et al. (1998) would suggest 85% (41ppm). Jonsson et al. (1997) only analyzed urine and his study suggests 27% (13 ppm) of the nitrogen in wastewater comes from urine. Siegrist et al. (1976) study suggest that of the nitrogen in wastewater 5% (2.4 ppm) comes from clothes washers, 6.5% (3 ppm) comes from dishwasher and kitchen sink and 2% (1 ppm) comes from showers and baths. Data from Siegrist et al. (1976) would suggest 13.5% (1.85 ppm) of phosphate in wastewater is from urine and feces and data from Beckerus et al. (1998) would account for 36% (5 ppm). Data of only urine from

Jonsson et al. (1997) suggest 8.5% (1.15ppm) of phosphate in wastewater is from urine. Siegrist et al. (1976) suggest that of the PO_4 in wastewater 52% (7.1 ppm) is from clothes washers, 27% (4 ppm) comes from the dishwasher and kitchen sink and less than 1% is from showers and baths. Data from Medcalf and Eddy (2003) suggest Cl in urine and feces account for 41% (19 ppm) of the concentration in wastewaters. Jonsson et at. (1997) analysis of urine would account for 9% (3.96 ppm) of the Na and 30% (3.3 ppm) of the K in wastewater. Data from Lindberg (2004) suggest that urine from a typical healthy adult would for <1% (0.06 ppm) Ca, 1% (0.04 ppm) Mg and 19% (1.1 ppm) sulfur in wastewater.

$N\text{-}NO_3$ data for wastewater samples in Table 3 were for that of the influent and do not represent the nitrate concentrations entering the groundwater. Most of the nitrogen produced in a home is organic nitrogen and urea. Urea breaks down to form ammonia (NH_3). Total ammonia is usually reported as $NH_{3(gas)} + NH_{3(aq)} + NH_{4(aq)}$ (Stumm and Morgan, 1996). In the septic tank NH_3 quickly converts to ammonium, NH_4^+. Some organic nitrogen in the septic tank also breaks down to NH_4^+ but is predominantly present as organic nitrogen (Andreoli et al., 1977). Studies report around a 20% loss in total nitrogen between the waste that enters a septic tank and when it enters the cesspool (Porter, 1997; Andreoli et al., 1977). This loss is most likely as ammonia gas. In the cesspool the BOD (biological oxygen demand) is high and any oxygen present is quickly consumed. As the effluent travels away from the cesspool the biological oxygen demand decreases and the conditions become more oxidizing. Dissolved oxygen measurements from Stackelberg (1995) suggest that soils on Long Island are well drained and well aerated and that processes that deplete dissolved oxygen, such as nitrification, are insufficient to exhaust dissolved oxygen supplies. These conditions favor nitrification, the conversion of the various forms of nitrogen to nitrate by microbial bacteria. N_2O can occur as a by-product during

Table 3 Chemical data for nitrate sources

Concentrations in ppm

	B	Ca	K	Mg	Na	P	S	Cl	$N\text{-}NO_3$	SO_4	PO_4
Soil Water Influenced by Chemical Fertilizer							***n=***	***12***			
Median	0.66	38.19	3.10	67.33	26.99	0.45	8.93	5.04	0.78	81.23	0.05
Average	0.71	42.47	2.93	61.80	36.08	0.43	9.89	9.43	6.28	92.04	0.57
Stdev	0.37	20.19	0.96	19.60	26.25	0.38	4.90	13.05	16.27	131.08	0.86
Min	0.21	25.60	1.64	27.99	12.35	0.02	3.50	1.00	0.05	7.25	0.05
Max	1.42	75.41	4.25	78.97	69.98	1.04	16.94	49.09	59.63	513.96	2.54
Average Ratio	0.13	7.58	0.61	13.36	5.36	0.09	1.77	1.00	0.15	16.12	0.01
Soil Water Influenced by No Fertilizer							***n=***	***5***			
Median	0.27	25.53	4.56	27.93	47.66	0.18	41.66	9.02	2.11	102.70	0.05
Average	0.41	25.53	4.56	27.93	47.66	0.12	41.66	9.52	2.64	124.38	0.50
Stdev	0.30	5.80	0.47	14.42	45.66	0.10	56.64	8.08	3.21	61.18	1.00
Min	0.11	21.43	4.23	17.73	15.37	0.00	1.60	0.10	0.05	69.07	0.05
Max	0.77	29.63	4.89	38.13	79.95	0.21	81.71	19.98	8.15	217.18	2.29
Average Ratio	0.03	2.83	0.51	3.10	5.28	0.02	4.62	1.00	0.23	11.39	0.01
Soil Water Influenced by Organic Fertilizer							***n=***	***53***			
Median	0.23	45.57	1.99	12.49	17.75	0.01	16.71	7.58	1.49	88.36	0.05
Average	0.24	53.87	2.52	18.09	23.67	0.03	29.05	9.46	2.59	97.99	0.05
Stdev	0.14	29.71	1.75	11.90	16.13	0.05	25.63	8.65	3.07	74.72	0.00
Min	0.06	10.53	0.68	2.85	4.76	0.00	1.88	0.10	0.02	4.78	0.05
Max	0.78	118.20	6.91	45.49	54.58	0.25	99.46	50.89	15.25	406.66	0.05
Average Ratio	0.03	6.01	0.26	1.65	2.34	0.00	2.20	1.00	0.20	11.66	0.01
All Soil Water Samples Below Turf Grass Sites							***n=***	***70***			
Median	0.26	42.23	2.17	17.73	18.78	0.02	14.93	6.90	1.33	86.36	0.05
Average	0.34	50.62	2.69	24.90	26.82	0.11	27.03	9.46	3.27	98.76	0.18
Stdev	0.27	28.37	1.67	20.07	19.88	0.22	26.04	9.41	7.42	85.80	0.48
Min	0.06	10.53	0.68	2.85	4.76	0.00	1.60	0.10	0.02	4.78	0.05
Max	1.42	118.20	6.91	78.97	79.95	1.04	99.46	50.89	59.63	513.96	2.54
Average Ratio	0.04	6.12	0.31	2.57	2.72	0.00	2.16	1.00	0.19	12.52	0.01
Residential Septic Tanks/Cesspool Influent							***n=***	***12***			
Median	0.27	19.47	18.77	6.10	83.06	8.27	4.72	66.44	0.44	8.99	26.07
Average	0.34	21.90	38.66	6.32	106.31	9.36	9.44	190.11	0.44	49.17	41.76
Stdev	0.18	14.38	67.41	1.68	85.94	5.45	14.07	387.86	0.27	90.51	55.97
Min	0.15	5.59	10.40	3.86	38.94	4.22	2.25	25.64	0.12	1.64	0.05
Max	0.74	47.49	251.50	9.64	294.80	22.71	53.42	1410.74	1.03	288.14	204.01
Average Ratio	0.00	0.29	0.28	0.09	1.25	0.12	0.07	1.00	0.01	0.14	0.39
Sewage Treatment Plant Influent							***n=***	***21***			
Median	0.21	21.74	9.90	4.51	42.38	3.41	6.65	45.13	0.39	18.68	10.80
Average	0.31	23.80	11.65	4.83	47.22	4.19	10.88	52.12	1.70	35.03	13.96
Stdev	0.26	9.36	4.84	1.73	25.62	3.26	19.50	21.24	5.84	76.23	12.24
Min	0.11	7.37	6.02	1.23	26.41	1.02	2.45	20.69	0.35	6.50	2.75
Max	1.31	53.55	22.43	8.31	148.30	14.01	92.88	102.41	27.20	365.49	51.15
Average Ratio	0.00	0.48	0.22	0.10	0.94	0.08	0.15	1.00	0.01	0.41	0.24
All Wastewater Influent							***n=***	***33***			
Median	0.23	20.87	10.85	5.08	43.04	4.43	5.88	48.78	0.39	16.11	13.70
Average	0.32	23.11	21.47	5.37	68.71	6.07	10.34	102.30	1.24	40.18	24.07
Stdev	0.23	11.26	41.84	1.84	61.50	4.82	17.43	237.78	4.66	80.60	36.81
Min	0.11	5.59	6.02	1.23	26.41	1.02	2.25	20.69	0.12	1.64	0.05
Max	1.31	53.55	251.50	9.64	294.80	22.71	92.88	1410.74	27.20	365.49	204.01
Average Ratio	0.00	0.43	0.22	0.10	0.88	0.09	0.12	1.00	0.01	0.33	0.28
Rain											
Average	nd	0.32	0.28	0.22	1.56	nd	nd	2.81	0.50	3.23	nd
Average Ratio	nd	0.11	0.10	0.08	0.56	nd	nd	1.00	0.11	1.15	nd

nitrification (Stumm and Morgan, 1996) which may also explain small losses in total nitrogen from the cesspool to the groundwater. Losses here may also be due to soil adsorption of ammonium that doesn't convert to nitrate. More studies are needed to understand nitrogen speciation from the cesspool to the groundwater table. Nitrification occurs before denitrification, which is the reduction of NO_3^- to nitrogen gas. For denitrification to occur, the dissolved oxygen level must be at or near zero. The conditions near the cesspool favor denitrification yet the nitrogen species is ammonium. It is unlikely that much of the nitrogen is denitrified based on dissolved oxygen measurements in groundwater samples from Northport (Bleifuss et al., 2000) and other locations on Long Island (Leamond et al., 1992; Stackelberg, 1995). Porter (1977) assumed a 50% nitrogen reduction from the raw sewage to the groundwater although he reported only one study with reductions this high (Andreoli et al., 1977) on Long Island . This study however is a pilot study which introduced methanol in the leaching field to promote denitrification. A 50% reduction is thus a high estimate of nitrogen reduction. Porter (1977) does note that many studies are incomplete and contradictory, thus the need for future work. The Suffolk County Health Department requirements are for a septic tank attached to a single 12 foot high stack of , 8' diameter, pre-cast concrete leaching rings or alternatively, multiple shorter leaching stacks depending on the depth to groundwater and number of bedrooms (Mermelstein and Minei, 1995).

Nitrogen nitrate values for septic tank/cesspool samples were assumed to be the average sum of all nitrogen species in the influent for the sewage treatment plants for the month of September, a value of 48 ppm as nitrogen (Table 4). The average for September (48 ppm) and the year (46 ppm) were not significantly different. The sewage samples analyzed for major elements were also collected in September. Suffolk County Public Works intended to analyze the wastewater samples for total nitrogen at the time of collection. However, due to miscommunication analysis of the samples could not occur before degradation of the samples.

Table 4 Nitrogen analysis for public sewage treatment plants.

Sewage Treatment Plant	Yearly Results	Influent TKN	Effluent TKN	Influent NO_X	Effluent NO_X
1	Average	26.48	17.30	0.96	0.45
	StdDev	11.96	3.42	0.41	0.17
	n	51	51	27	46
	Max	82.90	29.00	1.90	1.10
	Min	13.40	5.30	0.30	0.30
5	Average	38.07	1.46	0.39	1.10
	StdDev	8.87	0.62	0.10	0.82
	n	51	52	23	47
	Max	74.70	3.30	0.60	3.90
	Min	25.50	0.60	0.30	0.30
6	Average	47.74	5.66	0.81	11.46
	StdDev	12.51	4.86	0.80	5.48
	n	50	52	7	52
	Max	92.90	24.60	2.60	25.00
	Min	28.50	1.10	0.30	0.80
9	Average	54.95	2.40	1.94	0.73
	StdDev	17.61	1.26	0.79	1.02
	n	51	52	33	12
	Max	96.70	6.90	3.50	3.80
	Min	18.80	0.80	0.30	0.30
11	Average	55.45	2.36	0.43	2.64
	StdDev	8.31	1.16	0.12	1.47
	n	50	51	10	52
	Max	97.60	8.80	0.70	5.60
	Min	40.80	1.20	0.30	0.40
12	Average	72.69	2.78	0.60	0.82
	StdDev	22.35	2.04	0.33	0.86
	n	51	52	11	45
	Max	198.00	15.50	1.30	4.90
	Min	23.00	1.10	0.30	0.30
13	Average	32.99	1.56	0.57	1.31
	StdDev	10.54	0.87	0.33	0.89
	n	51	50	15	50
	Max	56.60	4.90	1.40	5.70
	Min	10.60	0.40	0.30	0.40
14	Average	57.87	2.83	0.71	0.62
	StdDev	20.30	3.18	0.37	0.75
	n	51	52	9	9
	Max	190.00	19.10	1.30	2.60
	Min	43.10	0.90	0.30	0.30
15	Average	53.11	1.48	1.36	3.06
	StdDev	17.01	0.88	0.94	4.38
	n	50	51	25	25
	Max	150.20	6.10	3.50	20.20
	Min	26.30	0.30	0.30	0.30
21	Average	32.04	1.64	1.65	1.65
	StdDev	8.26	0.97	2.05	1.46
	n	51	53	6	49
	Max	60.40	4.60	5.70	6.40
	Min	14.60	0.50	0.30	0.30
22	Average	43.20	2.86	0.57	2.74
	StdDev	10.30	3.33	0.48	2.86
	n	50	52	12	14
	Max	79.80	18.50	1.60	8.80
	Min	20.10	0.80	0.30	0.30

Sewage Treatment Plant	Yearly Results	Influent TKN	Effluent TKN	Influent NO_X	Effluent N_{OX}
23	Average	47.52	4.39	0.69	1.35
	StdDev	10.30	1.07	0.59	1.60
	n	51	52	17	32
	Max	66.10	8.70	2.70	6.10
	Min	12.70	2.60	0.30	0.30
28	Average	48.34	2.36	1.71	1.78
	StdDev	11.72	0.91	0.97	0.67
	n	49	52	41	50
	Max	93.00	6.10	4.50	3.10
	Min	27.30	1.10	0.40	0.70
7p	Average	52.96	2.46	0.88	1.22
	StdDev	10.35	1.30	0.46	2.37
	n	46	49	6	12
	Max	88.10	6.00	1.50	8.50
	Min	32.00	0.30	0.30	0.30
7w	Average	68.33	2.68	3.36	8.14
	StdDev	13.90	0.93	7.23	5.83
	n	49	52	20	51
	Max	91.90	6.10	30.40	26.60
	Min	25.40	0.70	0.30	0.80
18i	Average	31.59	9.67	2.58	10.03
	StdDev	13.45	6.04	2.94	7.42
	n	49	51	15	46
	Max	71.30	24.80	9.40	21.10
	Min	10.10	2.10	0.30	0.60
18n	Average	31.18	3.99	3.23	3.12
	StdDev	15.21	3.94	3.71	3.08
	n	49	50	33	34
	Max	73.20	21.50	22.80	13.50
	Min	4.00	1.10	1.20	0.30
20e	Average	35.66	4.11	1.41	1.48
	StdDev	12.71	4.34	1.03	0.90
	n	50	51	15	43
	Max	73.50	26.20	4.00	4.50
	Min	15.30	0.30	0.30	0.40
20w	Average	55.23	6.88	0.35	2.15
	StdDev	10.40	5.77	0.11	1.13
	n	50	50	8	52
	Max	82.10	21.00	0.60	5.00
	Min	33.30	1.20	0.30	0.30
40	Average	38.34	5.00	2.46	2.36
	StdDev	12.69	1.74	1.65	3.38
	n	48	52	43	36
	Max	96.70	8.20	8.00	20.20
	Min	19.20	0.60	0.30	0.30
60	Average	55.82	3.09	9.33	2.99
	StdDev	30.88	0.99	17.59	1.15
	n	18	18	4	18
	Max	93.80	5.30	35.70	4.60
	Min	3.80	1.70	0.30	0.50
All *(n=21)*	**Average**	**46.19**	**4.25**	**1.77**	**3.36**
	StdDev	**20.71**	**4.81**	**3.24**	**4.70**
	n	**1116**	**1145**	**480**	**875**
	Max	**198.00**	**29.00**	**35.70**	**26.60**
	Min	**3.80**	**0.30**	**0.10**	**0.17**

As a result total nitrogen values were not measured for the influent. It is assumed that all nitrogen will be converted to nitrate once discharged into the subsoil. Wastewater concentrations entering a septic tank/cesspool system and a sewage treatment plant should be the same. As evident in Table 4, the sewage treatment plants in this study reduce nitrogen concentrations to below the drinking water standard and usually below 5 ppm before discharge. Therefore the effluent for a sewage treatment plant has much lower concentrations of nitrogen than a septic tank/cesspool system and yield similar ratios of the elements to chloride as rainwater in the source plots. It was therefore decided not include them as a source field in the data plots since their influence of nitrate concentrations in groundwater is likely to be minimal.

G***eochemical tracer source plots***

A combination of the elements N-NO_3, SO_4, Na, Ca, Mg and Cl plotted on binary plots and a ternary diagram can place constraints of nitrate sources for a given groundwater. The most useful groundwater geochemical tracer is a conservative element, which is one that does not adsorb to the soil surfaces, or degrade with time due to biological or physical processes. N-NO_3, Cl and SO_4 are the most conservative elements utilized here. The cations Ca, Mg and Na tend to adsorb to negatively charged soil particles but with accurate sorption modeling such as done by Voegelin et al. (2000) and an understanding of plant uptake, concentrations in groundwater may be predicted.

Density contours were created for the two source fields 1) soil water collected below turfgrass sites treated with traditional chemical fertilizer, natural organic fertilizer or no fertilizer (gray scale) and 2) wastewater from septic tank/cesspool systems (color scale). Although there is a statistical difference in the concentrations of the soil waters their fields overlapped and therefore all soil water data is plotted as one field. Since the public sewage treatment plants analyzed in this study reduce nitrate concentrations before discharge they are contributing fewer nitrates to the groundwater and are not plotted as a source on the plots. They are however a source of groundwater recharge when the discharge location for the sewage treatment plant is within the capture zone for a given groundwater well.

Density contours for binary plots were created using the Fortran 77 programming language and Absoft compiler (complied by Professor Daniel Davis, SUNY Stony Brook, 2003). For this method the X and Y data ranges were divided into 151 segment each, for a total of 22,801 bins for each plot. A Gaussian (normal) bivariate distribution is calculated for each data point, distributing that data point among bins with an assumption that the standard deviation in each axis equals 10% of the measured value in that axis. A normal distribution for a data point X with mean (μ) and standard deviation (σ) is a statistical distribution with a probability function

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2 / (2\sigma^2)} \qquad \text{eq. 1}$$

(Mathworld, WOLFRAM Research, http://mathworld.wolfram.com). Eq. 1 is applied in both the X and Y directions. For values approaching zero, a minimum standard deviation is defined, equal to 0.05 in X and Y. A Gaussian distribution (defined as a bell shaped curve) is defined out to 3 sigma in both the X and Y directions, such that the integral over the curve equals one (except when part of the curve falls in the range of impossible negative values). The contribution to a given bin from a given point corresponds to the probability that that value actually falls with in the X-Y range defined by that bin. The contribution from each data point is summed for each of the bins, producing a data density plot that represents the best available estimate of the likely distribution for the variables.

Twenty two Suffolk County Water Authority public supply wells and eight monitoring wells from Bleifuss et al. (2000) were chosen to represent a range of land use and locations in

Table 5 Groundwater Chemistry

Well Id	Location		Depth	Land Use	Ca	K	Mg	Na	Cl	N-NO_3	SO_4	PO_4
			feet		*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*	*ppm*
J	Northport	monitoring	75	Ag	43.01	4.89	10.50	7.20	22.01	11.40	92.04	nd
S-103523	Southold	SCWA	88	Ag	15.90	6.12	6.38	26.30	54.40	6.92	36.10	dc
S-105669	Southold	SCWA	106	Ag	12.80	1.98	8.55	20.70	32.70	7.01	28.30	dc
S-24850	Southold	SCWA	97	Ag	nd	3.67	13.68	nd	35.50	9.97	90.20	dc
S-72271	Smithtown	SCWA	681	HD	10.80	0.92	4.60	8.20	11.00	5.09	10.10	dc
D	Northport	monitoring	13	LD	7.21	1.60	3.60	14.00	23.11	2.51	15.28	nd
S-20530	Huntington	SCWA	607	LD	3.60	0.63	1.33	5.30	7.20	2.69	dc	dc
S-72326	Huntington	SCWA	297	LD	2.00	0.45	0.53	3.50	4.20	0.77	dc	dc
B	Northport	monitoring	132	MD	13.99	3.09	4.11	12.99	18.11	7.10	21.71	nd
F	Northport	monitoring	123	MD	29.02	4.89	7.80	30.00	24.82	18.90	53.70	nd
G	Northport	monitoring	70	MD	19.00	3.28	4.40	34.99	56.51	8.70	24.88	nd
I	Northport	monitoring	42	MD	21.00	3.91	9.31	60.99	115.39	8.40	17.10	nd
S-100453	Babylon	SCWA	\	MD	4.30	1.18	2.54	8.10	11.70	2.39	8.50	dc
S-105300	Huntington	SCWA	\	MD	8.30	0.93	3.63	7.30	13.20	4.52	4.90	dc
S-11105	Huntington	SCWA	517	MD	17.20	1.28	6.96	10.80	20.00	7.45	24.00	dc
S-15514	Huntington	SCWA	595	MD	17.80	1.05	6.77	9.50	15.60	7.41	34.60	dc
S-16309	Brookhaven	SCWA	251	MD	11.20	0.72	3.96	8.30	9.20	4.55	4.10	0.24
S-25776	Huntington	SCWA	587	MD	22.80	1.18	8.22	11.10	17.10	8.27	43.20	dc
S-33820	Huntington	SCWA	408	MD	21.00	1.73	8.90	16.50	24.20	4.79	15.60	0.16
S-39536	Huntington	SCWA	615	MD	12.00	1.16	4.71	10.30	18.30	7.11	12.60	dc
S-53747	Huntington	SCWA	453	MD	12.50	1.22	4.86	9.40	14.50	7.32	20.20	dc
S-56133	Huntington	SCWA	332	MD	17.10	1.30	8.22	14.60	21.90	7.01	15.10	dc
S-88463	Huntington	SCWA	493	MD	18.60	1.17	6.89	18.10	19.20	8.03	29.50	dc
A	Northport	monitoring	102	MD/GC	16.99	2.11	7.39	18.00	25.98	9.30	31.03	nd
E	Northport	monitoring	105	MD/GC	18.00	1.68	8.10	16.99	23.89	6.25	22.58	nd
S-57961	Brookhaven	SCWA	\	OS	4.10	0.52	1.69	4.90	7.60	0.46	7.40	dc
S-59347	Islip	SCWA	463	OS	4.30	0.61	1.20	3.40	3.30	0.20	3.90	dc
S-70155	E.Hampton	SCWA	240	OS	14.90	1.68	9.36	28.80	56.70	0.19	16.40	dc
S-82174	Brookhaven	SCWA	187	OS	3.80	0.71	1.64	4.60	6.40	0.25	8.10	dc
S-100608	Brookhaven	SCWA	434	Vacant	7.60	0.39	1.38	3.90	4.90	dc	7.20	0.15

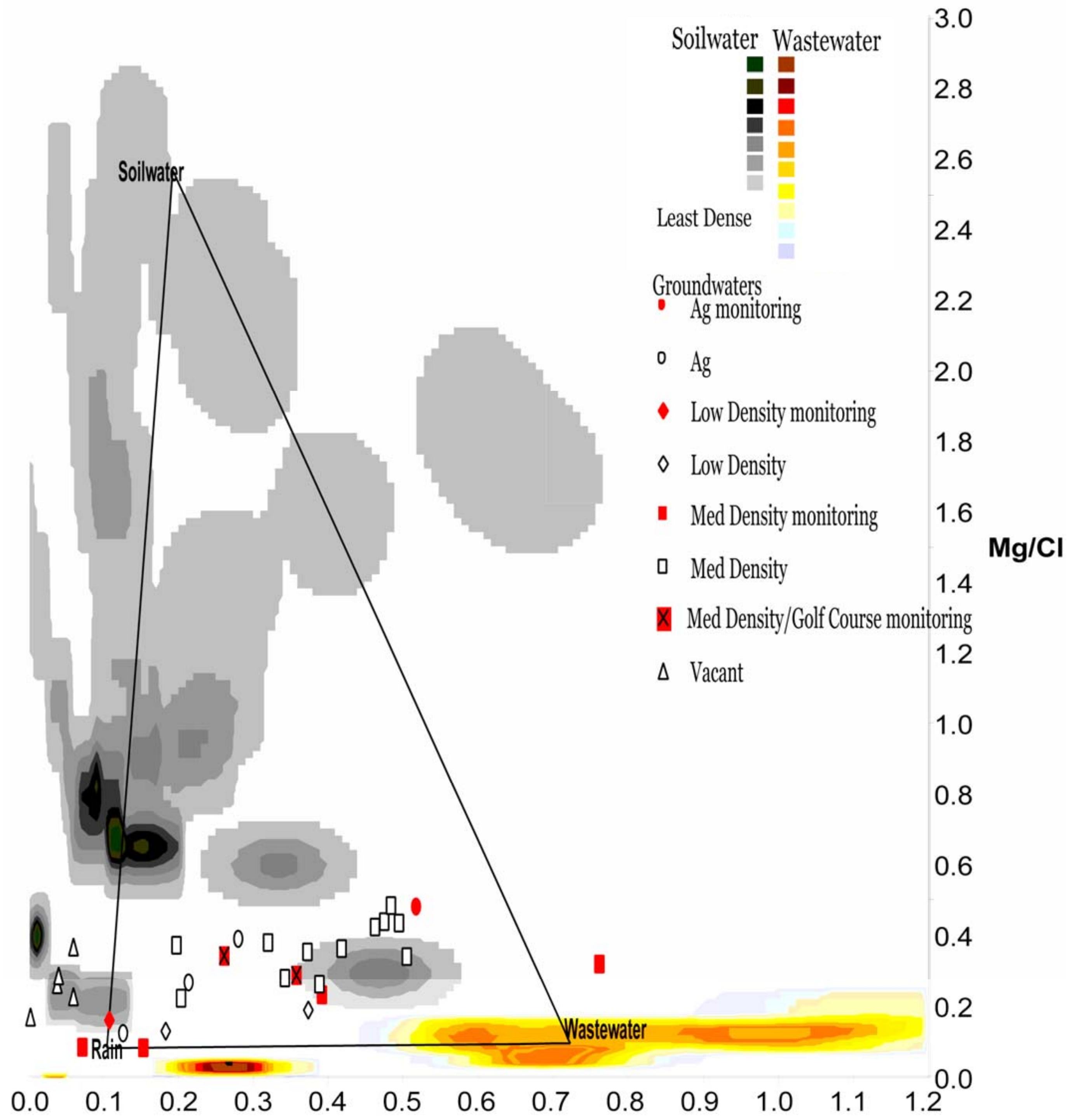
nd=not determined, dc=detection limit (2.5ppm SO4 and 0.1ppm PO4), monitoring wells from Bleifuss et al. (2000), depth is feet to top of well screen .Land Use abbreviations: Ag=agricultural, HD=high density residential, MD=medium density residential, LD=low density residential, GC=golf course, OS=open space

Suffolk County. Data acquired for these wells are presented in Table 5. The data for the groundwater and the wastewater and the soil water are compared in Figures 4-11. The groundwater data is plotted as a function of primary land use. Land use was determined from modeling capture zones (CMD, 2003) for all Suffolk County Water Authority supply wells. The data for the top three land uses in each capture zone for Suffolk County Water Authority supply

Table 6 Groundwater capture zone land use (CDM, 2003)

Well Number	**Land Use**	**Total %**	**Well Number**	**Land Use**	**Total %**
S-72271	High Density Residential unsewered	40.2%	**S-57961**	Open Space	100.0%
	Transportation	30.0%	**S-59347**	Open Space	95.0%
	Medium Density Residential unsewered	21.1%		Vacant	3.2%
S-100453	Medium Density Residential unsewered	28.6%		Transportation	1.8%
	Low Density Residential unsewered	25.8%	**S-70155**	Open Space	89.9%
	Transportation	19.9%		Waste Handling and Maintance	3.8%
S-105300	Medium Density Residential unsewered	59.4%		Transportation	3.3%
	High Density Residential unsewered	14.4%	**S-82174**	Open Space	96.0%
	Transportation	10.9%		Vacant	3.3%
S-11105	Medium Density Residential unsewered	61.2%		Agricultural	0.7%
	Transportation	24.1%	**S-100608**	Vacant	56.5%
	High Density Residential unsewered	9.0%		Low Density Residential unsewered	21.2%
S-15514	Medium Density Residential unsewered	70.3%		Transportation	11.8%
	Transportation	25.6%	**S-20530**	Low Density Residential unsewered	19.4%
	Low Density Residential unsewered	1.6%		Medium Density Residential unsewered	19.2%
S-16309	Medium Density Residential unsewered	50.7%		Agricultural	18.8%
	Transportation	21.8%	**S-72326**	Low Density Residential unsewered	54.8%
	High Density Residential unsewered	21.1%		Medium Density Residential unsewered	28.8%
S-25776	Medium Density Residential unsewered	67.9%		Transportation	13.1%
	Transportation	27.4%	**S-103523**	Agricultural	58.9%
	Low Density Residential unsewered	2.5%		Transportation	11.1%
S-33820	Medium Density Residential unsewered	34.0%		Vacant	9.4%
	Transportation	23.5%	**S-105669**	Agricultural	54.8%
	High Density Residential unsewered	22.5%		Low Density Residential unsewered	20.4%
S-39536	Medium Density Residential unsewered	62.3%		Vacant	10.7%
	Transportation	19.5%	**S-24850**	Agricultural	69.3%
	High Density Residential unsewered	6.8%		Utilities	7.8%
S-53747	Medium Density Residential unsewered	57.6%		Commercial unsewered	7.4%
	Transportation	21.3%			
	Commercial unsewered	5.4%			
S-56133	Medium Density Residential unsewered	49.5%			
	Transportation	22.8%			
	High Density Residential unsewered	16.3%			
S-88463	Medium Density Residential unsewered	63.6%			
	Transportation	33.0%			
	Low Density Residential unsewered	1.5%			

wells are reported in Table 6. Primary land use is defined to be the land use that most affects the groundwater in the capture zone. For groundwater wells characterized by agricultural land use the percent land use is >54% agriculture, for high density residential (>10 dwelling units/acre (DU/acre)) and medium density residential (2-10 DU/acre) land use the percent land use is >28% high or medium density residential, for low density residential (1 or less DU/acre) land use the percent land use is >20% low density residential and for vacant or open space land use the percent land use is >56% vacant or open space. Land use for monitoring wells was determined by Bleifuss et al. (2000) from Regional Planning Board Land Use maps. Although this method is less precise than modeling it is considered accurate for these shallow monitoring wells.



$N\text{-}NO_3/Cl$

Figure 4 Mg/Cl vs $N\text{-}NO_3/Cl$. *Names of source fields are near the median ratio for that source. Refer to legend for density contours and groundwater sample identification.*

Since both axes are normalized to the same element, chloride, Figures 4-7 are equivalent to element-element plots in that mixing of end members (or mixing sources, i.e. rain water, wastewater and soil water) is along straight lines (Langmuir et al., 1978). Multiple groundwater samples with differing element concentrations can yield the same ratio (i.e. similar proportions of the elements) therefore these plots can not be used to evaluate mixing percents but are used to asses mixing relationships. Plotted in these figures are mixing lines for the median ratio of rain water mixing with the median ratio of soil water, the median ratio of rain water mixing with the median ratio of septic tank/cesspools and mixing the median ratio of soil water and wastewater. These lines form a mixing triangle, so that any data point falling within this triangle is presumably mixing with all three sources. The name of the source fields are near the median ratio for that field.

Figures 4 through 7 plot N-NO_3/Cl on the x-axis. Septic tank/cesspool systems (referred to on the plots and in the text as wastewater) have higher nitrogen as nitrate and chloride concentrations than soil water collected below turfgrass sites that were fertilized with traditional chemical fertilizer, natural organic fertilizer or no fertilizer (referred to on the plots and in the text as soil water) but the values of the ratio of N-NO_3/Cl overlap for both sources with it generally being higher for wastewater. Mg/Cl and Ca/Cl ratios are greater in soil water samples than in wastewater samples as shown in Figures 4 and 5. Concentrations of SO_4 are higher for soil water than waste water. Also Cl concentrations for wastewater are 10x higher than they are for soil waters, thus the SO_4/Cl ratio is higher in soil water. Figure 6 shows that many of the soil water samples fall close to the average rain water composition but since many samples have high SO_4/Cl ratios the median value is closer to 12. All wastewaters have a SO_4/Cl ratio less than 1. Figure 7 is a plot of Na/Cl vs. N-NO_3/Cl. There is some overlap of the source fields. Ratios of soil waters are most dense at Na/Cl value below 2.

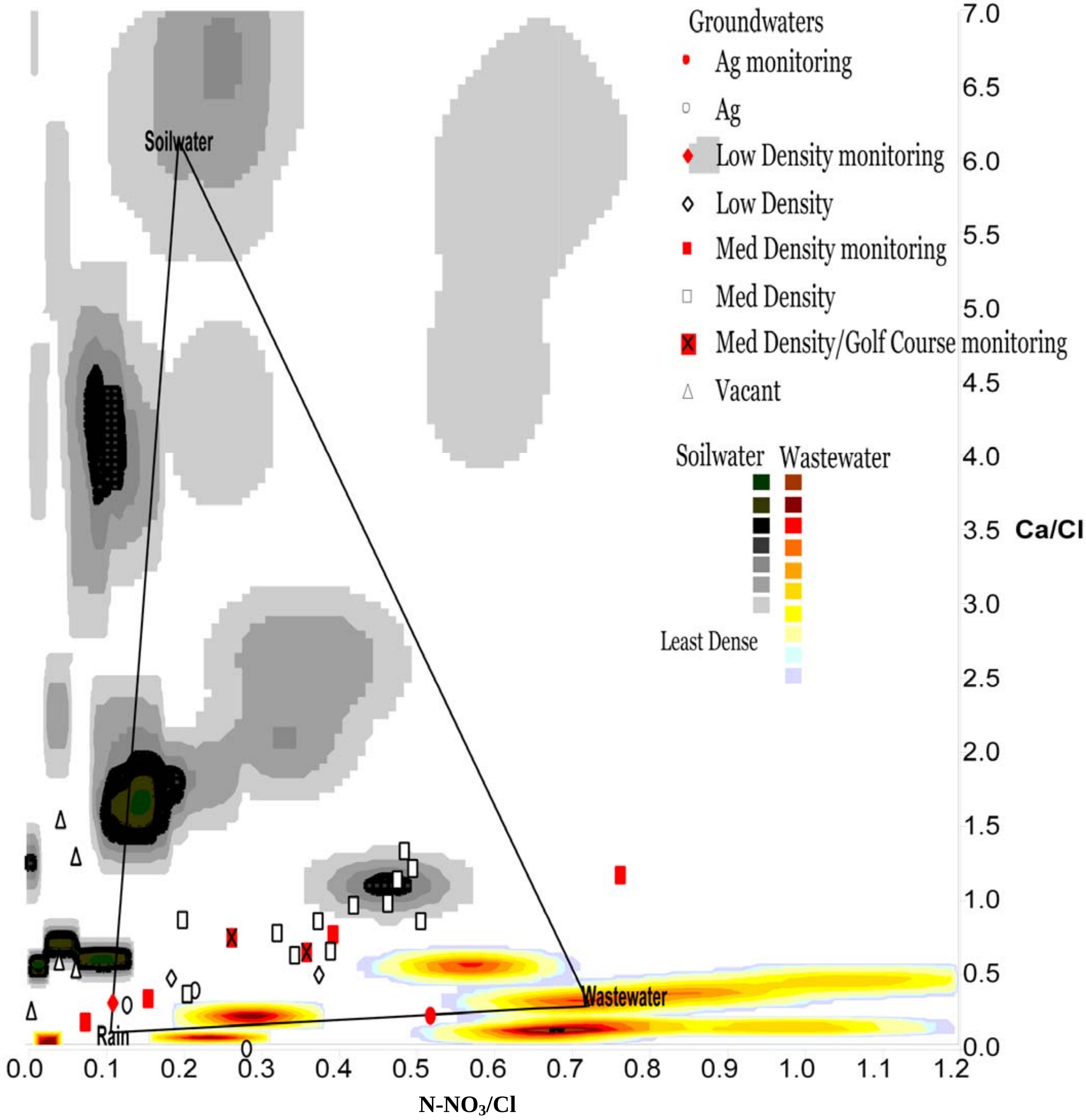


Figure 5 Ca/Cl vs N-NO$_3$/Cl. *Names of source fields are near the median ratio for that source. Refer to legend for density contours and groundwater sample identification.*

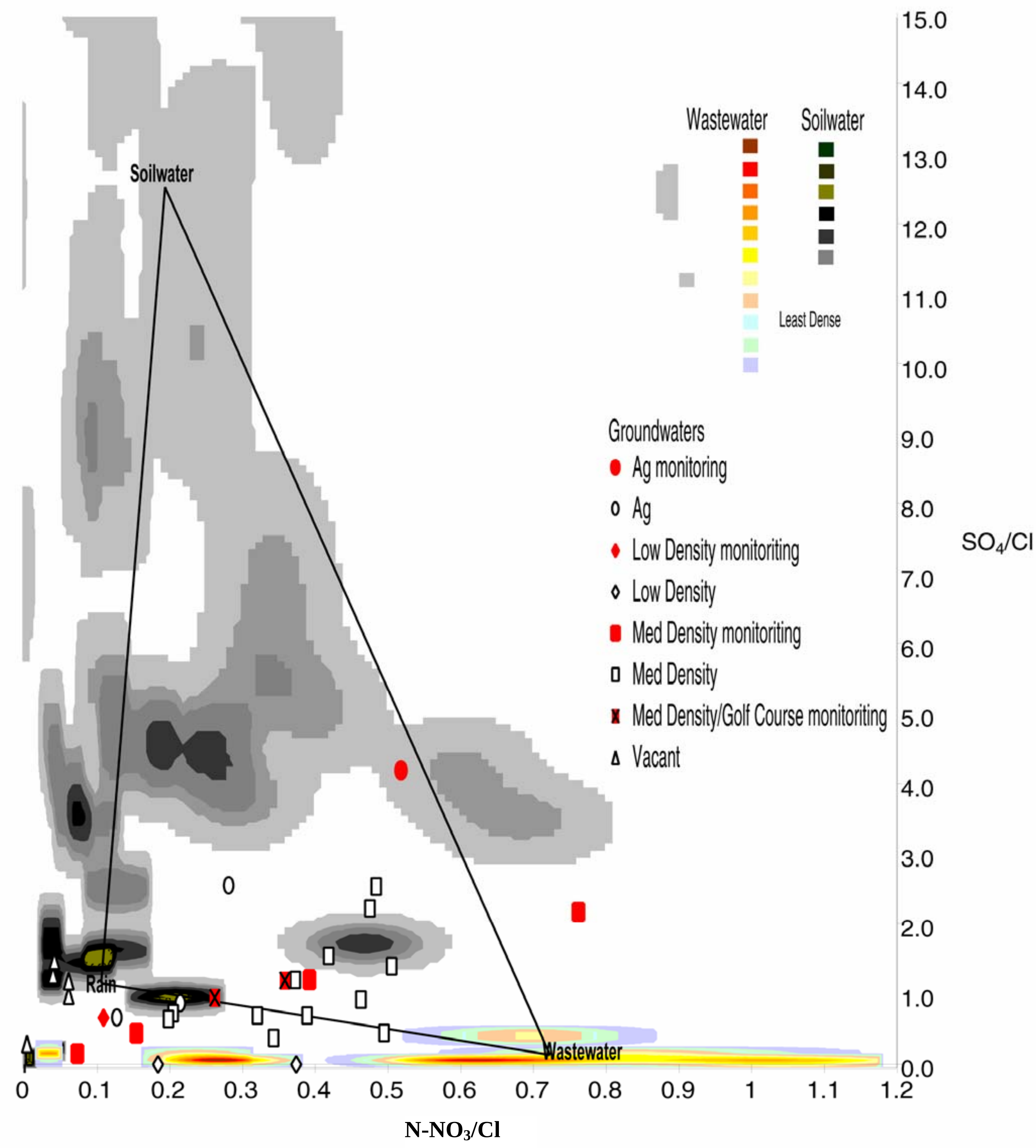


Figure 6 SO_4/Cl vs N-NO_3/Cl. *Names of source fields are near the median ratio for that source. Refer to legend for density contours and groundwater sample identification.*

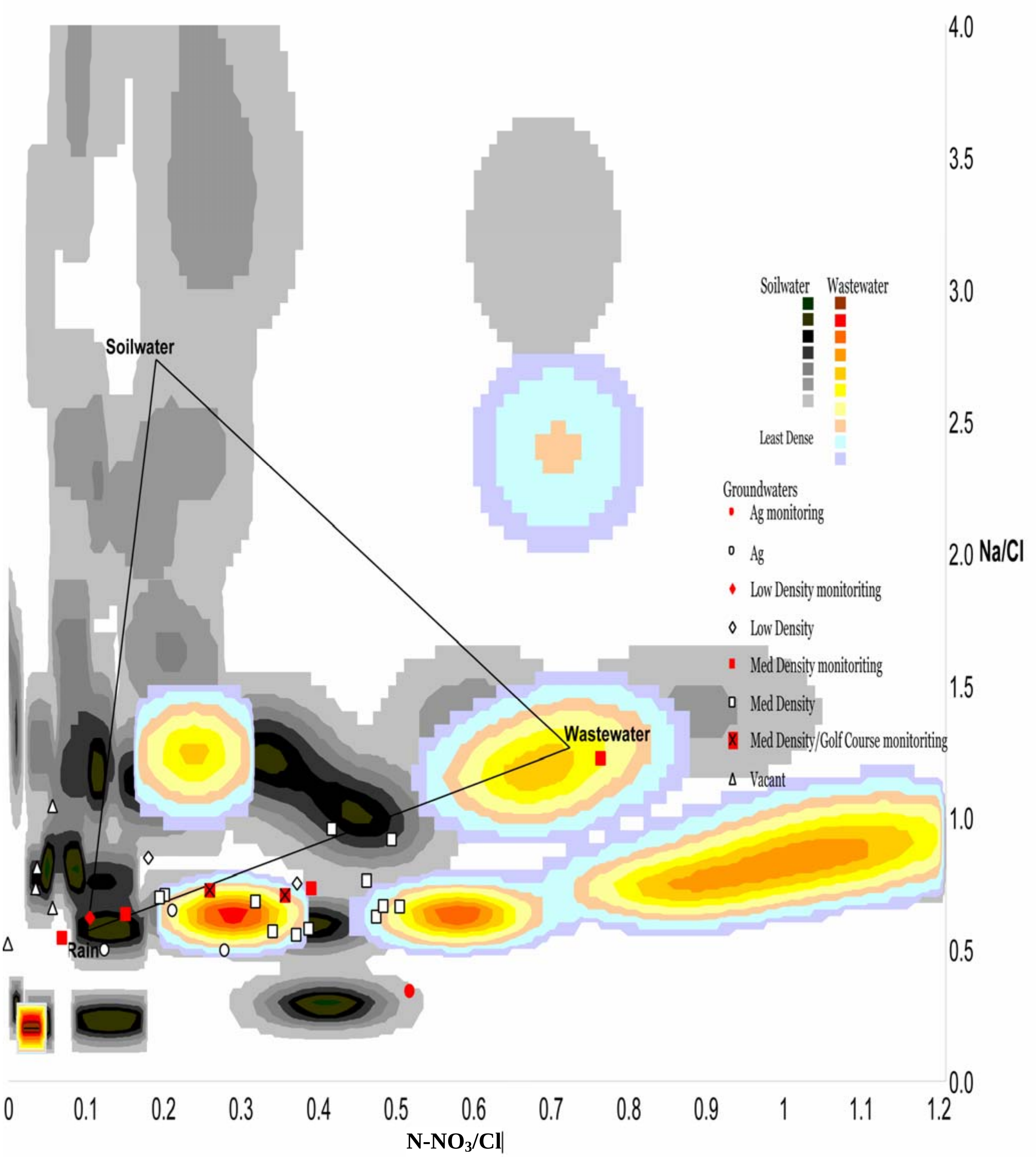


Figure 7 Na/Cl vs N-NO$_3$/Cl. *Names of source fields are near the median ratio for that source. Refer to legend for density contours and groundwater sample identification.*

Since the elements used in this study do not behave the same in the aquifer that is some will be more readily adsorbed to the aquifer than others or utilized by plants, all plots must be used in conjunction with each other to access mixing of a given groundwater. Groundwater samples sourced in vacant land use show the same mixing trend on Figures 4-7, which is mixing rain water and soil water. These samples do not lie in the mixing triangle presumably because they are only mixing with two sources, rain water and soil water. Groundwater samples sourced in low density residential land use plot similarly on Figures 4-7. The monitoring well sourced in low density residential land use plots as a mix of soil water and rain water. The public supply wells sourced in low density residential land use plot in the mixing triangle on Figures 4 and 5, which would indicate mixing with all three sources. In Figure 7 one of the wells plot in the mixing triangle and the other as a mix between wastewater and rain water. On Figure 6 both wells plot with zero sulfate concentrations. Groundwater with sulfate concentrations lower than rain water indicate pre industrial groundwater (Schoonen and Brown, 1994), since at present high sulfate concentrations in rain water are from the influence of acid rain.

Groundwater samples sourced in medium residential land use plot as a mixing trend in Figures 4-7. Figures 4 and 5 suggest rain mixing with an end member that is a mix of soil water and wastewater. All samples except two monitoring wells plot in or on the mixing triangle. Figure 5 would also suggest an end member that is a mix of soil water and wastewater yet some of the samples fall below the rain and wastewater mixing line and thus outside the mixing triangle. Since this is a plot using sulfate concentrations the samples falling below rain water could be older waters. This is unlikely since sulfate concentrations in the groundwaters are greater than rain. More likely is that these samples are mixing more with wastewaters than soil waters since the median mixing concentration of soil water is 86 ppm compared to below 10 ppm for both wastewater and rain water. Figure 7 further confirms this hypothesis. The residential land use samples plot close to the mixing line between rain water and wastewater and indicate little mixing with soil water. The groundwater data suggest an end member with a lower Na/Cl ratio than the wastewater analyzed in this study. This may be an influence of road salt. Road salt has a Na/Cl of 0.65. The groundwaters suggest an end member with a Na/Cl ratio of 1, which is likely a mix of wastewaters and road salt. Road salt has been shown to contribute a significant amount of chloride and sodium to shallow groundwater near the East Meadow Brook in central Long Island (Brown and Scorca, 1995) and Southold in eastern Long Island (Fuller and Bova, 2004).

Since this study analyses nitrate sources for residential areas specifically wastewater and soil water it was assumed that agricultural samples would not stand out on these plots. Groundwaters sources in agricultural land use may be similar to soil waters influenced by turfgrass fertilization but that is not what this study showed. Although fertilizer sources may be similar nutrient uptake will vary depending on the crop. In Figures 4 and 7 groundwater samples sources in agricultural land use plot within the medium density residential samples. In Figure 5 they plot with lower Ca/Cl ratios and in Figure 6 they plot with higher SO_4/Cl ratios.

Figures 8-10 are element-element plots not normalized. Mixing constraints for rain water, soil water and wastewater can be placed on each groundwater using mass balance equations. Fraction mixing (F) of a nitrate source, for a two source system, is calculated as

$$C_{mix}{}^{Y} = C_1{}^{Y}(F) + C_2{}^{Y}(1-F) \qquad \text{eq. 2}$$

Where C denotes concentration of element Y, C_{mix} is the composition at a given point along the mixing line, C_1 and C_2 are the concentrations for two end members mixing. The mixing lines are estimates of percent mixing. Because there is a relatively large range in compositions of the sources and because there may also be other sources, for example, road salt and agricultural inputs all groundwater samples will not lie directly on a mixing line or in the mixing field. It is therefore important to remember that the plots and mixing calculations must be used in conjunction with each other to assess estimates of mixing. A sample will fall within the mixing triangle if mixing with all three sources. Percent mixing contours are shown for both soil water (blue dashed lines) and wastewater (dotted red lines). Density source fields are not calculated for these plots.

Using Figures 8-11 in conjunction with relative proportions of groundwater concentrations and water budgets for each capture zone, mixing constraints can be placed on a given groundwater. Sulfate concentrations of the nitrate sources were highest for water collected below turfgrass sites. The percent mixing of soil water in a given groundwater can be assessed by dividing the SO_4 concentration in a groundwater by the median SO_4 concentration in soil water. For wastewater Cl and $N\text{-}NO_3$ median concentrations were used. Another source of Cl in Long Island groundwater is from road salt. If road salt is a significant source for a given groundwater this method may over estimate the contribution from wastewaters, as seen in Figure 8 where a majority of the groundwater samples have higher Cl concentrations than this ternary system would predict and plot outside the mixing triangle. Concentrations of the elements in rain water are low enough that mixing may not reduce concentrations significantly. The percent mixing of rain is the difference of 100% minus the soil water and wastewater mixing.

Mixing percents were also assessed using water budgets for a given groundwater capture zone according to land use (CDM, 2003). This was only calculated for Suffolk County Water Authority supply wells where a detailed description of the capture zone was available. This method is a rough estimate of the volume of recharge from rain, wastewater and soil water. Rain is the only pure end member. A large portion of fluid in a cesspool is water used to flush toilets or is rinse water from clothes washing, bathing and dishwashing. This flush water is water pumped from groundwater wells which in fact is rainwater that recharged any where from 10-8000 years ago (Buxton and Modica, 1992). If the water is young enough it is possible that it was already mixed with wastewater and soil water. Wastewater and soil water are mixing with rain water in the vadoze zone and aquifer. Recharge from rain was calculated as the yearly recharge rate (22” per year) multiplied by the area of the capture zone. Wastewater recharge was estimated by multiplying the total number of dwellings within the capture zone by the average discharge rate per cesspool per year using a discharge rate of 240 gallons per cesspool per day. Total dwellings were calculated assuming 1 dwelling per acre for low density residential land use, 5.5 dwellings per acre for medium density residential land use and 11 dwellings per acre for high density residential land use (CDM, 2003). The average dwellings per acre was multiplied by acre of land use for each residential land use and then added for all residential land use. Estimates of the amount of soil water influenced by turfgrass are more difficult to determine. Not all lawns are fertilized or watered at the same rate or at all. The influence of rain infiltrating turfgrass is also difficult to discern. Porter (1977) conducted a survey of turfgrass fertilization at more than 50 homes in seven towns in Suffolk and Nassau Counties, Long Island, NY. He found that fertilizer use increased as family income increased and that water applied was erratic and some individuals apply water excessively. Using percent of area turfed and fertilized according to land use from Porter (1977) the area of turfgrass fertilized for each capture zone was estimated. These values are 33% for low density, 36% medium density and 28% high density residential land use. Since the volume of water infiltrating fertilized lawns is difficult to

Table 7 Mixing estimates of groundwater wells

Well Id	**Location**		**Land Use**	**Rain**	**Waste**	**Soil**	**Rain**	**Waste**	**Soil**
				L/yr x10^{6}	*L/yr x10*^{6}	*L/yr x10*^{6}	range %	range %	range %
J	Northport	monitoring	Ag	nd	nd	nd	0	20-100	5-100
S-103523	Southold	SCWA	Ag	106	8	4	0-90	5-70	5-50
S-105669	Southold	SCWA	Ag	97	11	8	30-90	5-40	5-40
S-24850	Southold	SCWA	Ag	64	2	1	0-100	0-80	5-100
D	Northport	monitoring	LD	nd	nd	nd	60-80	0-30	10-20
S-20530	Huntington	SCWA	LD	441	81	48	70-100	0-20	0-10
S-72326	Huntington	SCWA	LD	381	119	89	60-100	0-20	0-20
B	Northport	monitoring	MD	nd	nd	nd	60-70	10-20	20-30
F	Northport	monitoring	MD	nd	nd	nd	0-20	20-40	60-70
G	Northport	monitoring	MD	nd	nd	nd	0-40	20-80	20-30
I	Northport	monitoring	MD	nd	nd	nd	0-70	20-100	0-20
S-53747	Huntington	SCWA	MD	506	258	92	50-70	10-30	10-40
S-16309	Brookhaven	SCWA	MD	261	195	52	50-90	10-40	0-10
S-56133	Huntington	SCWA	MD	1171	779	223	50-70	20-40	10-20
S-100453	Babylon	SCWA	MD	260	70	40	70-90	0-20	5-10
S-33820	Huntington	SCWA	MD	821	524	127	50-80	20-40	5-20
S-11105	Huntington	SCWA	MD	107	69	22	40-60	10-40	10-30
S-88463	Huntington	SCWA	MD	434	227	84	40-60	20-30	10-40
S-25776	Huntington	SCWA	MD	719	396	149	20-40	20-50	10-50
S-39536	Huntington	SCWA	MD	256	156	51	60-80	10-30	5-20
S-15514	Huntington	SCWA	MD	1004	581	214	30-50	15-33	10-40
S-105300	Huntington	SCWA	MD	63	45	13	50-90	10-37	0-10
S-72271	Smithtown	SCWA	HD	282	231	44	50-90	9-42	5-20
A	Northport	monitoring	MD/GC	nd	nd	nd	40-50	20-30	30-36
E	Northport	monitoring	MD/GC	nd	nd	nd	50-70	14-28	20-26
S-57961	Brookhaven	SCWA	OS	125	0	0	80-100	0-6	0-9
S-59347	Islip	SCWA	OS	113	0	0	90-100	0-2	0-5
S-70155	E.Hampton	SCWA	OS	155	0	0	10-100	0-80	0-19
S-82174	Brookhaven	SCWA	OS	1179	0	0	90-100	0-5	0-9
S-100608	Brookhaven	SCWA	Vacant	64	7	6	80-100	0-10	5-8

monitoring wells from Bleifuss et al. (2000), depth is feet to top of well screen .Land Use abbreviations: Ag=agricultural, HD=high density residential, MD=medium density residential, LD=low density residential, GC=golf course, OS=open space

distinguish a simple estimate was to assume a value based on the needs of the turf, which is 1.5" of water per week (Porter, 1977) for three months out of the year (summer months). Table 7 reports the water budget and estimated percent contribution for all three nitrate sources, as described above.

Groundwater samples sourced in vacant land use plot as a mix between rain and soil water as shown in Figures 8, 9 and 11. Figure 10 shows less mixing with soil water and some mixing with wastewater. Mixing proportions (Table 7) for rain range from 80-100% with one sample showing as low as 10%. This sample S-70155 is influenced by discharge from a sewage treatment plant showing as high as 80% mixing with wastewater. The other samples show no more than 10% wastewater mixing and 20% soil water mixing.

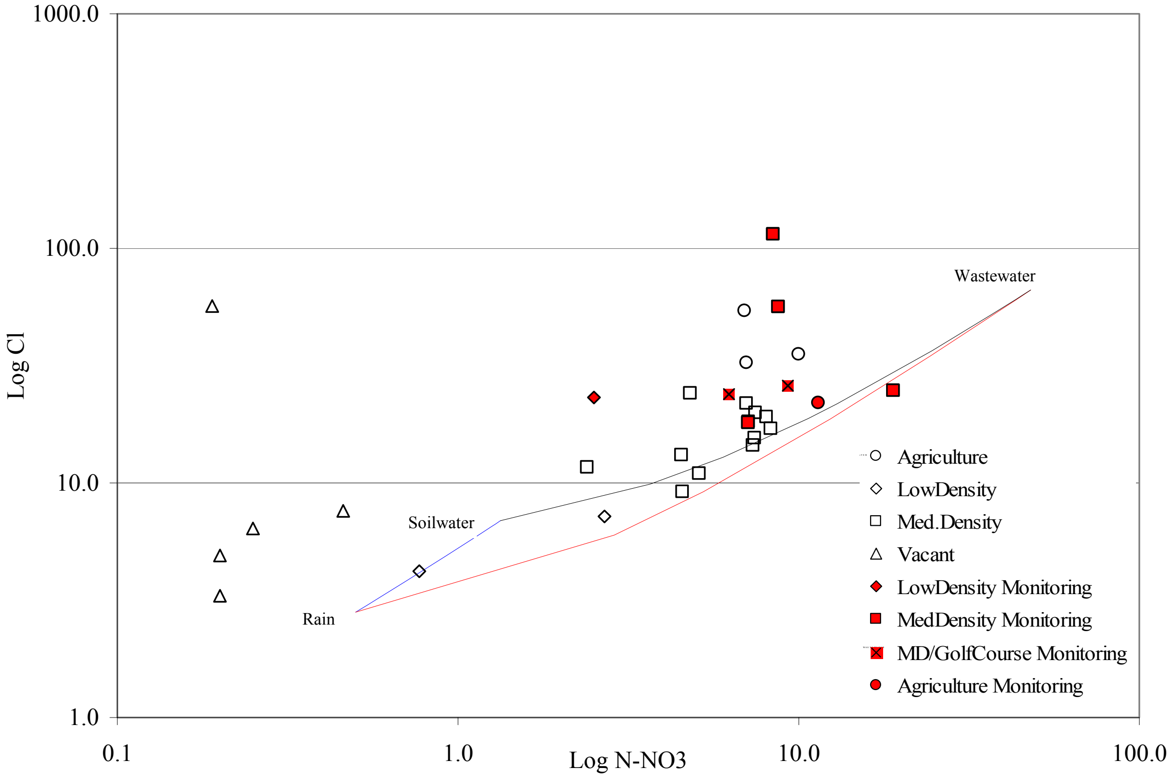


Figure 8 Log Cl vs. Log N-NO$_3$. *Mixing lines are indicated between end members. Refer to legend for groundwater sample identification.*

Sulfate concentrations are low in public supply wells sourced in low residential density land use, indicating groundwater older than the onset of sulfur-rich acid rain. These two samples plot close to rain water in Figure 10. Figure 8 show some mixing with soil water and wastewater. The monitoring well sourced in low residential density land use plots as a mix of all three sources in Figures 9 and 10 and outside the mixing triangle in Figures 8 and 11. This sample could be influenced by road salt. Mixing proportions (Table 7) for all three samples show 60-100% mixing of rain water, 0-30% mixing with wastewater and 0-20% mixing with soil water.

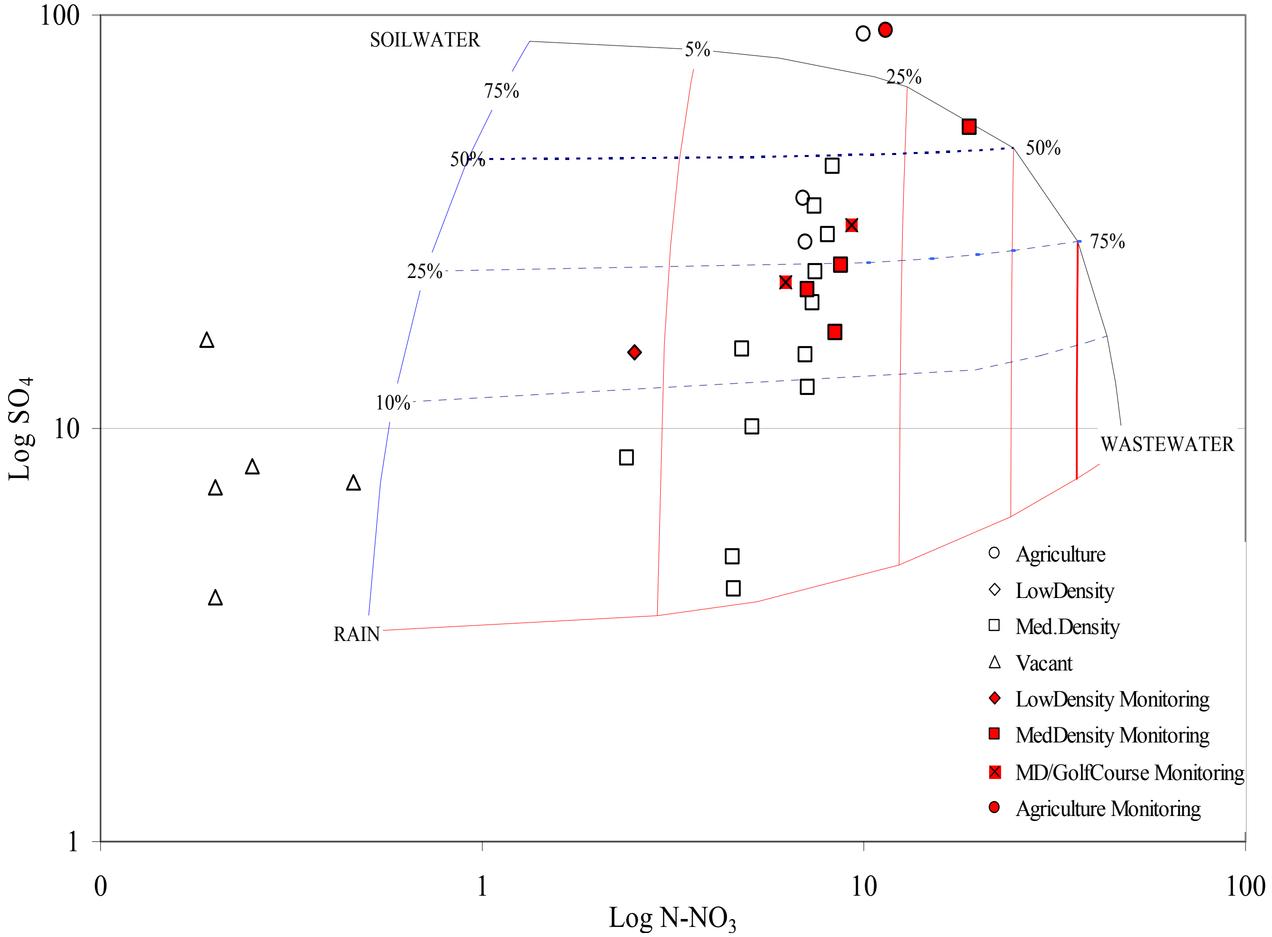


Figure 9 Log SO_4 vs. Log N-NO_3. *Mixing lines are indicated between end members. Refer to legend for groundwater sample identification. Red solid mixing contours are for wastewater and blue dashed contours are for soil water.*

Most groundwater samples sourced in medium residential land use plot within the mixing triangle on Figures 9 and 10 indicating mixing of rain, soil water and wastewater. Both plots suggest less than 50% mixing of soil water. Figure 9 suggest up to 25% mixing with wastewater and Figure 10 suggest less than 50%. Two monitoring wells plot outside the mixing triangle on Figure 10. This could indicate a large contribution from wastewaters or be an influence of road salt on the chloride concentrations. It is likely road salt is an influence on one of the samples since it plots within the mixing triangle on Figure 9. The other sample plots on the mixing line between soil water and wastewater on Figure 10 and I would suggest that it is highly influenced by wastewater. Monitoring wells are shallow and usually reflect land use to a greater degree than deeper supply wells since there is less time for dispersion and dilutions of contaminants. Many groundwater samples sourced in medium residential land use plot outside the mixing triangle on Figure 8. Road salt is a likely contaminant since for most groundwater wells transportation, i.e. roads, are among the top three land uses in the capture zone (Table 6). The 16 groundwaters sourced in medium residential density land use range in percent mixing.

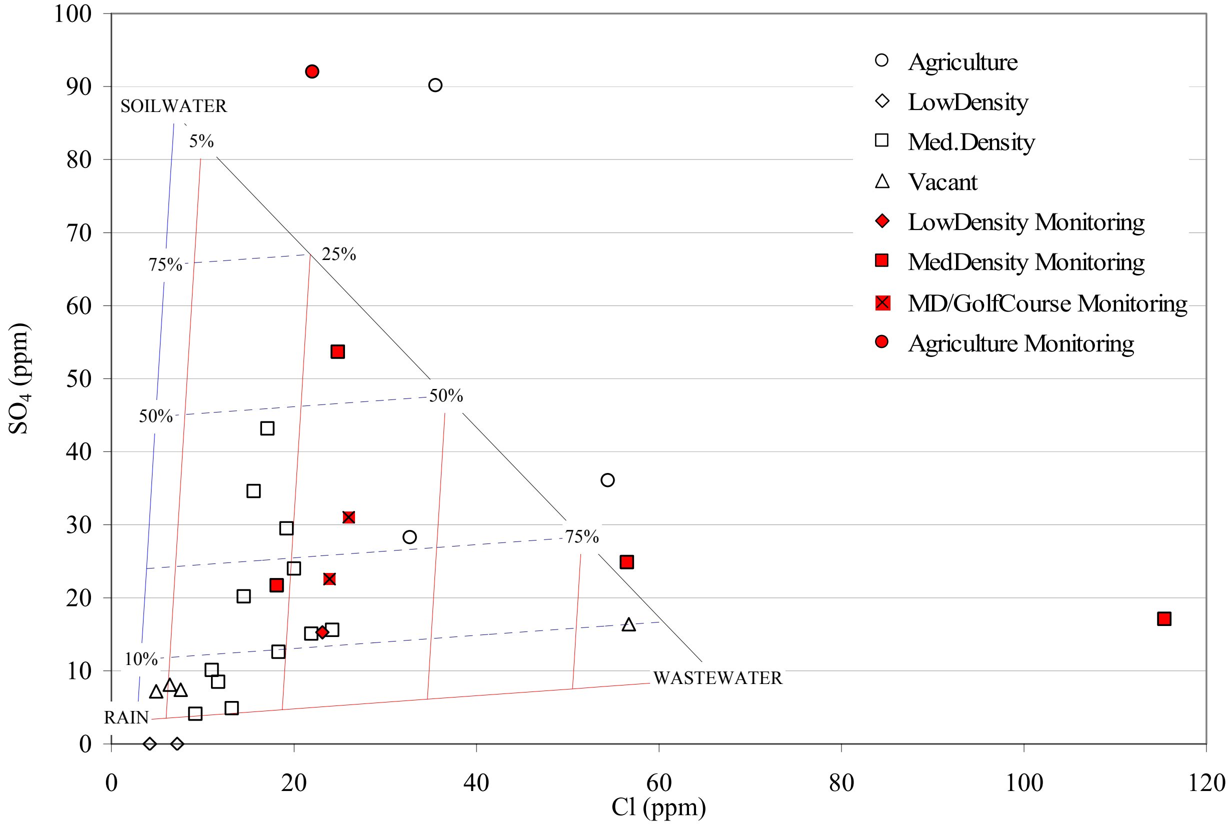


Figure 10 SO_4 vs. Cl. *Mixing lines are indicated between end members. Refer to legend for groundwater sample identification. Red solid mixing contours are for wastewater and blue dashed contours are for soil water. Source name is near median value.*

Rain water is 0-90%, soil water is 0-70% and wastewater is 0-100%. It is obvious that these groundwaters are influenced by both soil water and wastewater but the relative proportions vary greatly from sample to sample. When the portion of rain mixing for a given sample is zero the mixing proportions of the other two sources will be overestimated. This is why mixing percents are as high as 70% in soil water and 100% in wastewater. Excluding the samples with 0% rain gives a maximum of 50% for both sources, in agreement with Figures 9 and 10.

Groundwater samples sourced in agricultural land use yield mixing proportions for all nitrate sources between 0 and 100%. It is obvious that these groundwaters can't be characterized by the ternary system presented for residential land use but in fact are mixing with other sources, such as agricultural practices.

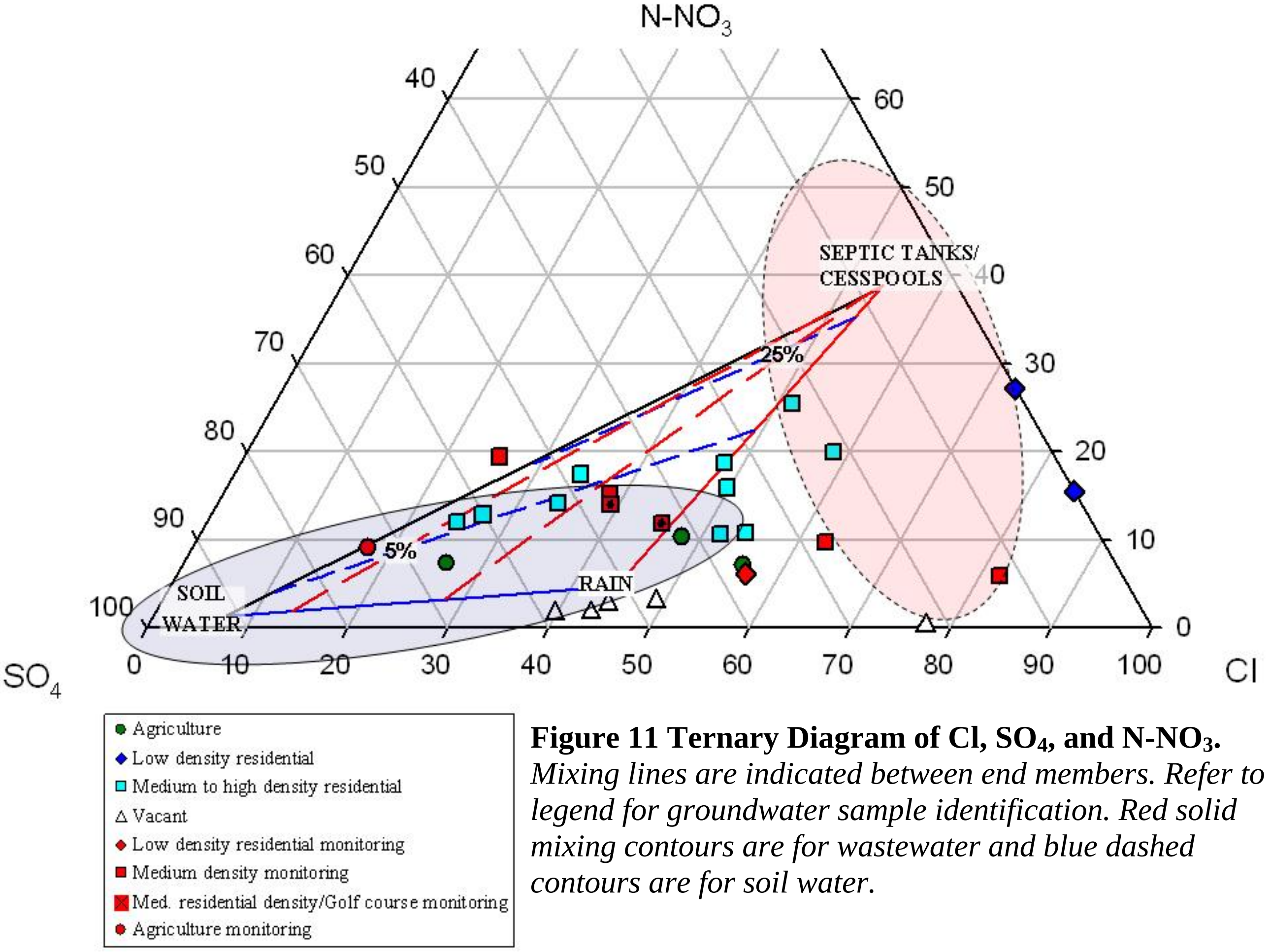


Figure 11 Ternary Diagram of Cl, SO_4, and $N\text{-}NO_3$. *Mixing lines are indicated between end members. Refer to legend for groundwater sample identification. Red solid mixing contours are for wastewater and blue dashed contours are for soil water.*

Figure 11 is a ternary diagram of Cl, N-NO_3 and SO_4. Again, groundwaters influenced by low residential land use are low in SO_4 and plot on the zero SO_4 contour line possibly indicating old groundwater (Schoonen and Brown, 1994). The groundwater samples sourced in vacant land use plot close to rain water. Groundwater samples influenced by residential land use would suggest mixing of all three sources with mixing greater than 5% with wastewater and for soil water. The groundwaters sourced in agricultural land use plot close to groundwaters sourced in medium residential density land use samples.

iv. Conclusions

Major element data along with nitrate compositions of groundwater show a distinct relationship between land use and sources of nitrate contamination such that the geochemistry of groundwater associated with (1) vacant or open land use has a signature close to rain water (2) low residential density land use is mostly influenced by rain water with some contributions of soil water and wastewater (3) medium residential density land use plots as a mixture of rain, soil water and wastewater and (4) agricultural land use is not distinguishable from groundwater associated with urban land use.

These data allow estimates but do not allow precise calculations of the proportions of rainwater, soil water and waste water in groundwater because of the rather large ranges in the concentrations of the elements in the sources. Sulfate concentrations give the best estimate for contributions by soil water. Nitrate concentrations give the best estimate for contributions by wastewater. Water budgets for capture zones aid in placing constraints on mixing proportions of nitrate sources for a given groundwater.

v. References

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