MAJOR ION CHEMISTRY AND MIXING PROPORTIONS OF NITRATE SOURCES IN GROUNDWATER

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ABSTRACT. The purpose of this study is to place constraints on the sources of nitrate in groundwater using major ion chemistry. Nitrate contamination of drinking water is a concern in residential areas. To accurately evaluate contamination of groundwater it is essential to determine the chemistry of known sources. We characterized the geochemistry of soil water samples from below maintained turfgrass sites and sewage from septic tank/cesspools. Our data show a distinct difference in the major ion chemistry between these sources. Groundwater wells plotted according to their major land use on binary ion diagrams and show that wells of similar land use have similar geochemistry and similar source contributions. Although volumetric source proportions to groundwater wells are similar for soil water and sewage within a given land use, sewage contributes a greater proportion to the nitrate concentration in groundwater wells. For example, sewage contributes between 86-100% of the nitrate in wells sourced in medium density residential land use, even when accounting for a 50% reduction in nitrate concentrations from the septic tank/cesspool system. Our results indicate that to decrease the nitrate concentrations in groundwater one must reduce the load from septic tank/cesspool systems.

Introduction

Nitrate concentrations of groundwater in residential areas are steadily increasing across the United States (Nolan and Stoner, 2000). In these areas, contamination is in part due to nonpoint sources. The two main types of nonpoint sources of nitrate contamination in residential areas are turfgrass fertilizers and sewage from septic tank/cesspool systems. Any increase of nitrate concentrations can be alarming, since nitrate is a health concern. For example, blue baby syndrome develops at levels above the EPA drinking water standard of 10 ppm nitrate as nitrogen. Excess nitrate also causes eutrophic conditions in receiving waters, which may compromise ecosystem health.

In order to place constraints on sources of nitrate concentrations of residential well water in Suffolk County, New York, we have analyzed the major ion chemistry of the two main sources. These are soil water collected below turfgrass sites managed in one of three ways (chemical fertilizer, organic fertilizer or no fertilizer), and residential sewage from septic tank/cesspool systems. Major ion concentrations for groundwater from monitoring wells and Suffolk County Water Authority municipal wells were then evaluated according to land use. The available data for the groundwater were next compared to those for rain, sewage and soil water on binary diagrams. Cation concentrations, since they are not conservative, were evaluated using a non-linear, multi-component, interactive, sorption model. Estimates of mixing proportions from each source to a given groundwater well were calculated using mass balance and a water budget approach. This approach can have wide application since major ion data are routinely monitored by local water agencies, who can use this method with minimal effort.

Methods

To evaluate the chemical signature of lawn maintenance, ceramic suction lysimeters were installed under seven fertilized lawns and one unfertilized lawn at depths less than 150 cm, beneath Suffolk County Water Authority property and at Stony Brook University (Munster, 2004). Two locations underwent chemical turfgrass treatment while the other five were treated with organic fertilizer. Chemical fertilizers (Scotts and Lesco brands) were applied according to the manufactures guidelines. Pro Grow, the organic fertilizer, was applied by an organic landscaper. Soil water samples from lysimeters were acquired monthly during 2003, totaling 70 samples. Literature based data were used to define the composition of rain for Suffolk County (Proios and Schoonen, 1994; Schoonen and Brown, 1994).

Twelve sewage samples from residential septic tanks/cesspool systems and 21 public sewage treatment plant influent samples, which may include residential and industrial sources, were acquired from the Suffolk County Department of Public Works. All sewage samples were prepared by centrifuging to separate the solids from the liquid. If necessary the supernate was decanted and centrifuged again. The supernate was then filtered with Millipore AP15 glass fiber filters.

Both soil water and sewage samples were collected in polypropylene bottles. Bottles for cation analysis were acid rinsed and these samples were preserved to a pH of 2, with a few drops of concentrated HCl. All samples were stored at 4ºC until analyzed. The samples were analyzed by the Cornell University Nutrient and Elemental Analysis Laboratory. Cation concentrations were determined using inductively coupled plasma optical emission spectroscopy. Anion concentrations were determined using ion chromatography.

Binary ion plots and calculating mixing proportions. Three mixing lines were calculated (as in Figures 1, 2); rain mixing with soil water, rain mixing with sewage and soil water mixing with sewage for the binary ion plots. Mass balance of nitrate sources, for a two source system, is calculated as

$$C_{mix}^{Y}=C_{1}^{Y}(F) + C_{2}^{Y} (1-F)$$

where C denotes concentration of ion Y, F is the fraction of source 1 and 1-F is the fraction of source 2, C_1 and C_2 are the concentrations of Y for each of the two sources and C_{mix} is the concentration in groundwater for a given value of F. Because there is a relatively large range in compositions of the sources and because there may also be other sources, for example road salt, groundwater samples may not lie directly on a mixing line or in the mixing field; therefore multiple plots and mixing calculations should be used in conjunction with each other to assess estimates of mixing. Normalizing to a conservative ion, such as chloride, minimizes the effects of dilution and dispersion because Cl rarely enters into oxidation-reduction reactions and is not readily sorbed. Plots normalized to the same ion, as in Figures 1, are equivalent to binary ion plots and mixing of end members is along straight lines (Langmuir et al., 1978). Mixing lines of three sources on binary ion plots form a mixing triangle. Groundwater compositions falling within this triangle include water from all three sources.

To calculate the dashed mixing lines (as in Figure 2) for a ternary system the following equation is used:

$$C_{mix}^{Y}=C_{1}^{Y}(F_{1}) + C_{2}^{Y} (F_{2}) + C_{3}^{Y} (F_{3}); \text{ where } F_{1}+F_{2}+F_{3}=1$$

This approach allows us to estimate the proportions of soil water, sewage and rain water on binary ion plots for a given groundwater.

Mixing percents were evaluated by calculating the water budgets for each groundwater capture zone (CDM, 2003) for Suffolk County Water Authority public supply wells where the capture zones were available. This method estimates the volume of recharge from rain, sewage and soil water based on land use in each capture zone.

Pristine water from groundwater wells is from rain that recharged in undeveloped areas from 10-8000 years ago (Buxton and Modica, 1992). The composition of pristine groundwater is dry and wet precipitation whose composition will have been affected by reaction with the sediments in the soil and along the path of the groundwater. Pristine groundwater will also have changed composition over time as precipitation composition has changed with development. For example, recently acid rain would have added more SO_4 and NO_3. Because the soil and sediments on Long Island are high in quartz, reaction of water with sediments probably does not change the composition of precipitation significantly. Recharge from rain was calculated as the yearly recharge rate (56 cm per year; Koppelman, 1984) multiplied by the area of the capture zone.

Sewage recharge was estimated by multiplying the total number of dwellings within the capture zone by the average discharge rate per cesspool per year (900 L per cesspool per day; Flynn et al., 1969). Total dwellings were calculated using the definitions of 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 density of dwellings per acre was multiplied by acre of land use for each residential land use and then added together.

An estimate of the amount of soil water influenced by turfgrass that recharges to the groundwater is difficult to determine. Not all lawns are fertilized or watered at the same rate or at all. Porter (1980) 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. Using percent of area turf and fertilized according to land use (Porter, 1980), 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.

The influence of rain vs. irrigation water infiltrating turfgrass is difficult to discern. Porter (1980) found in his survey that water application was erratic and some individuals apply water excessively. We used a simple estimate based on the needs of the turf, which is 3.8 cm of water per week (Porter, 1980) for the three summer months out of the year.

Results and Discussion

We calculated mixing proportions for 21 public supply wells and 8 monitoring wells using two approaches 1) a mass balance approach and 2) one based on capture zones of public supply wells, which we call a water budget approach. The groundwater wells are predominantly influenced by a sewage signature (Figure 1). Companion plots, as shown in Figure 1, are used to evaluate mixing relationships. Normalizing the data to a conservative element, such as chloride, reduced the effects of dilution and dispersion but one can not use ratios to evaluate mixing percentages.

Evaluating the mixing proportions using the mass balance approach (Table 1, Figure 2) shows that soil water and sewage account for similar proportions in the groundwater wells according to major land use. These calculated percents are volumetric proportions. When one takes into account the concentrations of nitrate in the end members the contribution of sewage is overwhelming (Table 2). Even when accounting for a 50% reduction of nitrate in sewage from the source to the well sewage contributed between 46-97% for groundwater wells sourced in low residential density land use, 84-100% for groundwater wells sourced in medium residential density land use and between 0-87% in groundwater wells sourced in open space land use. It is clear that in order to reduce the nitrate impact to Suffolk County groundwater the load from sewage must be reduced.

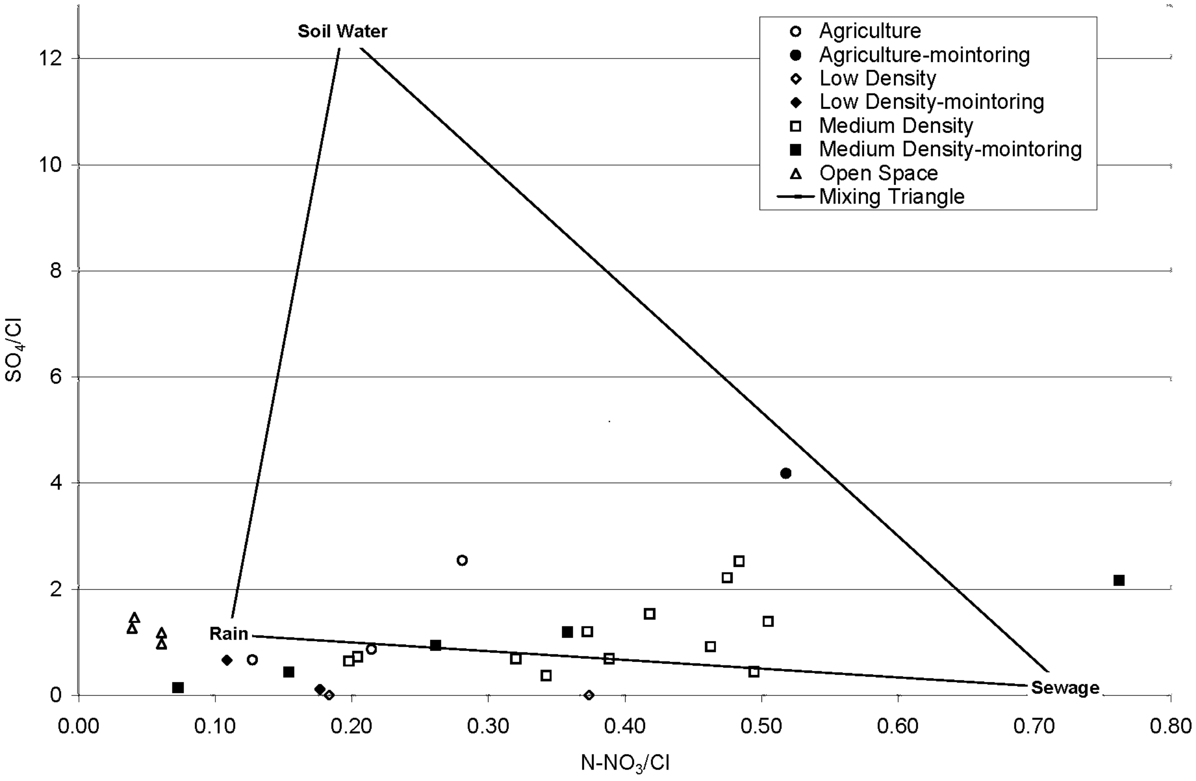

Figure 1. Companion plot. Demonstrates mixing relationships but not mixing proportions.

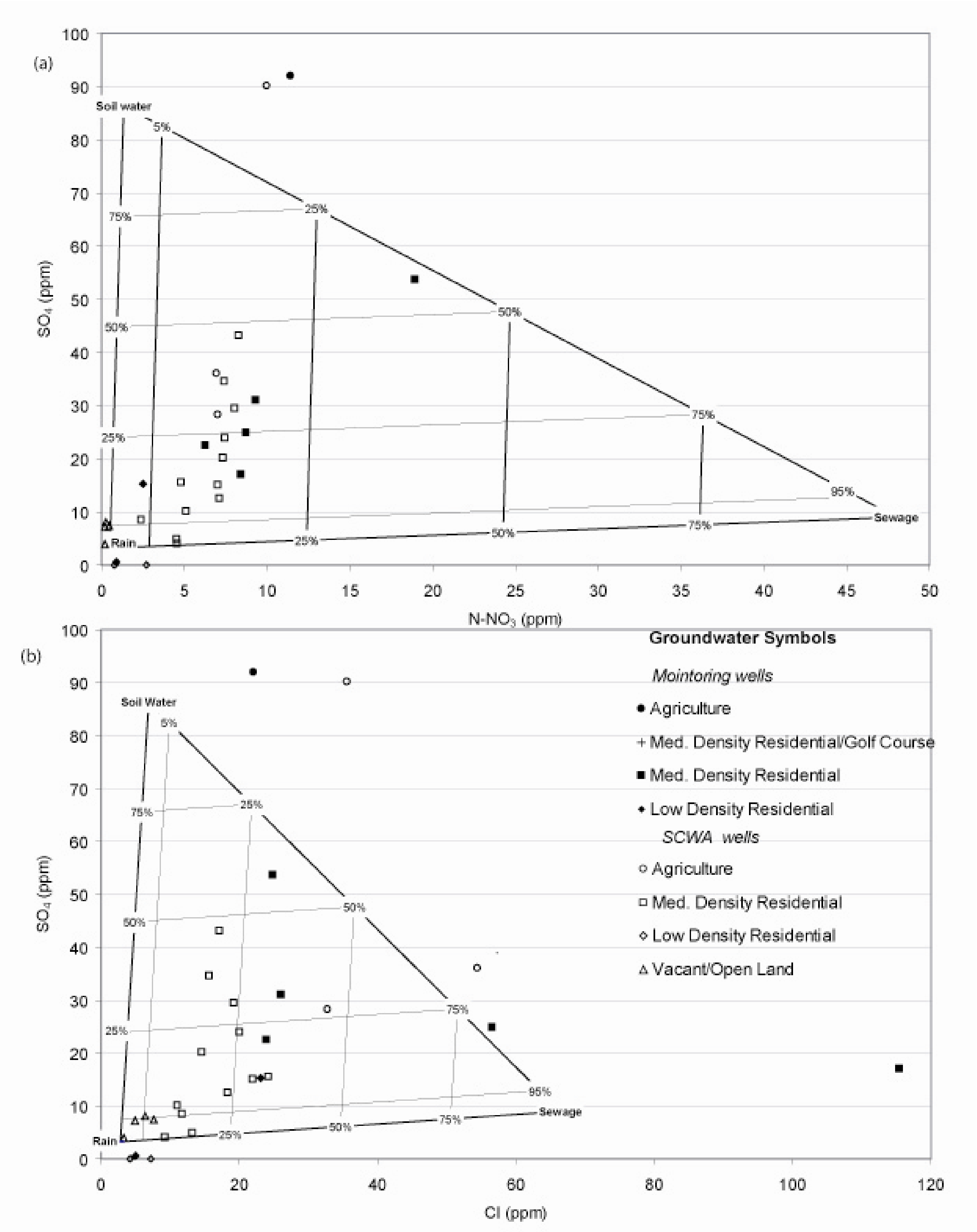

Figure 2. Binary Ion Diagrams. (a) SO$_4$ vs N-NO$_3$ (b) SO$_4$ vs Cl, used to evaluate mixing proportions.

Table 1. Mixing estimates based on the water budget and mass balance approach.

				Water Budget			SO_4 vs. Cl			SO_4 vs. N-NO_4		
	Land Use	**Location**	**Well Type**	**Rain**	**Sewage**	**Soil Water**	**Rain**	**Sewage**	**Soil Water**	**Rain**	**Sewage**	**Soil Water**
	(%)			*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*	*(%)*
1	Ag	Northport	monitoring	90	7	3	0	23	105	0	21	105
2	Ag (59)	Southold	SCWA	83	10	7	0	79	34	49	13	39
3	Ag (55)	Southold	SCWA	95	3	2	28	45	27	58	13	29
4	Ag (69)	Southold	SCWA	nd	nd	nd	0	45	102	0	18	103
5	LD	Northport	monitoring	nd	nd	nd	57	31	12	82	4	14
6	LD	Northport	monitoring	nd	nd	nd	100	4	0	102	1	0
7	LD (40)	Huntington	SCWA	77	14	8	97	7	0	100	5	0
8	LD (55)	Huntington	SCWA	65	20	15	102	2	0	103	1	0
10	MD/GC	Northport	monitoring	nd	nd	nd	35	34	31	50	18	32
11	MD/GC	Northport	monitoring	nd	nd	nd	47	32	21	66	12	22
12	MD	Northport	monitoring	nd	nd	nd	11	31	59	4	38	58
13	MD	Northport	monitoring	nd	nd	nd	0	83	20	58	17	25
14	MD	Northport	monitoring	nd	nd	nd	0	177	4	68	16	16
9	MD (60)	Smithtown	SCWA	51	41	8	80	12	7	83	10	8
15	MD (54)	Babylon	SCWA	70	19	11	81	14	5	90	4	6
16	MD (74)	Huntington	SCWA	52	37	11	83	16	1	90	8	1
17	MD (61)	Huntington	SCWA	54	35	11	51	26	23	62	14	24
18	MD (70)	Huntington	SCWA	56	32	12	46	18	37	49	14	37
19	MD (78)	Brookhaven	SCWA	51	38	10	90	10	0	91	9	0
20	MD (68)	Huntington	SCWA	57	31	12	34	19	47	37	16	47
21	MD (58)	Huntington	SCWA	56	36	9	55	33	13	77	9	14
22	MD (69)	Huntington	SCWA	55	34	11	67	24	10	76	14	10
23	MD (59)	Huntington	SCWA	59	30	11	64	17	19	67	14	19
24	MD (66)	Huntington	SCWA	54	36	10	59	29	12	73	13	13
25	MD (64)	Huntington	SCWA	58	30	11	46	24	30	54	15	31
26	OS (100)	Brookhaven	SCWA	100	0	0	88	7	5	95	0	5
27	OS (95)	Islip	SCWA	100	0	0	99	1	1	100	0	1
28	OS (90)	Brookhaven	SCWA	100	0	0	89	5	5	95	0	6
29	OS (96)	Brookhaven	SCWA	100	0	0	92	3	5	96	0	5

Nd=not determined, \=below detection limit, SCWA=Suffolk County Water Authority, Ag=agricultural; HD=high density residential; LD=low density residential; MD=medium density residential; GC=golf course; OS=open space.

Table 2. Contribution of nitrate to groundwater.

	Land Use	**Location**	**Well Type**	**Measured N-NO_3**	**Predicted N-NO_3 values from Mixing Estimates**		**Percent contribution of nitrate from sewage**	
	(%)				*with 50% Denitrification*	*with out*	*with 50% Denitrification*	*with out*
1	Ag	Northport	monitoring	11.40	2 - 7	4 - 13	77 - 89	87 - 89
2	Ag (59)	Southold	SCWA	6.92	3 - 19	5 - 38	82 - 99	89 - 99
3	Ag (55)	Southold	SCWA	7.01	1 - 11	2 - 22	58 - 98	73 - 98
4	Ag (69)	Southold	SCWA	9.97	6 - 12	10 - 23	89 - 94	86 - 94
5	LD	Northport	monitoring	2.51	2 - 8	3 - 15	94 - 97	76 - 97
6	LD	Northport	monitoring	0.88	1 - 1	1 - 2	58 - 78	45 - 78
7	LD (40)	Huntington	SCWA	2.69	2 - 4	3 - 7	78 - 93	82 - 93
8	LD (55)	Huntington	SCWA	0.77	1 - 5	1 - 10	46 - 95	37 - 95
10	MD/GC	Northport	monitoring	9.30	5 - 9	9 - 17	93 - 97	93 - 97
11	MD/GC	Northport	monitoring	6.25	3 - 8	6 - 16	94 - 97	90 - 97
12	MD	Northport	monitoring	18.91	8 - 10	16 - 19	90 - 96	95 - 96
13	MD	Northport	monitoring	8.70	5 - 20	9 - 40	99 - 99	93 - 99
14	MD	Northport	monitoring	8.40	4 - 42	8 - 85	100 - 100	93 - 100
9	MD (60)	Smithtown	SCWA	5.09	3 - 10	5 - 20	86 - 98	90 - 98
15	MD (54)	Babylon	SCWA	2.39	1 - 5	2 - 10	87 - 95	78 - 95
16	MD (74)	Huntington	SCWA	4.52	2 - 9	5 - 18	90 - 98	90 - 98
17	MD (61)	Huntington	SCWA	7.45	4 - 9	7 - 17	92 - 98	92 - 98
18	MD (70)	Huntington	SCWA	7.41	4 - 8	7 - 16	86 - 97	90 - 97
19	MD (78)	Brookhaven	SCWA	4.55	3 - 10	5 - 19	84 - 98	90 - 98
20	MD (68)	Huntington	SCWA	8.27	5 - 8	8 - 15	86 - 97	90 - 97
21	MD (58)	Huntington	SCWA	4.79	3 - 9	5 - 17	95 - 98	88 - 98
22	MD (69)	Huntington	SCWA	7.11	4 - 9	7 - 17	93 - 97	93 - 97
23	MD (59)	Huntington	SCWA	7.32	4 - 8	7 - 15	88 - 97	92 - 97
24	MD (66)	Huntington	SCWA	7.01	4 - 9	7 - 18	94 - 98	92 - 98
25	MD (64)	Huntington	SCWA	8.03	4 - 8	8 - 15	90 - 97	92 - 97
26	OS (100)	Brookhaven	SCWA	0.46	1 - 2	1 - 4	0 - 87	0 - 87
27	OS (95)	Islip	SCWA	0.20	1 - 1	1 - 1	0 - 41	0 - 41
28	OS (90)	Brookhaven	SCWA	0.25	1 - 2	1 - 3	0 - 83	0 - 83
29	OS (96)	Brookhaven	SCWA	0.20	1 - 1	1 - 2	0 - 73	0 - 73

SCWA=Suffolk County Water Authority, Ag=agricultural; HD=high density residential; LD=low density residential; MD=medium density residential; GC=golf course; OS=open space.

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