Nonpoint sources of nitrate and perchlorate in urban land use to groundwater, Suffolk County, NY

A Dissertation Presented

by

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to

The Graduate School

in Partial Fulfillment of the

Requirements

for the Degree of

Doctor of Philosophy

in

Geosciences

Stony Brook University

August 2008

Stony Brook University

The Graduate School

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Abstract of the Dissertation

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More than fifty percent of the population in the United States relies on groundwater as the sole source of potable water. Groundwater in Suffolk County, NY, the study area, provides all potable water to the residents. Regrettably, urban contamination is increasingly threatening groundwater supplies. Two common inorganic contaminates in urban settings are nitrate (NO_3) and perchlorate (ClO_4). The U.S. Environmental Protection Agency national drinking water standard is 10 mg/L for N-NO_3. No national drinking water standard has been set for ClO_4 but many states have set advisory levels. The contaminant planning level in New York State is 5 µg/L and the maximum allowable level is 18 µg/L.

Nitrate and perchlorate are common co-contaminants in urban settings. Both ions are mobile in groundwater, moving quickly from the source of contamination. The goal of this research is to identify likely sources of these ions in urban areas. Once identified, hopefully contamination can be reduced at the source. Urban sources are identified as residential sewage, road runoff from highways, and organic fertilizer applied to urban lawns. The lawns are dominantly turfgrass and were sampled for soil water affected by turfgrass fertilizer, lawn clippings, soil cores, and bulk precipitation. In addition to N-NO_3 and ClO_4, the sources were analyzed for ion concentrations of Ca, Na, K, Mg, Cl, SO_4, PO_4, Br, I, B, Sr, and N-NH_4.

Perchlorate concentrations of bulk precipitation are between 0.2 to 3 µg/L, with the highest concentrations influenced by atmospheric fallout from firework displays. The ion content of bulk precipitation is predominantly influenced by sea spray with minor components (<16%) of anthropogenic contamination and terrestrial dust. The average soil water concentrations of perchlorate, collected at 100 cm, beneath lawns treated with organic fertilizer is 90 μg/L which is 45 times higher than concentrations beneath lawns treated with chemical fertilizer or lawns that were not fertilized. However, nitrate concentrations of soil water beneath the lawns treated with chemical fertilizers are statistically higher than the lawns treated with organic fertilizer, with average values of 9.7 mg/L and 6.5 mg/L respectively.

Perchlorate concentrations in sewage range from below detection (0.1 μg/L) to 260 μg/L, with an average concentration of 2.2 μg/L. Perchlorate from sewage will likely raise the concentration in the groundwater above natural levels and depending on the density of septic systems and the amount of perchlorate reduction by bacteria, the groundwater concentrations may increase to near or above the NY State advisory level of 5 μg/L. Road runoff collected in catch basins and recharge basins have, on average, 3 μg/L ClO_4 and 2 mg/L Total Inorganic N (nitrate and ammonium). In areas where road runoff directly recharges to groundwater, the concentrations from these areas are of concern for groundwater quality. While the average concentration, 3 μg/L, is below the NY state drinking water planning level, some samples are above this level at concentrations as high as 18 μg/L. As a result, we have to be concerned about the risk of concentrations of perchlorate in groundwater increasing to above the New York State planning level.

Perchlorate was found in nearly all samples analyzed in this study. Concentrations of some samples are a concern for groundwater quality. However, without a clear understanding of the health impacts of perchlorate ingestion it is difficult to clearly assess impacts to groundwater quality. What is clear is that perchlorate contamination is likely widespread and more research is needed in understanding nonpoint source pollution in addition to a clear understanding of health impacts.

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Acknowledgments

This research would not have been possible without the support of the Suffolk County Water Authority (SCWA). It is encouraging to see a business invested in more than the bottom line. I would personally like to thank Steve Jones, Michael Stevenson and Michael DeBlasi for the support and encouragement. I would especially like to thank Jeff Rinker and Steve Brozyna for their help in maintaining the lawns on SCWA property and Ed Truskol for providing groundwater data.

I have had many helping hands conducting six years of fieldwork including Sunny Xu, Soma Sen, Shuangtao Zhang, Valerie Slonecki and Caitlin Young. Caitlin is now carrying on the torch of sampling the sites Peter Schumann and I established. Their support in the field was greatly appreciated, especially on the beautiful days which included sleet and rain. I would also like to thank Valerie Slonecki for taking the time to proof read most of my chapters. It was helpful to get a fresh perspective on the data I've spent the last four years thinking about.

In the lab, I would like to thank Dr. David Hirshberg who, over time, trusted me with a very new expensive piece of equipment. I appreciated his patience and trust. Besides helping to analyzing hundreds of samples David was a positive influence on my experience at Stony Brook University.

Staying on the theme of lab work I like to thank Dr. Todd Anderson for responding to an anonymous e-mail and allowing a desperate student looking for a lab to analyze samples for perchlorate content to collaborate with him and eventually leading to my collaboration with Dr. Andrew Jackson's lab at Texas Tech. I would like to thank Dr. Jackson and the students in his lab. I would especially like to thank Srinath Rajagopalan and Brad Thornhill for training me in the lab and allowing me to interrupt their schedule to analyze my samples.

At Stony Brook University I would like to thank Ben Vitale for all his help in the Isotope Lab. I would like to thank Claire Ondrovic, Owen Even, Loretta Budd and Diana Isgro for their administrative help.

I would like to thank my committee members and especially Gil Hanson, my adviser. His guidance in my research was helpful and insightful although at times, frustrating. Gil is very skeptical and it takes a lot of hard work and understanding of ones' subject to convince Gil your concept is correct, this of course, makes you more confident in your work and makes the final project much more thorough, concise and accurate. Henry Bokuniewicz was involved in my research and provided much appreciated guidance. I also appreciate him connecting me with the Long Island Groundwater Planning group. It was always a great experience to present my work to that diverse group of scientists and government, state and city officials. I would also like to thank Troy Rasbury as she has been an excellent role model as a successful women scientist. Although our research isn't closely related she always gave helpful comments and incites about my presentations in Dirt Group. We also work together frequently to solve problems in the Isotope Lab.

To finish I would like to acknowledge my husband, C. Dave Martin, for all he has done. I appreciate him for believing in me when sometimes I didn't believe in myself, and for his help in proof reading some of my work over my graduate career.

1. Introduction

1.1. Study Area

The study area, Suffolk County, NY, (Figure 1.1) is the easternmost county on Long Island, covering approximately 2,300 square kilometers. Long Island extends eastward from New York City, separated by the Hudson and East Rivers. Until World War II Suffolk County was dominantly rural or forested; since then residential land use has steadily increased eastward from New York City. Population of Suffolk County as of 2005 was 1.47 million.

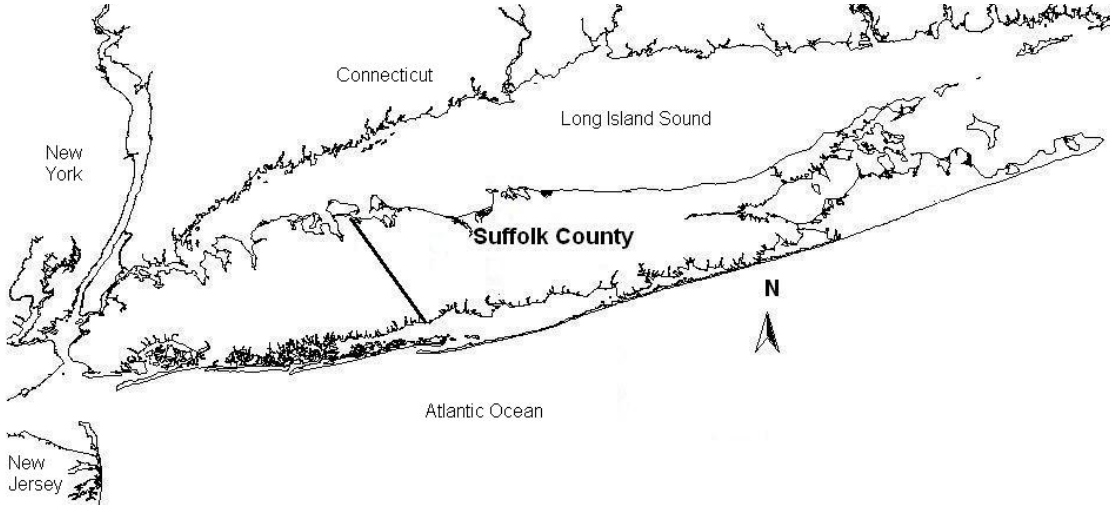

Figure 1. 1. Map showing the study area, Suffolk County, Long Island, NY.

Groundwater provides drinking water for more than 50% of the population in the United States (Nolan and Stoner, 2000). In Suffolk County, all potable water comes from groundwater, which is derived locally from precipitation. Long Island receives an average of 112 cm of precipitation annually (Busciolano, 2004). Half of this is lost to evapotranspiration or loss to the sea, the other half recharges to groundwater in an amount equivalent to 4.3 billion liters of water per day in Suffolk County (Buxton and

Modica, 1992). Precipitation falling on impervious surfaces is usually redirected to groundwater through recharge basins.

Groundwater wells in Suffolk County tap two aquifers sourced in Atlantic Coastal Plain siliciclastic sediments. The near surface sediments are dominated by Pleistocene glacial deposits of unconsolidated sands, gravels, silts and clays (Fuller, 1914), defining the Upper Glacial Aquifer. The water in this aquifer is generally less than a few decades old, and is highly susceptible to contamination due to the high permeability of the aquifer. Immediately underlying the Upper Glacial Aquifer (in most parts of Suffolk County) are Upper Cretaceous deltaic sand, gravel, silt and clay. Water from this aquifer, the Magothy Aquifer, can be more than 1,000 years old in its deepest location underlying the south shore (Buxton and Modica, 1992). Below the Magothy Aquifer is the Raritan Clay Formation which overlays the Lloyd Aquifer. There are very few wells that pump from the Lloyd Aquifer, the lower most water-bearing unit, composed mainly of white medium to coarse sands and gravels. Paleozoic metamorphic bedrock is one to two hundred meters below the surface on the north shore and about 600 meters below the surface along the south shore.

Table 1. 1 Concentrations of pristine groundwater and bulk precipitation.

Ion *(mg/L)*	**Magothy Aquifer**	**Upper Glacial Aquifer**	**Precipitation**
Ca	1.2	3.0	1.3
Mg	0.6	0.9	0.26
Na	3.3	<3.0	2.0
K	0.4	0.6	0.56
Cl	4.0	4.0	3.3
N-NO_3	0.2	<0.01	0.24
TDS	25	24	ND
SO_4	9.0	6	2.6
DO	ND	11	ND
Fe	0.002	<0.05	ND

Groundwater concentrations are from Stackelberg, (1995) and the Suffolk County Water Authority on-line database. Precipitation data from this study. ND=not determined.

Background concentrations of major ions in pristine groundwater of aquifers in Suffolk County are low (Table 1.1), due to the quartz-rich nature of the aquifers and thus their low reactivity. The aquifer sediments typically have a cation exchange capacity of about 1 meq per 100 gram, which is mainly associated with coatings on the mineral grains (Boguslavsky, 2000). These aquifers are considered well aerated with high dissolved oxygen measurements, which limit the amount of free ammonia in the aquifers (Bleifuss et al., 2000; Leamond et al., 1992; Stackelberg, 1995). In fact, as reported on their web site, free ammonia is rarely detected in groundwater wells monitored by the Suffolk County Water Authority. However, there are at least localized anaerobic conditions in the Magothy Aquifer (Brown and Scorca, 1995).

1.2. Background on nitrate contamination

The main sources of nitrate in groundwater of residential areas of Suffolk County are turfgrass fertilizers and sewage via septic systems and discharge from sewage treatment plants (Flipse et al., 1984; Kimmel, 1984; Munster, 2004). About two-thirds of the population (Allee et al., 2001) in Suffolk County dispose of sewage through cesspools, most of which have a secondary septic tank, that leach sewage directly to groundwater. Nitrogen in sewage is mostly from human excretion. Farming was extensive on Long Island before World War II but since then a higher proportion of land is being used for residential purposes. A study conducted in the 1970's determined that turfgrass occupied 25% of the land use in Suffolk County (Koppelman, 1978), either as golf courses, parks and residential or commercial lawns. It is likely this value has increased since residential land use has increased. Suffolk County Water Authority estimates 80 million liters per day, or 30% of pumped groundwater is used for the sole purpose of lawn irrigation (Written Communication, Michael Stevenson Suffolk County Water Authority, 2003). Nitrogen is a major nutrient needed to keep turfgrass healthy and green, and is applied in the form of fertilizer as natural conditions of Long Island do not naturally support turfgrass.

The U.S. Environmental Protection Agency (EPA) has set the maximum level of nitrogen as nitrate in drinking water at 10 mg/L N-NO_3. Infants who consume water with concentrations greater than this may develop blue baby syndrome, or methemoglobinemia. Nitrate in the digestive system may be converted to nitrite which interacts with hemoglobin in red blood cells reducing the amount of oxygen transported to the body's cells and tissues and eventually causes the infants death. Health effects of nitrate consumption on adults and children are inconclusive (Weyer, 1999).

The New York State Department of Health Bureau of Water Supply Protection developed the New York State Source Water Assessment Project (SWAP), and directed the implementation of the project for over 1,300 public supply wells that provide drinking water to nearly 3 million people in Nassau and Suffolk Counties. These modeling efforts by the SWAP characterized capture zones, travel time, and land use data for approximately 1000 wells in Suffolk County (CDM, 2003). The SWAP determined that 2% of 1000 wells exceeded the 10 mg/L N-NO_3 drinking water standard and 8% had between 6 to 10 mg/L N-NO_3. When assessing susceptibility of Suffolk County municipal supply wells for nitrate contamination, 66% had a rating of high to very high susceptibility; taking into account prevalence (occurrence), concentration, sensitivity and mobility based on land use and travel time in a well capture zone. This study indicates that nitrate contamination is and will continue to be a threat to drinking water quality in Suffolk County.

1.3. Background on perchlorate contamination

Perchlorate was placed on the EPA contaminant candidate list in 1998, the list of potentially harmful drinking water contaminants for which more data are needed (EPA, 1998). Since 1998, perchlorate has been studied extensively to understand natural and anthropogenic sources in addition to health effects from perchlorate ingestion.

Perchlorate inhibits iodide uptake by the sodium iodide symporter of the thyroid gland. Disruption of the thyroid gland can cause significant growth problems for a developing fetus and growing children. The extent of this health concern is still not fully understood, yet for the population with sufficient iodide uptake in their diet perchlorate does not seem to cause a significant effect on the thyroid gland. The current reference dose is 0.0007 mg per kg body weight per day (NRC, 2005), although this value is debated (Gibbs et al., 2005; Ginsberg and Rice, 2005). Assuming all ingested perchlorate comes from drinking water, a 70 kg body weight and a consumption of 2 liters of water per day would correspond to a drinking water equivalent of 24.5 μg ClO_4 per L. However, no national drinking water standard has been set and many state action levels are lower than this.

Perchlorate is a strong oxidizer and is a primary ingredient in solid propellants in rockets and missiles, fireworks, road flares, air bag inflators and matches. Perchlorate is a byproduct during the breakdown of hypochlorite (bleach) and chlorate, chlorate also forms during the breakdown of hypochlorite. Perchlorate is also present in nitrate fertilizers derived from Chilean ore. It has been estimated that over the last 60 years perchlorate production in the United States were 10.6 Gg per year as an oxidizer, 0.75 Gg per year as Chilean nitrate fertilizer and 0.13-0.64 Gg per year from natural production (Dasgupta et al., 2006). As an oxidizer perchlorate content decreases as it is used in the product, thus the 10.6 Gg per year estimate is more likely closer to the input from Chilean nitrate fertilizer.

Decreasing detection limits in analytical methods have allowed a better understanding of perchlorate concentrations at low levels and thus in natural conditions. Perchlorate has been detected in precipitation from Texas, U.S. (Dasgupta et al., 2005), and Ireland (Barron et al., 2006), measuring between 0.02 and 2.8 μg/L. It was predicted from observed perchlorate concentrations in uncontaminated groundwater from north-central New Mexico that precipitation in the Holocene had an average ClO_4 concentration of 0.093 μg/L leading to groundwater concentrations as high as 4 μg/L, depending on the extent of evapotranspiration (Plummer et al., 2006).

Perchlorate salts are very soluble in water. Perchlorate is non-reactive and highly mobile in the groundwater. Once perchlorate enters the groundwater system it moves quickly from the source, making it difficult to remediate, although perchlorate specific resins have been developed (Gu et al., 2004; Gu et al., 2005). Naturally occurring bacteria can reduce perchlorate (Coates et al., 1999; Coleman et al., 2003), thus there is the potential to reduce perchlorate in the natural environment where reducing conditions exist (Nozawa-Inoue et al., 2005; Tan et al., 2004).

The first detection of perchlorate in Suffolk County occurred in 1998, analyzed by a private lab due to concerns of the Suffolk County Water Authority (SCWA). Subsequently, a well in Westhampton, NY was taken out of service. SCWA now routinely monitors for perchlorate throughout their supply wells. In 2002, perchlorate content was confirmed in 6% of all community supply wells and 7% of all non-community supply wells. The maximum contaminant level goal in New York State is 5 μg/L and the maximum contaminant level is 18 μg/L. As of December 2005, SCWA identified 104 wells with perchlorate concentrations above 0.5 μg/L with 58 of these wells having concentrations below 2 μg/L, 25 wells between 2-4 μg/L, 14 wells between 4-6 μg/L and 7 wells above 6 μg/L. One additional well in Northport has been taken out of service where the other wells in that well field are being treated by a combination of perchlorate specific resins and blending techniques. SCWA divides their distributing area into 31 service areas (for service area map see, www.scwa.com/sitemap.cfm#), of which eight had no measurable detection of perchlorate in 2006. In many other areas perchlorate was detected infrequently at concentrations ranging between 0.2 and 2 μg/L. Concentrations above 2 μg/L were located in the service areas of Huntington and Northport (service areas 6, 9, 10), in central Suffolk County from Deer Park to Yapank (service area 12), in the north central part of Suffolk County (service area 15), the southern portion near Shirley and Westhampton (service area 20), and in the north fork (services areas 30 and 45).

1.4. Research Plan and Objectives

The goal of my dissertation research is to understand and identify sources of nitrate and perchlorate contamination in Suffolk County, NY groundwater. As such, I undertook multiple distinct projects that were related, as nitrate and perchlorate are commonly co-contaminants.

I sought to understand the chemistry of bulk precipitation by measuring monthly concentrations of inorganic ions, including nitrate and perchlorate, of bulk precipitation at six locations in Suffolk County (Chapter 2). These measurements establish background concentrations for groundwater of Long Island (which includes both Suffolk and Nassau County), aid in understanding the components in bulk precipitation from sea spray and from anthropogenic sources and quantify concentrations of perchlorate - a measurement that is lacking in the literature.

Fertilizers are commonly applied to lawns, which are primarily turfgrass, in areas where turfgrass does not normally grow. Nitrate is a major component of lawn fertilizers and perchlorate is associated with fertilizer products that contain a Chilean ore. Chilean nitrate is minded from a desert deposit in Chile which is considered an organic source of nitrate by the U.S. Department of Agriculture. There is a high probability of excess fertilizer leaching to groundwater in Suffolk County due to the sandy nature of the soils, the large amount of rain and irrigation water applied to lawns and due to fertilizer applied improperly, i.e. at the wrong time or in the wrong quantities. To measure the amount of nitrate and perchlorate leaching beneath fertilized lawns I measured monthly concentrations of nitrate, perchlorate and other ions in soil water collected beneath lawns fertilized with chemical fertilizer, organic fertilizer, no fertilizer and beneath a forested site. Grass clippings and soil cores were also collected and analyzed (Chapters 3 and 6).

About 75% of the population in Suffolk County operates on septic systems which leach sewage directly to the groundwater. Due to the large volume of recharge from sewage I was interested if perchlorate was present in sewage. It seemed probable that perchlorate was present in sewage since it is a breakdown product of bleach which is present in many household products. To test this hypothesis I measured perchlorate content in sewage from thirty five residential septic systems (Chapter 4).

Road flares have been identified as a possible source of perchlorate pollution yet only one study has measured perchlorate content in road runoff. In Suffolk County road runoff is collected in stormwater catch basins or recharge basins which recharged to groundwater. As such, road runoff is a possible nonpoint source of perchlorate pollution. I measured perchlorate and ion chemistry in road runoff collected from stormwater catch basins and recharge basins in two areas with high incidents of traffic accidents within the Brookhaven Township (Chapter 5).

Ions that accompany contamination can assist in identifying the sources of contamination. As part of these studies data for inorganic ion chemistry of perchlorate and nitrate sources in residential areas which include bulk precipitation, soil water, sewage, and road runoff were compiled. The ions analyzed were Ca, Mg, Na, K, B, Br, I, Cl, NH_4, NO_3, ClO_4 and SO_4 and are presented in Appendix 1.

This study is unique and significant for a few reasons (1) this was the first major study undertaken on nonpoint sources of perchlorate in urban areas (2) this is the most extensive study of the geochemistry of sewage and soil water beneath urban lawns and (3) to my knowledge this is the first extensive study to document the concentrations of inorganic ions in precipitation collected on Long Island.

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2. Bulk Precipitation

2.1. Perchlorate content of bulk precipitation

2.1.1. INTRODUCTION

While perchlorate is known to inhibit iodide uptake of the thyroid gland, whether low microgram levels of perchlorate in drinking water are a health concern is still highly debated (Blount and Valentin-Blasini, 2006). The U.S. Environmental Protection Agency has yet to establish a national drinking water standard, while many states have set advisory levels. New York State has implemented advisory levels of 18 µg/L ClO_4 for public notification level and 5 µg/L ClO_4 for drinking water planning levels in groundwater. Advisory levels are as low as 1 µg/L in Massachusetts, Maryland and New Mexico (EPA, 2005). Establishing background concentration of perchlorate in precipitation and groundwater, and determining whether the perchlorate is natural or anthropogenic is a prerequisite for determining drinking water standards.

Since the presence of perchlorate in precipitation has only recently been measured (Dasgupta et al., 2005, Barron et al., 2006), the sources of perchlorate in precipitation are not well known. A major source could be the formation of perchlorate in the atmosphere from chlorine species (Dasgupta et al., 2005).

Perchlorate in the atmosphere may also be from sea spray since perchlorate is present in seawater (Martinelango et al., 2006). Perchlorate is present in surface soils of the southwest (Rao et al., 2007), thus it is conceivable that perchlorate in dust is picked up by wind, transported and deposited as dry deposition. An anthropogenic source of perchlorate in bulk precipitation may be fireworks. Atmospheric fallout from fireworks consists of fine particles of burnt black powder, paper debris and residue. Perchlorate in paper debris ranges from 302 to 34,200 µg kg-1 (2006). Two studies (Backus et al., 2005; Wilkin et al., 2007) show direct perchlorate contamination of lake water from fireworks displays.

The Massachusetts Dept. of Environmental Protection has determined that historic fireworks displays are the likely source of perchlorate contamination in 2 of the 9 public water supply systems showing levels above 1 μg/L (DEP, 2006). Although little information is available on the perchlorate content in fireworks their model predicts that groundwater should be contaminated to the tens of μg/L within 100 meters of the fireworks display. This assumes 1000-2000 aerial shells weighing a total of 1361 kg, of which 40% is ClO_4 and the contaminated area (fireworks fallout area) is equal to 3600 m^2.

To establish perchlorate concentrations in precipitation we collected bulk precipitation samples monthly from six locations in Suffolk County, Long Island, NY from November 2005 to July 2007 (Figure 1). We analyzed samples for ClO_4 and also NO_3, NH_4, Cl, Br, I, SO4, Na, Mg, K, Ca, Sr and B.

2.1.2. METHODS

A total of one hundred and eight samples of bulk precipitation (wet plus dry) were collected monthly for 20 months between November 30, 2005 and July 5, 2007 at six locations in Suffolk County, NY. Suffolk County is the eastern most county on Long Island, which extends east from Queens and Brooklyn. All sample sites are in or near urban areas (Figure 1).

Samples were collected using All-Weather Precipitation Gauges purchased from Fisher Scientific. These gauges sample both wet and dry deposition since they are not covered during dry periods. The sampling area of the gauge is 10 cm in diameter. The inner sampling device, used to determine rainfall, is 26 cm in height and 3.2 cm in diameter. Evaporation from the samplers is minimal due to the small opening at the top of the gauge. For example, annual rainfall totals for 2006 at our sites ranged from 110 to 130 cm which are only slightly less than the 137.4 cm value for 2006 reported by Weather Underground for Islip, NY which is in the center of Long Island.

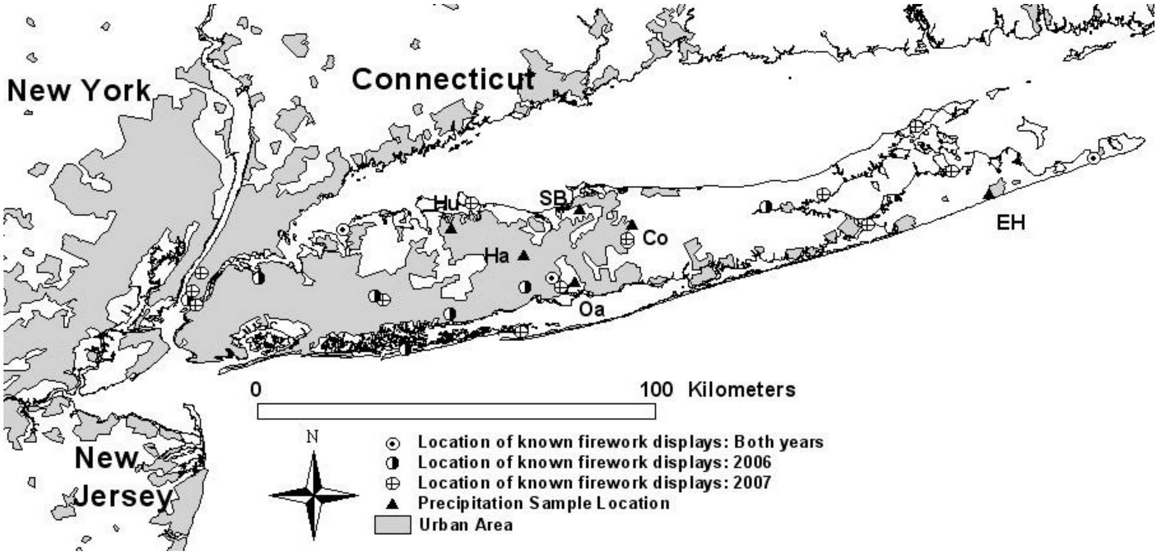

Figure 2. 1. Location of precipitation gauges in Suffolk County, Long Island, NY. Locations names are abbreviated. Hu=Huntington, Ha=Hauppauge, SB=Stony Brook, Co=Coram, Oa=Oakdale and EH=East Hampton. Gray areas are urban as mapped by the U.S. Geological Survey according to the Digital Chart of the World, revised version of 1998 data. In general, urban areas are a concentration of at least 5,000 persons in continuous collection of houses where the community sense is well developed and the community maintains public utilities, such as, roads, street lighting, water supply, sanitary arrangements etc. Note that two firework display locations overlap near the Coram precipitation gauge. The covered symbol had firework displays both years.

Samples were filtered in the field using a 0.2 μm surfactant-free cellulose acetate (SFCA) filter for perchlorate analysis and 0.45 μm glass fiber filters for all other analysis. Samples were stored in sample rinsed, polypropylene vials untreated for all samples except nitrogen. Vials for nitrogen were acid rinsed with a 10% HCl solution before sample collection. Samples were stored in a cooler while in the field and then at 4°C until analyzed. Samples for nitrogen, once in the laboratory, were frozen until analyzed.

Perchlorate was analyzed using a sequential ion chromatography-mass spectroscopy/mass spectroscopy (IC-MS/MS) technique (Aribi and Sakuma, 2005) with a method detection limit of 0.005 μg/L. To account for matrix effects, all samples were spiked with an oxygen-isotope (^{18}O) labeled ClO_4 internal standard. Each sample was measured in duplicate or triplicate and the precision was on average ± 5%. B, Br, I, Mg, Na, Ca, K, Sr, Cl, N-NO_3, NH_4 and SO_4, were analyzed using standard methods.
We used the program Minitab to perform One-way Analysis of Variance (ANOVA, unstacked) Turkey tests, with a 95% confidence interval. A One-Way Analysis of

Variance is a way to test the equality of three or more means at one time by using variances.

2.1.3. RESULTS

The mean monthly perchlorate concentration of bulk precipitation is 0.21 ± 0.04 (standard error) µg/L. The maximum monthly value is 2.78 µg/L. The mean value is similar to that reported from Lubbock, TX, 0.20 µg/L (Dasgupta et al., 2005), while the maximum is similar to the highest value reported in Ireland, 2.82 µg/L (Barron et al., 2006). What is striking about our data set is the large peak in perchlorate concentration in the July samples for both 2006 and 2007 collected after the Fourth of July (Figure 2). Many communities in and around the Metropolitan New York area, which includes Long Island, have large firework celebrations on the evening of, and leading up to the Fourth of July. Although fireworks are illegal in New York State, residents also set off fireworks in their neighborhoods. We have located (Figure 1) known displays during the Fourth of July celebrations reported in Newsday (July 2, 2006 and July 4, 2007), using oral communication with local town clerks, and from other sources (www.grucci.com, http://hamptons.plumtv.com; http://www.sagharboryc.com). We have not located all the firework displays, but we believe that we have located the larger ones.

Excluding the samples from July the mean concentration of perchlorate in precipitation is 0.12 ± 0.03 (standard error) µg/L. Perchlorate concentrations are significantly higher in July compared to all months except August ($p<0.05$). Mean values vary between the six locations, although there was no statistical difference ($p<0.05$). Coram has the highest mean value of 0.40 ± 0.70 (standard deviation) µg/L. East Hampton has the lowest mean of 0.06 ± 0.06 µg/L. Hauppauge has a mean value of 0.27 ± 0.14 µg/L, Huntington a value of 0.14 ± 0.06 µg/L, and Stony Brook a mean value of 0.25 ± 0.09 µg/L. There was no significant correlation (significant defined as a $R^2>0.5$) between ClO_4 and the other anions and cations analyzed.

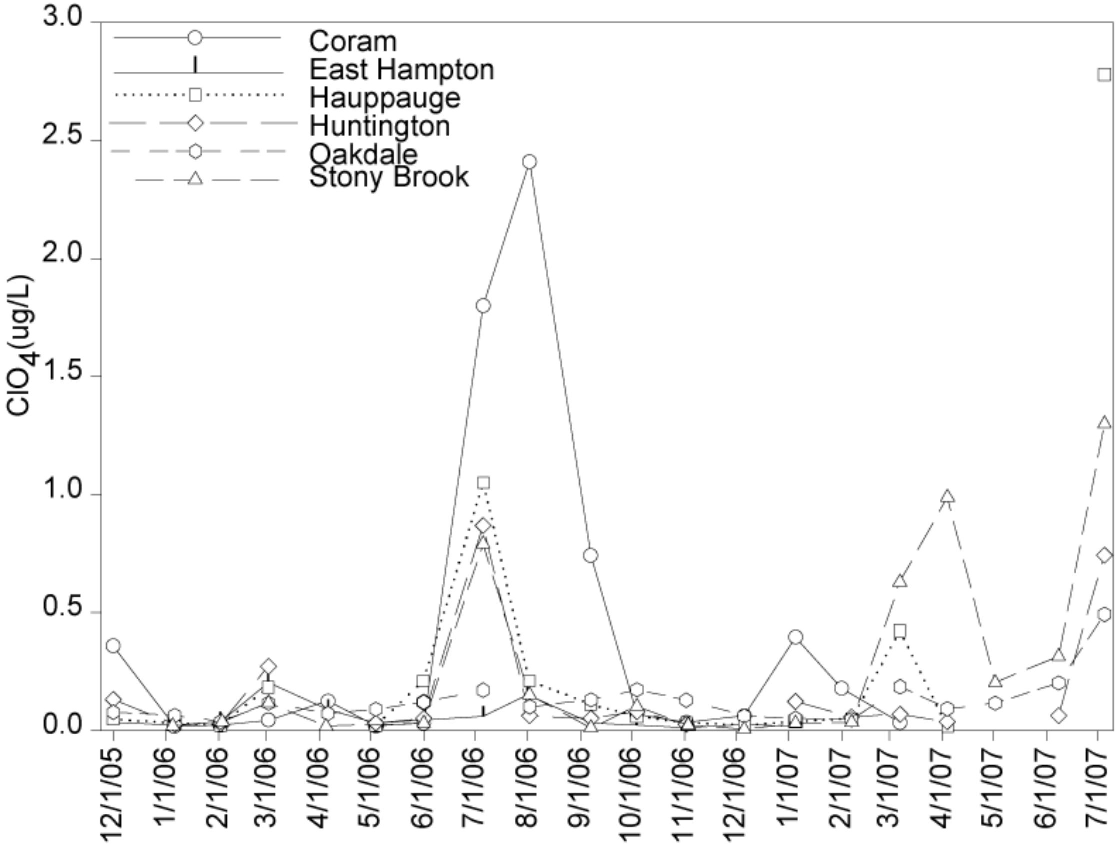

Figure 2. 2. Monthly perchlorate concentrations in bulk precipitation. Collection at Coram was discontinued after March 2007 and discontinued at East Hampton after January 2007.

2.1.4. DISCUSSION

Fireworks are most likely responsible for the high concentrations of ClO_4 in the July 7, 2006 and July 5, 2007 samples (Figure 2). The effects of atmospheric pollution from fireworks is reported in other studies noting increases in SO_2, NO_2, suspended particles and metallic elements (Moreno et al., 2007; Ravindra et al., 2003). Precipitation scavenging can effectively remove pollutants from the atmosphere, with wet deposition being more effective than dry deposition (Loosmore and Cederwall, 2004). In our study area, wet deposition occurred between the Fourth of July and the time of sample collection for both years of this study (Weather Underground). These three storms originated inland and progressed in a west to east direction, moving slightly north during the 2006 events, as noted on NOAA archived radar images (www4.ncdc.noaa.gov).

Two studies (Backus et al., 2005; Wilkin et al., 2007) which show direct contamination of lake water from firework displays measured perchlorate concentration adjacent to the displays. Our rain gauges are, at the closest, a few km from known displays (Figure 1). Thus wind properties and storm direction play a role in where the firework fallout eventually settles. Our rain gauges are mostly in areas zoned for business, except for Stony Brook which is on a university campus and Coram, which is in a residential neighborhood. Coram, coincidentally, had the highest concentration in July 2006. Sampling at that location was discontinued after March 2007. Coram is near known public firework displays (approximately 1.5 km). Oakdale, which is also near known firework displays, has relatively low concentrations with a value of 0.17 µg/L on July 6, 2006 and 0.49 µg/L on July 5, 2007. It is likely that the wind and storm direction did not carry fireworks contamination towards the Oakdale study site in 2006 but that some contamination was received in 2007. Hauppauge measured 2.78 µg/L on July 5, 2007. There are no known fireworks displays near Hauppauge, yet fireworks fallout from the south shore or in western Long Island may have traveled around 40 km and contaminated Hauppauge rain water. Additionally, there may have been fireworks near Hauppauge that we are unaware of. It is likely that the perchlorate from fireworks in our precipitation samples have traveled the atmosphere and perchlorate concentrations of precipitation adjacent to large fireworks displays may be much higher than we report.

2.1.5. CONCLUSIONS

Precipitation concentrations after Fourth of July firework displays can be 18 times as much as background levels confirming that, “fireworks constitute a potential source of increasing importance, as fireworks use is rising exponentially with average consumption at 4.5 x 10^7 kg per year” (Dasgupta et al., 2006). As a result we need to be concerned about the potential impact on our groundwater of increased perchlorate in precipitation associated with fireworks. It is likely that perchlorate is not a recent trend in bulk precipitation but is a natural occurrence. Further monitoring of perchlorate locally and nationally is important to better understand the natural contribution.

2.1.6. REFERENCES

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2.2. *Ionic composition and sources of bulk precipitation*

2.2.1. INTRODUCTION

Precipitation is an efficient scavenger of the particles and gases dispersed in the atmosphere, making precipitation chemistry a good indicator of the pollutants in our air. Determining the chemical composition of bulk precipitation (1) provides an understanding of the source types that contribute to precipitation chemistry and (2) enhances the understanding of local and regional dispersion of pollutants and their potential impact to groundwater and surface water chemistry.

Precipitation is the sole source of all fresh groundwater on Long Island. In order to preserve groundwater quality precipitation chemistry should be fully understood; yet, a thorough study of precipitation chemistry on Long Island is not available. Locally, previous work has measured quantities of acid rain (Peters et al., 1982; Schwartz, 1989) and trends in precipitation volume (Colle and Yuter, 2007; Dike and Tilburg, 2007; Spar and Ronberg, 1968), but few measured concentrations of or examined sources of precipitation chemistry (Lee et al., 1986; Pearson and Fisher, 1971; Peters and Bonelli, 1982). Sources of ions in precipitation are predominantly (1) marine sea-salt aerosols, (2) natural emissions, such as those from volcanoes and forest fires, (3) anthropogenic emissions, such as those from power plants, other industrial operations and traffic emissions, and (4) dust from natural sources of soil and rock or anthropogenic sources such as suspension of road particles. Marine sea-salt aerosols are produced by breaking waves and photochemical and biological processes in the near surface marine water (Keene et al., 1986). Sea-salt aerosols from breaking waves may still influence atmospheric chemistry as far as 25 km from the coast (de Leeuw et al., 2000).

Water quality studies of Long Island Sound indicate that precipitation adds about 8% of the pollutant loads of sulfur, nitrogen, and phosphorus to the Sound (LISS, 1990). Prevailing winds over the Long Island Sound are from the southwest, indicating that the industrialized regions of New York and New Jersey are major sources of pollutants to the Sound (Xu et al., 1997), and could also be a major source in Long Island precipitation. Data collected from October 1940 to September 1965 (Miller and Frederick, 1969) indicate that much of the winter precipitation on Long Island is caused by low-pressure systems which move roughly NE along the Atlantic Coast. In the summer, precipitation is dominantly from thunderstorms. Tropical storms occur throughout the year but with greatest frequency from June to November. These storms are from the Atlantic, Caribbean or Gulf of Mexico. Storms originating in different localities will bring variable atmospheric sources affecting precipitation chemistry differently throughout the year on Long Island.

The objective of this study is to gain an understanding of the variation and distribution of bulk precipitation composition and to identify the possible sources of the ions in precipitation in the study area by monthly sampling of six locations in Suffolk County, Long Island, NY and analyzing for B, Br, I, Ca, Mg, Na, K, Sr, Cl, N-NO_3, N-NH_4, SO_4, PO_4 and ClO_4.

2.2.2. METHODS

A total of one hundred and eight samples of bulk (wet and dry) deposition were collected monthly between December 1, 2005 and July 5, 2007 at six locations in Suffolk County, NY (Figure 2.3) and analyzed for ion chemistry. Suffolk County is the eastern most county on Long Island, which extends east from Manhattan. The study locations are in or near urban areas. Oakdale is approximately 11 km from the Atlantic Ocean. East Hampton is 2 km from the Atlantic Ocean. These sites are the most coastal sites. Hauppauge and Coram are the most inland sites of the study area. Huntington is 4 to 10 km and Stony Brook is 2 to 6 km from the Long Island Sound. The precipitation samples were collected using All-Weather Precipitation Gauges purchased from Fisher Scientific. These gauges sample both wet and dry deposition since they are not covered during dry periods. The gauges were mounted at least 5 feet above the ground surface. After a vandalism event, the Stony Brook gauge was relocated to the roof of the Earth and Space Sciences Building at Stony Brook University. The sampling area of the gauge is 10 cm in diameter. The inner sampling device, used to quantify precipitation volume, is 26 cm in height and 3.2 cm in diameter. Evaporation is thought to be minimal in the precipitation gauges due to the small opening at the top of the gauge. However, some evaporation surely occurs, which we have not quantified. Yearly totals for our sites range from 110 to 130 cm, which are slightly below the total reported by Weather Underground for Islip, NY, a value of 137.4 cm for 2006 (www.wunderground.com). The variation between our sites and Islip, NY could be due to spatial differences as wet precipitation can vary as much as 20.3 cm (8”) across Long Island (Busciolano, 2004). The historical yearly average from 1950-2000 ranges from 109 to 124 cm across Long Island (Busciolano, 2004).

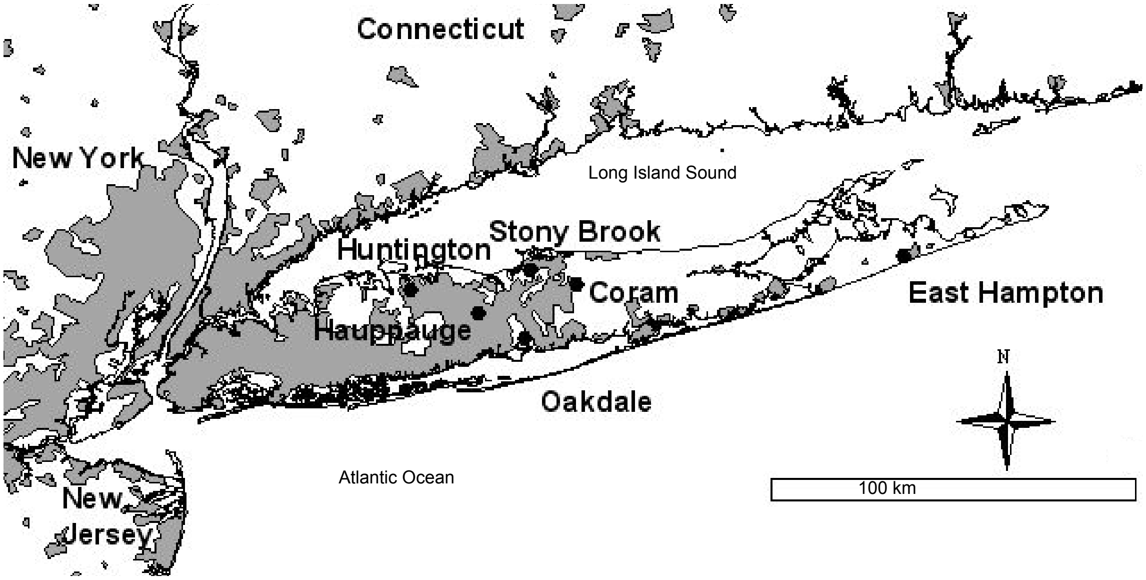

Figure 2. 3. Location map of bulk precipitation gauges (dark circles). Gray areas are urban areas as mapped by the U.S. Geological Survey according to the Digital Chart of the World, revised version of 1998 data.

Samples were filtered in the field using a 0.2 μm surfactant-free cellulose acetate (SFCA) filter for perchlorate analysis and 0.45 μm glass fiber filters for all other analyses. Samples were stored in sample rinsed, polypropylene vials, untreated for all samples except nitrogen, where the vials were acid rinsed with a 10% HCl solution before sample collection. Samples were stored in a cooler while in the field and then at 4°C until analyzed. Samples for nitrogen were frozen on arrival to the laboratory until analyzed. EMD colorpHast® pH strips, narrow range, with a sensitivity of 0.2–0.3 pH units were used in the field to determine pH.

Perchlorate was analyzed using a sequential ion chromatography-mass spectroscopy/mass spectroscopy (IC-MS/MS) technique (Aribi and Sakuma, 2005) with a method detection limit of 0.005 μg/L. To account for matrix effects, all samples were spiked with an oxygen-isotope (^{18}O) labeled ClO_4 internal standard. Each sample was measured in duplicate or triplicate and the precision was on average 5%. The ions B, Br, I, Ca, Mg, Na, K and Sr were analyzed by Activations Laboratory using ion coupled plasma mass spectrometry. Detection limits were as follows: Sr is 0.04 μg/L, B and I are 1 μg/L, Mg is 2 μg/L, Br is 3 μg/L, Na is 5 μg/L, K is 30 μg/L, and Ca is 700 μg/L. The ions Cl, PO_4, N-NO_3, N-NH_4, and SO_4 were analyzed using the Lachat's QuickChem 8500 Flow Injection Analysis System (which is a colorimetric method, designed by HACH Spectrometry), in the Marine Science Research Center at Stony Brook University. Detection limits were 0.1 mg/L for N-NO_3, 0.01 mg/L for N-NH_4 and PO_4, and 1 mg/L for SO_4 and Cl.

Data quality was checked by ionic balance (Figure 2.4). The acceptable range according to the U.S.EPA for the ionic difference in precipitation samples, having total ion concentrations >100 μeq/L, is 15-30% (Rastogi and Sarin, 2005). Most samples are within this range. A deficit of anions could be due to lack of bicarbonate and organic acid analysis of the samples.

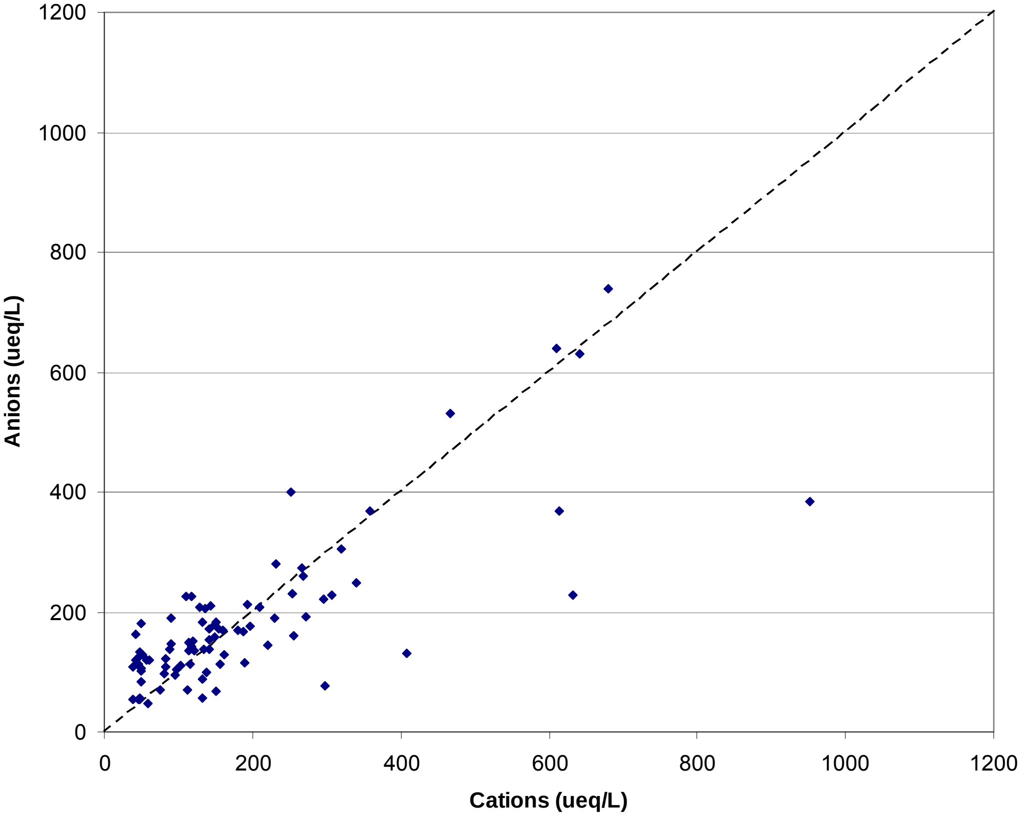

Figure 2. 4. Charge balance for bulk precipitation samples that were analyzed for all ions. The 1:1 line is shown on the plot.

I used the program Minitab to perform One-way Analysis of Variance (ANOVA, unstacked) Turkey tests, with a 95% confidence interval. A One-Way Analysis of Variance is a way to test the equality of three or more means at one time by using variances. Samples below analytical detection limits for the ions were assigned a value of zero for calculating ANOVA and average values.

Principle Component Analysis (PCA) was calculated using the build in function of the program Matlab. PCA, a multivariate statistical method, detects linear dependencies between variables and replaces groups of correlated variables by new uncorrelated variables, the principal components. The sources of precipitation can be inferred from the correlations within a principle component. Each component groups together variables that are highly correlated with one another, presumably because they all are influenced by the same underlying sources.

To perform PCA on the data I first excluded samples that were not analyzed for all ions, as the calculations can not account for missing data points. This reduced the sample size from 108 to 89. In addition, seventy one samples were below detection for PO_4 and 77 samples were below detection for Ca. Due to such a large number of samples below the detection limit these ions were excluded from the analysis as a high amount of zeros (non detect) would skew the data. Initially, PCA was performed for 89 samples with ionic concentrations in μeq/L of Na, Cl, Mg, K, SO_4, N-NH_4, N-NO_3, Sr, Br, I and ClO_4. No correlations were noted for the ions Sr, Br, I and ClO_4 with the other ions and zero loads were noted for these ions in the first five principle components. These ions were excluded and the analysis was performed again; the removal of these ions did not significantly adjust the results. This final analysis on 89 samples with ionic concentrations of Na, Cl, Mg, K, SO_4, N-NH_4 and N-NO_3 is presented in the results section.

2.2.3. RESULTS

Mean concentrations (μeq/L) of the ions measured in bulk precipitation collected in Suffolk County, NY are in order of concentration as follows: Na>Cl>Ca> SO_4>N-NH_4>Mg>N-NO_3>K>PO_4>B>Br>I>Sr>ClO_4. Sodium and chloride are commonly the dominant species of bulk precipitation. On average, these ions account for 47% of the total ion concentration in bulk precipitation. In July and August, SO_4 is the dominant anion. In June, July and October, Ca is the dominant cation.

The ions measured in this study vary over a large range of concentrations (Figure 2. 5). The average pH value is 4.7 ± 0.5 (2σ). Average concentrations for all sites grouped by month sampled are presented in Table 2.1. Only a few of the ions measured showed significant variations (ANOVA, $p<0.05$) between sample months. These ions are Na, Cl, N-NO_3, ClO_4, SO_4 and K (Figure 2. 6). Nitrate was the most variable ion throughout the study period. Concentrations of N-NO_3 are highest from January through April. Concentrations of ClO_4 were highest in July. Concentrations of Na and Cl show a similar pattern to each other, with higher concentrations from February through April than from May through January. Concentrations of SO_4 indicate no systematic variability in monthly concentrations. The ions Mg, Ca, Sr, Br, I, B and N-NH_4 were not variable during the year.

There was no statistical difference (ANOVA, $p<0.05$) in yearly concentrations between sample locations for pH, I, N-NO_3, N-NH_4, SO_4, ClO_4, B and Ca (Table 2.2). The ions Na, Cl, Mg, Br and Sr varied between locations. Concentrations at East Hampton and Oakdale varied most from the other locations, with concentrations at these locations higher than the other locations.

The only significant relationship for all sites between the ions is between Na and Cl (Figure 2. 7a) with a linear relationship and a R^2 value of 0.82 for all samples ($p<0.05$). This linear correlation varied between the sites with a R^2 value of 0.82 at East Hampton, 0.89 at Oakdale, 0.68 at Coram, 0.56 at Huntington, and about 0.30 at both Hauppauge and Stony Brook. Although significant relationships are not observed for the other ions for all samples there are significant correlations of the other ions according to location. Sodium and magnesium were correlated at East Hampton (R^2, 0.75) and Stony Brook (R^2, 0.60) (Figure 2. 7b). Bromide and chloride were correlated at East Hampton (R^2, 0.76) (Figure 2. 7c). Bromide and sodium were correlated at East Hampton (R^2, 0.69) and Stony Brook (R^2, 0.51) (Figure 2. 7d). A majority of the samples fall near the ratio for marine sea-salt aerosols for the ions Br, Cl, Mg and Na, while some samples may be influenced by a road salt ratio (Figure 2. 7). Four samples collected at Oakdale in

March and April consistently fall outside the range of the other samples on all plots of Figure 2. 7.

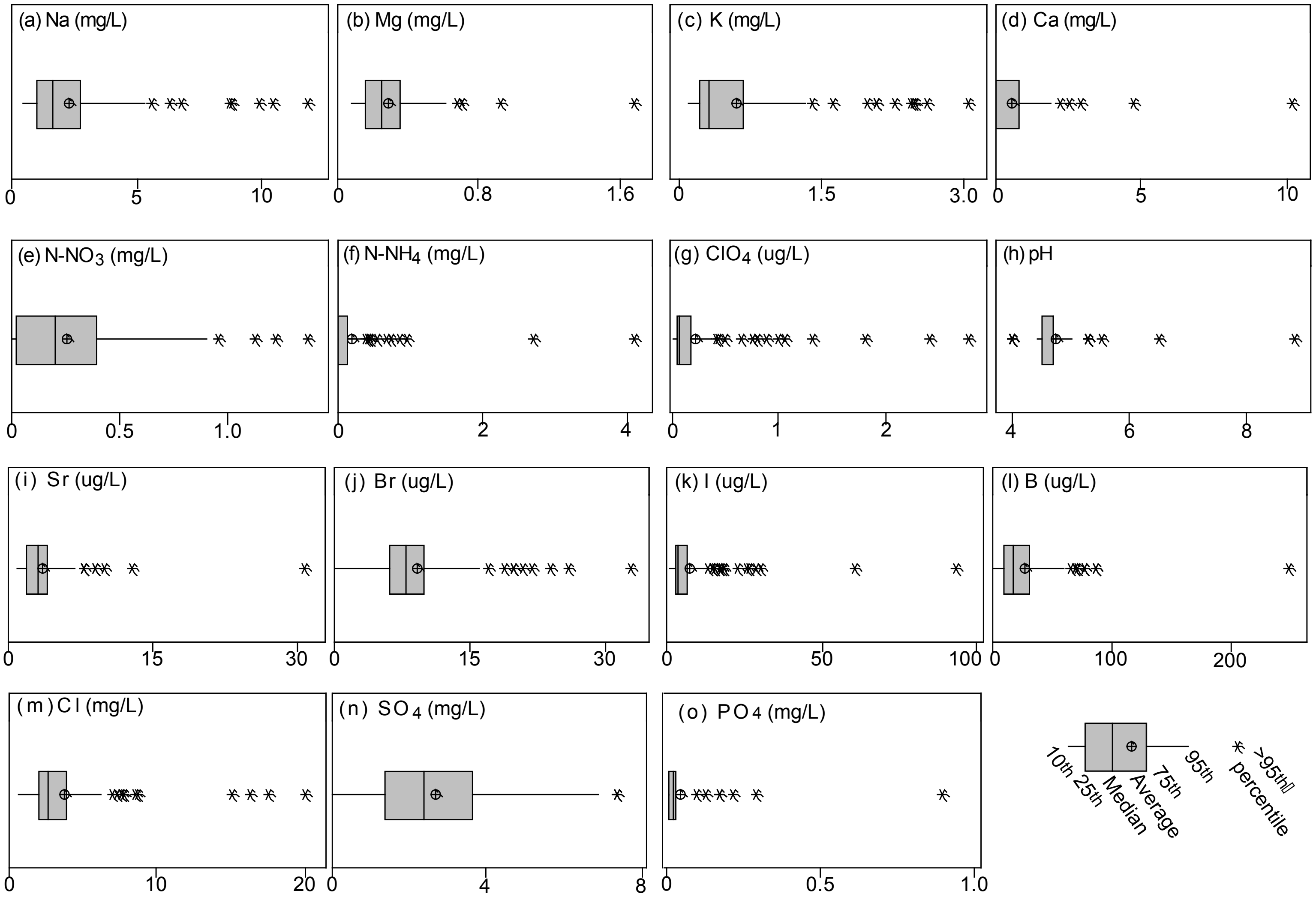

Figure 2. 5. Box plots of ion concentrations for all bulk precipitation samples. Ion concentrations for plots (a) through (f) and (m) through (o) are in mg/L. The other plots, besides (h), are in µg/L. Note the variability in scale.

Table 2. 1. Average ion concentrations for bulk precipitation as calculated according to sample month. Value next to month is maximum sample size, some samples could not be analyzed for all ions. *Not enough data for calculations.

	January (12)		February (11)		March (11)		April (10)		May (9)		June (9)	
Variable	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev
pH	4.5	0.2	4.7	0.2	5.1	0.2	4.6	0.3	4.5	0.3	5.1	0.6
Na *(mg/L)*	1.5	1.1	2.8	1.2	4.2	3.0	4.9	3.9	1.7	1.0	1.8	1.9
Mg *(mg/L)*	0.20	0.12	0.23	0.08	0.27	0.12	0.39	0.15	0.24	0.11	0.41	0.5
K *(mg/L)*	0.38	0.66	0.29	0.32	0.34	0.18	0.33	0.16	0.43	0.36	0.96	0.61
Ca *(mg/L)*	0.07	0.23	0.16	0.35	0.5	0.62	1.22	0.8	0.17	0.33	1.66	3.34
N-NO_3 *(mg/L)*	0.42	0.40	0.38	0.17	0.41	0.18	0.74	0.26	0.18	0.19	0.05	0.05
N-NH_4 *(mg/L)*	0.03	0.05	0.18	0.17	0.21	0.21	0.3	0.24	0.11	0.31	0.59	1.36
Cl *(mg/L)*	2.6	1.7	3.9	1.6	6.2	5.4	7.5	6.1	2.8	0.38	2.9	2.5
SO_4 *(mg/L)*	1.4	0.8	1.5	0.84	2.5	0.7	4.5	1.1	2.7	0.8	2.8	2.1
PO_4 *(mg/L)*	0.09	0.27	0.00	0.00	0.00	0.00	0.04	0.06	*	*	0.06	0.13
ClO_4 *(ug/L)*	0.07	0.11	0.05	0.04	0.21	0.18	0.14	0.3	0.06	0.07	0.11	0.11
B *(ug/L)*	12	9	15	14	44	72	31	28	36	23	37	22
Sr *(ug/L)*	2	1	2	1	3	1	6	2	3	1	6	10
Br *(ug/L)*	8	6	9	4	10	4	10	3	11	5	7	6
I *(ug/L)*	2	1	14	26	9	6	12	10	13	19	8	8

	July (10)		August (6)		September (6)		October (6)		November (6)		December (12)	
pH	4.6	0.3	5.2	1.8	4.7	0	4.5	0.4	4.6	0.2	4.7	0.1
Na *(mg/L)*	1.5	2.0	1.8	1.2	1.5	0.8	1.3	0.4	2.2	1.9	1.7	0.5
Mg *(mg/L)*	0.24	0.28	0.34	0.17	0.30	0.11	0.25	0.12	0.35	0.27	0.23	0.08
K *(mg/L)*	0.63	0.58	1.54	1.1	1.1	1.1	0.57	0.53	0.73	0.81	0.57	0.62
Ca *(mg/L)*	0.64	1.56	0.73	0.61	0.55	0.45	0.68	0.88	0.23	0.57	0.06	0.20
N-NO_3 *(mg/L)*	0.09	0.15	0.07	0.09	0.03	0.05	0.02	0.02	0.07	0.08	0.11	0.18
N-NH_4 *(mg/L)*	0.28	0.85	0.00	0.00	0.05	0.10	0.00	0.00	0.00	0.00	0.07	0.08
Cl *(mg/L)*	2.1	0.9	2.2	0.27	3.1	1.3	2.6	0.5	4.4	2.9	2.7	1.1
SO_4 *(mg/L)*	3.5	1.7	5.0	3.4	3.8	2.4	2.6	0.5	1.8	1.6	1.5	0.8
PO_4 *(mg/L)*	0.01	0.01	0.07	0.06	0.08	0.08	0.02	0.01	0.02	0.01	0.01	0.01
ClO_4 *(ug/L)*	1.0	0.8	0.51	0.93	0.18	0.28	0.08	0.05	0.04	0.04	0.08	0.1
B *(ug/L)*	32	15	42	22	11	6	18	15	8	3	20	17
Sr *(ug/L)*	4	4	6	2	4	1	4	3	3	2	2	1
Br *(ug/L)*	6	7	8	5	10	5	7	2	15	12	9	3
I *(ug/L)*	7	8	7	10	4	1	3	1	2	1	2	0

Table 2. 2. Average ion concentrations for bulk precipitation as calculated for each study location. Value next to site name is maximum sample size, some samples could not be analyzed for all ions.

	Coram (16)		**East Hampton (13)**		**Hauppauge (20)**		**Huntington (20)**		**Oakdale (20)**		**Stony Brook (19)**	
Variable	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev	Avg	StDev
pH	4.6	0.3	5.1	1.1	4.7	0.6	4.7	0.2	4.7	0.4	4.7	0.2
Na *(mg/L)*	1.5	0.7	3.3	1.5	1.4	0.8	2.0	1.9	4.4	3.5	1.4	0.6
Mg *(mg/L)*	0.21	0.10	0.41	0.17	0.20	0.08	0.27	0.12	0.46	0.34	0.16	0.06
K *(mg/L)*	0.51	0.74	1.1	0.7	0.65	0.8	0.63	0.68	0.56	0.56	0.29	0.16
Ca *(mg/L)*	0.41	0.69	0.35	0.59	0.19	0.46	0.54	0.66	1.5	2.4	0.04	0.18
N-NO_3 *(mg/L)*	0.19	0.25	0.13	0.17	0.23	0.21	0.31	0.41	0.37	0.35	0.26	0.25
N-NH_4 *(mg/L)*	0.07	0.14	0.07	0.09	0.39	1.06	0.23	0.32	0.13	0.2	0.05	0.08
Cl *(mg/L)*	2.9	1.8	5.1	2.2	2.36	0.9	2.9	1.7	7.1	6.0	2.6	1.0
SO_4 *(mg/L)*	2.7	2.1	1.8	1.6	2.3	1.4	3.0	1.9	3.4	2.0	2.6	1.2
PO_4 *(mg/L)*	0.03	0.04	0.11	0.26	0.04	0.08	0.02	0.04	0.02	0.03	0.01	0.01
ClO_4 *(ug/L)*	0.40	0.70	0.06	0.06	0.27	0.64	0.14	0.24	0.13	0.1	0.27	0.39
B *(ug/L)*	28	26	42	74	22	20	31	25	20	16	22	17
Sr *(ug/L)*	3	2	4	2	3	1	3	2	7	6	2	1
Br *(ug/L)*	7	2	17	8	6	3	7	2	12	6	8	3
I *(ug/L)*	4	3	5	7	5	5	6	5	12	21	9	14

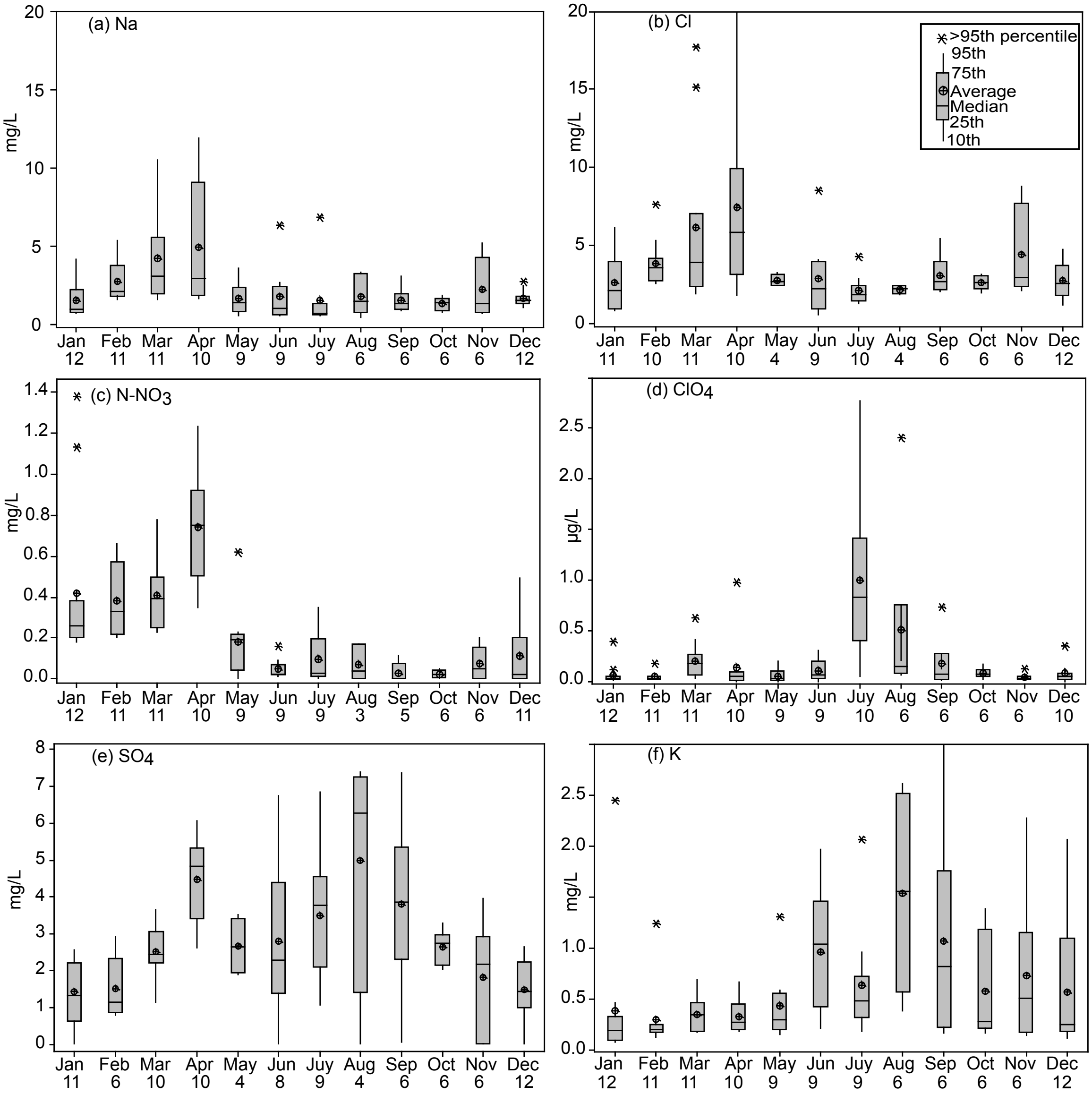

Figure 2. 6. Box plot, according to sample month, for the ions which were most variable throughout the year (a) Na, (b) Cl, (c) N-NO_3, (d) ClO_4, (e) SO_4 and (f) K. Values below the month are the number of samples collected and analyzed for that month.

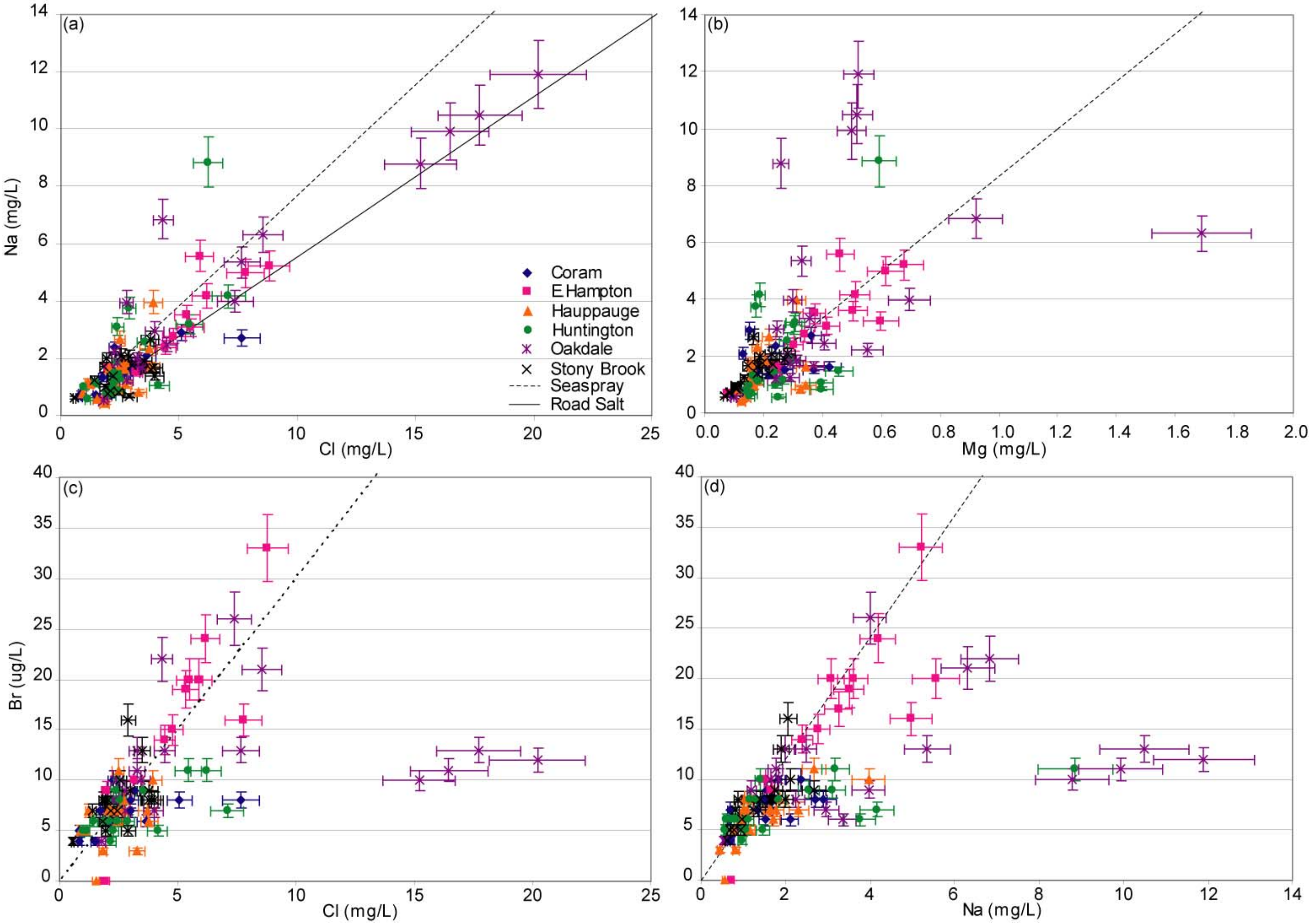

Figure 2. 7. Plots of the dominant ions in marine sea-salt aerosols, plotted by study location for (a) Na vs. Cl, (b) Na vs. Br, (c) Br vs. Cl, and (d) Br vs. Na.

Principle component analysis, a multivariate statistical method, detects linear dependencies between variables and replaces groups of correlated variables by new uncorrelated variables, the principal components. The sources of precipitation can be inferred from the correlations within a principle component. Each component groups together variables that are highly correlated with one another, presumably because they all are influenced by the same underlying sources. Eighty four percent of the variance in the bulk precipitation data is explained by a principle component dominated by Na and Cl (Table 2.3). This component is interpreted as influenced by marine sea-salt aerosols. To test for overestimating the influence of marine sea-salt aerosols due to contamination by road salt, the samples that were collected in February, March and April were removed (since concentrations of Na and Cl in these months are higher than the other months (Figure 2. 6)) and the PCA was performed again. Additionally, the samples with Cl concentrations higher than 7 mg/L (which is greater than 2σ of the mean (Figure 2. 5)) were removed instead and the PCA was performed again. Both analyses predicted a PC1 influenced by Na and Cl explaining around 60% of the variance, a decrease of 14% from the PCA analysis including all samples. No other components were influenced by Na or Cl.

From the initial analysis with all samples, 13% of the total variance is explained by the last three principle components. PC2, PC3 and PC4 are all influenced by SO_4 and N-NH_4. PC3 and PC4 are both influenced by Na and Cl. There are small principle component loads for K, Mg and N-NO_3.

Table 2. 3. Principle component loads for selected ions for all bulk precipitation samples (see methods).

Variable	PC1	PC2	PC3	PC4
Na	-0.71	0.01	-0.44	0.49
Cl	-0.69	-0.13	0.39	-0.57
Mg	-0.07	0.06	0.05	0.29
K	0.00	0.13	0.03	0.01
SO_4	-0.09	0.61	0.65	0.38
N-NH_4	-0.03	0.77	-0.45	-0.44
N-NO_3	-0.07	0.02	-0.15	0.11
Percent Explained	84	5	4	4

2.3.4. DISSCUSSION

The concentrations of the major ions in bulk precipitation measured in this study were compared with bulk precipitation samples collected from 1965 through 1978 at Mineola, NY in Nassau County and Upton, NY in Suffolk County, totaling more than 100 samples at each location (Peters et al., 1982). These sites are most similar to the locations Coram and Hauppauge in proximity to coastlines. At the time of the previous study, Upton was in a rural area and Mineola was in an urban area and today both sites are urban. Concentrations of Na and Cl at Upton and Mineola are most similar to the more inland sites of this study (Figure 2. 8), which is likely a function of proximity to the coastlines, as the sites closer to the coast have higher concentrations of Na and Cl. Potassium concentrations are higher in this study than the previous study. Potassium is predominately from dust, but less commonly K in the atmosphere can be from fertilizers (Berner and Berner, 1996). The previous study measured higher concentrations of nitrate and sulfate than this study, which is likely due to reductions in anthropogenic emissions from the Clean Air Act of 1990 (Lynch et. al., 1996). Peters et. al. (1982) found a four fold increase in nitrate concentrations after 1969, an artifact of increased industrial emissions. Concentrations from Peters et. al. (1982) is within range of this study for Mg, Ca and N-NH_4. Concentrations of Mg and Ca likely haven’t changed with time since their sources are largely natural.

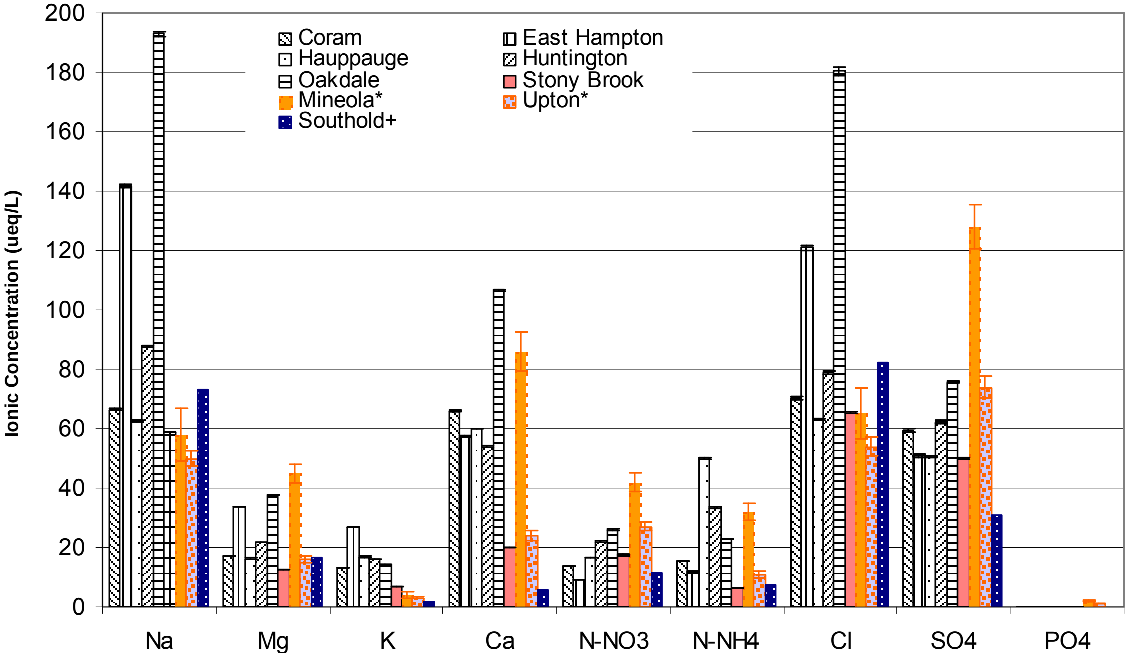

Figure 2. 8. Concentrations of major ions at the study locations compared to previous data. *Peters et al., 1982. +National Atmospheric Deposition Program/National Trends Network, 2006 Data for Site NY96-Southold, NY. Error bars are standard error of the mean, when not shown they are smaller than the data points. Statistical data was not available for Southold.

Recent data was acquired from National Atmospheric Deposition Program/ National Trends Network, 2006 Data for Site NY96-Southold, NY (http://nadp.sws.uiuc.edu/). Southold is located on the northeastern end of Long Island. Concentrations measured at Southold are within the range of concentrations measured in this study for Na, Mg, N-NO_3, N-NH_4 and Cl. Samples collected at this site are wet deposition only, which may explain the lower Ca and Mg concentrations. Lower SO_4 and low N-NO_3 and N-NH_4 concentrations compared to other locations may be due to the omission of dry deposition in Southold samples or due to Southold being farther than the other locations from the industrialized areas of New York and New Jersey.

An estimated 60-84% of the variation, as calculated using principle component anlysis, in the data can be explained by an influence from marine sea-salt aerosols (Table 2.3). This is evident by the strong relationship between Na and Cl in the bulk precipitation samples (Figure 2. 7a) and the relationships between the other major ions in marine sea-salt aerosols (Figure 2. 7). The ion concentrations measured at the study locations show variable influence by marine sea-salt aerosols. East Hampton and Oakdale (closest to the Atlantic Ocean) have the highest concentrations of Na and Cl (Table 2.2) and the most significant relationship between the two ions (Figure 2. 7a) likely due to the high influence from marine sea-salt aerosols. However, Na and Cl are also present in suspended road salt which may contaminate precipitation (Pearson and Fisher, 1971) and may cause overestimates of the marine sea-salt aerosols influence. Four samples collected at Oakdale in April and March are dissimilar to the other bulk precipitation samples (Figure 2. 7) and are likely highly influenced by road salt.

A high content of marine sea-salt aerosols can obscure identification of sources to precipitation, especially in bulk precipitation samples (Peters and Bonelli, 1982). It is also possible that trends and source identification are obscured since the bulk precipitation concentrations presented in this study are monthly averages or accumulations and not event samples. Composite samples are frequently mixtures of different types of storms (Junge and Werby, 1958). If the collectors receive much locally derived, resuspended, dry material, bulk precipitation is a poor source of data for determining aerial deposition patterns (Peters and Bonelli, 1982).

The remaining variance in the data can be explained as a mix of anthropogenic air pollution, atmospheric reactions, road dust, and soil dust. The association of SO_4 and N-NH_4 in PC2, PC3, and PC4 is a strong indicator of anthropogenic influences. The relationship between these ions can be due to acid neutralization and scavenging of aerosols containing $(NH_4)_2SO_4$ and NH_4HSO_4 (Zhang et al., 2007). The inverse relationship between Na and Cl in PC3 and PC4 is possibly from suspended road salt (Pearson and Fisher, 1971). Road salt likely contaminates bulk precipitation, as average concentrations of Na and Cl increase during the months of high salting (Figure 2. 6).

Nitrate and sulfate vary between sample months, suggesting that wind and storm direction are likely controlling the concentrations of these ions. Nitrate and sulfate are predominantly from anthropogenic emissions and these aerosols have residence times in the atmosphere from 1-10 days (Mihajlidi-Zelic et al., 2006). Concentrations of SO_4 vary between months due to variability in storm direction, which in turn affect sources of SO_4. Concentrations of SO_4 are highest in the summer months when storms, wet deposition, and winds are predominately from the west. These storms can scavenge pollutants from the industrialized areas of New Jersey and New York (Xu et al., 1997). Furthermore, it has been shown that scavenging of sulfur oxides decrease in the cold season (Hidy,1994; Meyers et al., 1991). Monthly averages are lowest in the cold season in this study.

Nitrate concentrations were found to be highest in snow or ice in a study measuring wet deposition of six sites in northeastern United States (Maxwell et. al., 1988) and concentrations of $N\text{-}NO_3$ in this study are highest in the winter months. Deposition of NO_3 usually occurs 400-1200 km from the source (Schwartz, 1989). Frequent small rains will concentrate pollutant deposition closer to the pollution sources than will large infrequent rains (Jordan et. al, 1995). Nitrate and sulfate concentrations are not variable between locations (Table 2) which indicate the concentrations of these ions are not controlled by location. Monthly variations of ClO_4 are due to firework peaks (see Chapter 2a).

Potassium and calcium are likely from natural dust sources. Transport of these ions is likely from the Midwest where the soils are calcareous. Potassium concentrations are higher from June to December than from January to May (Figure 2. 6f). Calcium shows a constant flux throughout the year although this ion is likely sourced in dust similar to K, however K may also be from fertilizer (Berner and Berner, 1996).

The mean concentration of B in marine derived wet deposition is 10 μg/L (Park and Schlesinger, 2002). This value is lower than the average for this study, 26 μg/L, suggesting that dry deposition contributes as much to the concentrations of boron in bulk precipitation as wet deposition, which has been suggested by others (Schlesinger, 1997). Atmospheric inputs of B may also be from soil dust, fossil fuel combustion, biomass burning and other human activities (Park and Schlesinger, 2002).

2.3.6. CONCLUSIONS

Bulk precipitation concentrations in Suffolk County, Long Island, NY are predominately influenced by a marine source with minor inputs from dust and anthropogenic sources. This indicates that reducing anthropogenic sources may not strongly influence bulk precipitation quality, depending on the concentration of anthropogenic contamination.

Concentrations of the ions in bulk precipitation are not near the maximum contaminate levels for drinking water, and have a low probability of reaching these levels. However, coupled with contamination on land, concentrations from the atmosphere could be enough to increase drinking water above levels of concern. Monitoring of bulk precipitation concentrations at these same locations should be continued in order to evaluate changes in concentrations over time.

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3. Perchlorate cycling and content in a lawn environment

3.1 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) placed perchlorate on its contaminant candidate list in 1998, yet there is still no national drinking water standard. Perchlorate is known to inhibit iodide uptake of the thyroid gland, which is of particular concern for women and children with iodide deficiencies. This heath concern coupled with the mobility of perchlorate poses a threat to groundwater. Our study area, Suffolk County, Long Island, NY (Figure 3. 1), is particularly sensitive to groundwater contamination as all potable water is derived from the local aquifers. New York State has implemented levels of 18 μg ClO_4 per L for the public notification level and 5 μg/L for the drinking water planning level in groundwater; however, state levels are as low as 1 μg/L in New Mexico, Maryland and Massachusetts (EPA, 2005).

Perchlorate contamination is commonly associated with rocket fuel propellant or Chilean nitrate use. Chilean nitrate was historically used in agricultural fertilizers before the Harbor-Bosch process of ammonium production (~1950) and is currently an acceptable form of nitrate used in organic fertilizers (The National Organic Program). Perchlorate is rarely detected in fertilizer products which don't contain the Chilean ore (Susarla et al., 1999a; Susarla et al., 1999b; Urbansky and Collette, 2001). The amount of perchlorate in Chilean nitrate has varied over time, with values as high as 6.8% (Dasgupta et al., 2007), decreasing recently to values between 0.15-0.18% (Urbansky and Collette, 2001). A modified refining process is currently producing Chilean nitrate containing 0.01% perchlorate (Dasgupta et al., 2007). Even at low concentrations, perchlorate from organic fertilizers could adversely affect groundwater concentrations depending on the dilution of Chilean nitrate in the fertilizer, the application rate of the fertilizer, and the imposed standards for drinking water quality.

Perchlorate uptake and bio-concentration in plant matter has been documented (Ellington and Evans, 2000; Jackson et al., 2005; Smith et al., 2001; Tan et al., 2004b; Yu et al., 2004), although it is not certain to what purpose plants take up ClO_4. Perchlorate retention in soil is negligible (Urbansky and Brown, 2003). Perchlorate concentrations in the unsaturated and saturated zones may decrease due to microbial degradation depending on the type of microbial community, the exposure time of ClO_4 in the environment, and the concentration of the competing ions, such as NO_3 (Coates et al., 1999; Nozawa-Inoue et al., 2005; Tan et al., 2004a).

Turfgrass in the United States is estimated to cover up to 14% of the total U.S. area, including residential, commercial and industrial lawns, parks, golf courses and athletic fields (Beard and Green, 1994; Milesi et al., 2005). A 1970's land use survey concluded that turfgrass covers more than 25% of the 2,300 km^2 which is Suffolk County, NY. This value has likely increased since then, as residential land use has increased. The soils in Suffolk County lack the needed nutrients for healthy turfgrass to grow; consequently, fertilizers are applied through out the year. The local water authority is promoting an organic fertilizer campaign in hopes of reducing nitrate leaching to groundwater and water demands from irrigation.

To understand the cycling of perchlorate in an urban lawn environment and evaluate the impact of perchlorate leaching beneath lawns to groundwater, soil water samples were collected monthly from suction lysimeters installed beneath turfgrass sites treated with organic fertilizer, chemical fertilizer or no fertilizer from June 2006 to January 2007. In addition, monthly samples were collected of bulk precipitation and turfgrass clippings and in November, 2006, soil cores were collected at three sites treated with organic fertilizer. All samples were analyzed for perchlorate, nitrate and chloride concentrations and soil cores were also analyzed for sulfate.

3.2 METHODS

Soil water samples were acquired from suction lysimeters at eleven sites (at five locations) in Suffolk County, NY (Figure 3. 1), collected monthly from June 2006 through January 2007. Lysimeters were installed in 2001 (Schuchman, 2001), 2002 and 2005 (Munster, 2004) at 60, 80, 100 and 120 or 150 cm depths. The sites were maintained lawns at either the Stony Brook University Campus or lawns at office buildings of the Suffolk County Water Authority. Two of the sites were not fertilized, four were treated with organic fertilizer and four were treated with chemical fertilizer. There was also one site in a forested area at the University. Only one sample, however, could be collected in the forested site due to low sample volumes. This sample contained less than 0.1 µg/L of ClO_4 and will not be discussed further.

The organic sites were fertilized with Pro Grow fertilizer once during the study period, in May 2006, receiving 244 kg fertilizer per ha (Table 3.1). The organic sites at Hauppauge and Oakdale-1 have been treated with organic fertilizer since 2002. A portion of the lawns at Huntington and Oakdale-2 switched from chemical fertilizer to organic fertilizer in early 2005. East Hampton was fertilized with organic fertilizer from 2002 to the end of 2004, at which time the site no longer was fertilized. The chemical sites were fertilized with Scotts or Lesco Brand fertilizer in early April and mid May also receiving 244 kg fertilizer per ha per treatment. On October 26, 2005, nine months before the study period, two sites at Oakdale received the incorrect fertilizer treatment by mistake; the organic site (Oakdale-2) was treated with chemical fertilizer and vice versa.

Table 3. 1. Dates of fertilizer application during and near the study period.

Site	Treatment Type	Application Dates			
Oakdale	chemical	10/26/2005*	4/6/2005	5/22/2006	10/23/2006
Oakdale-1	organic	10/26/2005*		5/11/2006	10/23/2006
Oakdale-2	organic	10/26/2005		5/11/2006	10/23/2006
Huntington	chemical	10/27/2005	4/6/2005	5/22/2006	10/23/2006
Huntington	organic	10/27/2005		5/11/2006	10/23/2006
Hauppauge	chemical	10/27/2005	4/6/2005	5/22/2006	10/23/2006
Hauppauge	organic	10/27/2005		5/11/2006	10/23/2006
Stony Brook	chemical	10/26/2005	4/7/2006	5/22/2006	11/06/2008

*incorrect treatment

Precipitation was collected monthly at the study sites using All-Weather Rain Gauges purchased from Fisher Scientific. These gauges sample both wet and dry deposition since they are not covered during dry periods. Soil water and bulk precipitation samples were filtered in the field using a 0.2 µm surfactant-free cellulose acetate (SFCA) filter and collected in untreated polypropylene vials. Samples were stored in a cooler while in the field and then at 4°C until analyzed.

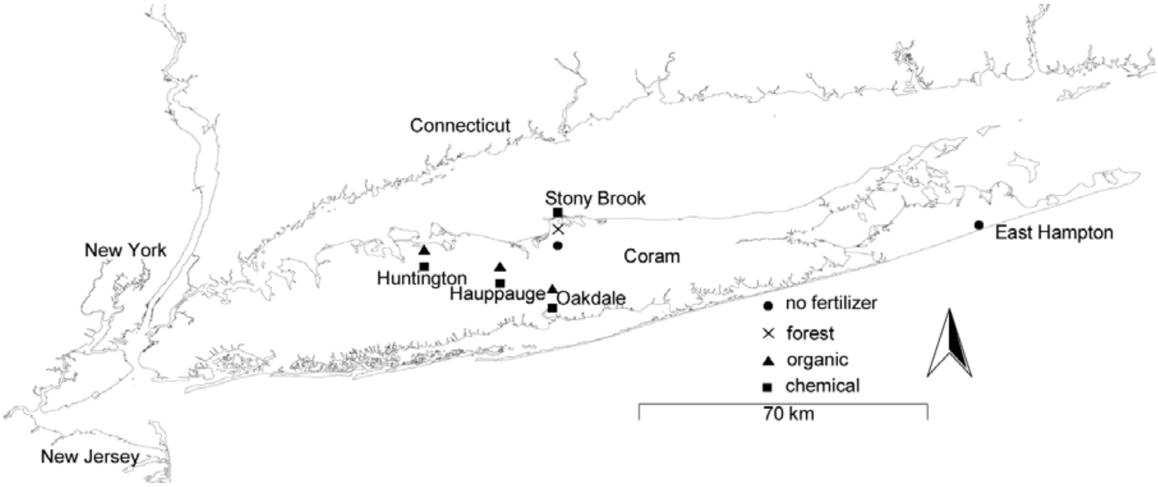

Figure 3. 1. Map of study locations. Most locations have multiple sites and all locations have a precipitation gauge. Coram only has a precipitation gauge. Oakdale has two sites treated with organic fertilizer, Oakdale-1 and Oakdale-2.

All locations were irrigated with an automatic sprinkler system in the summer months, except for Stony Brook. All lawns were mowed, once a week or once every other week, from April to November. The mowed grass was mulched and left on the lawns. Samples of the live grass were collected monthly from June 2006 through January 2007. A rectangular outline, 14 by 24.3 cm, was used so that a similar area of grass was collected each time. The grass was cut as close to the surface as possible being sure not to sample soil, fallen leaves or mulched grass. If species other than turfgrass, such as crabgrass, plantain, clover or dandelions were present they were not excluded in the samples. Lawn samples, collected in brown paper bags, were brought back to the lab and air dried, then oven dried at 105°C for 24 hours. Samples weighing from 0.5 to 1.5 g were cut into small pieces and placed into 30 mL of deionized water in a 50 mL centrifuge tube and boiled in a water bath for approximately an hour (Ellington and Evans, 2000; Tan et al., 2006). The tubes were then placed in the fridge and manually shaken every two hours for eight hours, then left over night. The following day the tubes were centrifuged at 2000 rpm for 30 minuets. The supernatant was filtered with a 0.45 µm glass fiber filter and then a 0.2 µm SFCA filter. Samples were stored at 4°C until analyzed.

Three soil cores were collected at sites treated with organic fertilizer in November 2006; one at Hauppauge, one at Oakdale-1 and one at Oakdale-2. The cores were sampled in 5 cm increments to approximately 100 cm using a combination of a soil auger and an AMS soil core sampler from Forestry Suppliers (Jackson, MS) in which internal rings can be disassembled to obtain intact samples. Samples were first air dried, then oven dried at 110°C for 24 hours. The soil was crushed using a shatterbox with an agate grinding bowl. Using a 1:1 ratio of soil to water, approximately 10 grams of crushed soil was added to 10 mL of deionized water in a centrifuge tube and shaken vigorously by hand. The tubes were then centrifuged at 2000 rpm for 30 minuets. The supernatant was filtered with a 0.2 µm SFCA filter and diluted in deionized water with a 1:4 soil to water ratio (Canas et al., 2006). Perchlorate in the deionized water was below the detection limit of 0.1 µg/L.

Perchlorate was analyzed using a sequential ion chromatography-mass spectroscopy-mass spectroscopy (IC-MS/MS) technique (Aribi and Sakuma, 2005) with a method detection limit of 0.1 µg/L for soil water and soil samples and a detection limit of 0.005 µg/L for bulk precipitation samples. To account for matrix effects, all samples were spiked with an oxygen-isotope (^{18}O) labeled ClO_4 internal standard. The precision determined from replicate analysis was ± 5%. Nitrogen as nitrate, chloride and sulfate concentrations was analyzed using a Lachat's QuickChem8500 Flow Injection Analysis System. These analyses have an uncertainty of 5% for $N\text{-}NO_3$ and 10% for Cl and SO_4 determined by anonymous standards and duplicate analysis. Detection limits are 0.1 mg/L $N\text{-}NO_3$ and 1 mg/L Cl and SO_4.

3.3 RESULTS[1]

3.3.1 *Soil water concentrations and turfgrass content*

Soil water concentrations of perchlorate at 100 cm are highest beneath lawns treated with organic fertilizer, with an average value of 90 μg ClO_4 per L and a maximum value of 625 μg/L (Figure 3. 2a). The average concentration of soil water collected beneath the sites treated with chemical fertilizer is 1.6 μg/L. The average concentration of soil water collected beneath the sites which were not fertilized is 0.34 μg/L. This value is similar to the average concentration of bulk precipitation, a value of 0.21 μg/L (see Chapter 2a). The same pattern is observed for the turfgrass (lawn) samples, with the highest concentrations at the organic sites (Figure 3. 2b). The average concentration is 4,163 μg ClO_4 per kg of grass (oven dry weight) for samples from sites treated with organic fertilizer. The average concentration is 242 μg/kg for the sites treated with chemical fertilizer and 120 μg/kg for the sites that were not fertilized.

No clear relationship is observed between soil water concentrations of ClO_4, Cl and N-NO_3 in soil water collected at 100 cm. Concentrations of perchlorate vary in soil water collected beneath sites treated with organic fertilizer, yet there is a general pattern of high concentrations from May to August and decreasing concentrations from September to January (Figure 3.3a). The ClO_4 to Cl ratio of soil water beneath the sites treated with organic fertilizer are highest in the beginning of the study and decrease over time (Figure 3.3c).

Patterns of ClO_4 concentrations of soil water are similar at the sites treated with chemical fertilizer and those not fertilized with the highest concentrations found in early Fall. The sites at East Hampton and Oakdale-1 differ from this general pattern (Figure 3.3b). Soil water concentrations at East Hampton are routinely below detection. As I will explain in detail later, concentrations of ClO_4 at the sites treated with chemical fertilizer and those not fertilized are dominantly controlled by bulk precipitation. Concentrations in

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[1] The major conclusions of this chapter for soil water, turfgrass content and soil core concentrations are presented in the results and discussion sections; however, other data was collected for these study sites in regards to perchlorate cycling and mobility which may be of interest to the reader. I have included these data as supplemental information at the end of this chapter.

precipitation are lower at East Hampton than at the other sites, which may explain the lower concentrations in soil water at this site. Concentrations at Oakdale are higher than the other sites since it mistakenly received an application of organic fertilizer in October, 2005. The ClO_4 to Cl ratio of the sites treated with chemical fertilizer and not fertilized vary over the study period (Figure 3.3d). This ratio is highest at Oakdale, likely due to the mistaken application of organic fertilizer.

Concentrations of ClO_4, Cl and N-NO_3 in the turfgrass samples do not mimic each other. Perchlorate in turfgrass varies among the sites (Figure 3.4a), with similar patterns of ClO_4 to Cl ratios (Figure 3.4c). Peak uptake of ClO_4 in the grass is observed in June, July, September and November for the sites treated with organic fertilizer and in June, July, August, October and November for the other sites. In general, concentrations decrease in late Fall for all sites. The variability of turfgrass uptake between the sites may be due to variability in lawn species, which was not documented, and differences in the health of the ecosystems, as growth rate in grasses are depended on the species of grass, availability of water and soil temperature.

Soil water concentrations (Figure 3.3b) and turfgrass content (Figure 3.4b) vary between the sites which are not fertilized, with Stony Brook having higher perchlorate than East Hampton in both cases. Bulk precipitation, turfgrass content and soil water concentrations are presented for the Stony Brook site which is not fertilized and receives no irrigation (Figure 3.5). The bulk precipitation spike observed in July is likely from firework fallout (see Chapter 2a). The turfgrass content peaks in August, likely as a response to the peak in precipitation, and decreases thereafter with lowest concentrations occurring when the grass is dormant. Cool season turfgrass, the common type on Long Island, is active (i.e. growing) from May to October (Emmons,1995). Soil water concentrations are highest in September and October, an increase which occurs after the increases in bulk precipitation and turfgrass content. The ClO_4 to Cl ratio is highest in the soil water samples from August to December. Bulk precipitation has a high ratio in July.

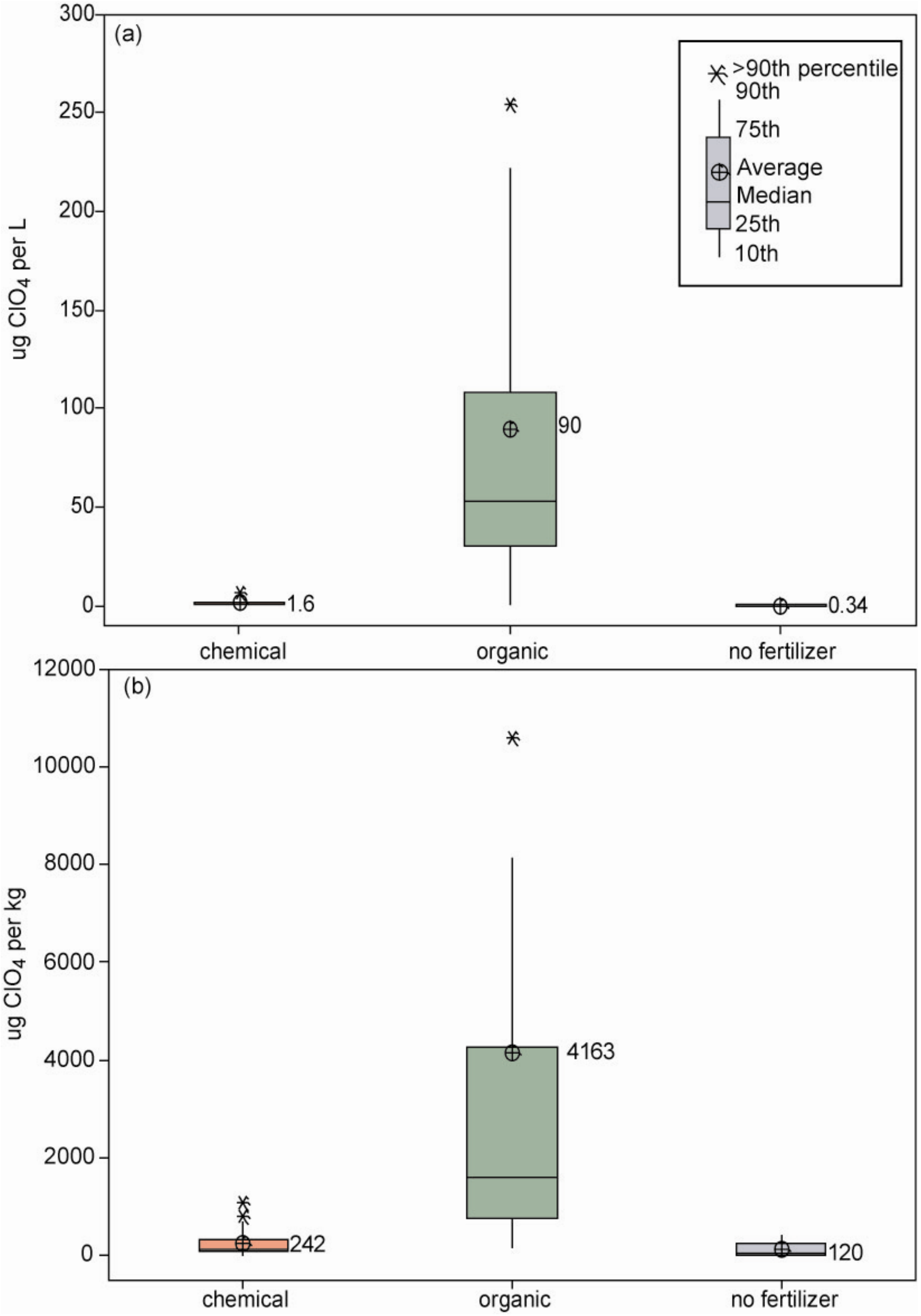

Figure 3. 2. Perchlorate content of (a) soil water samples collected at 100 cm from all sites and (b) turfgrass samples from all sites. Outliers not showed (a) 625 ug/L for the organic sites and (b) 47,145 ug/kg for the organic sites.

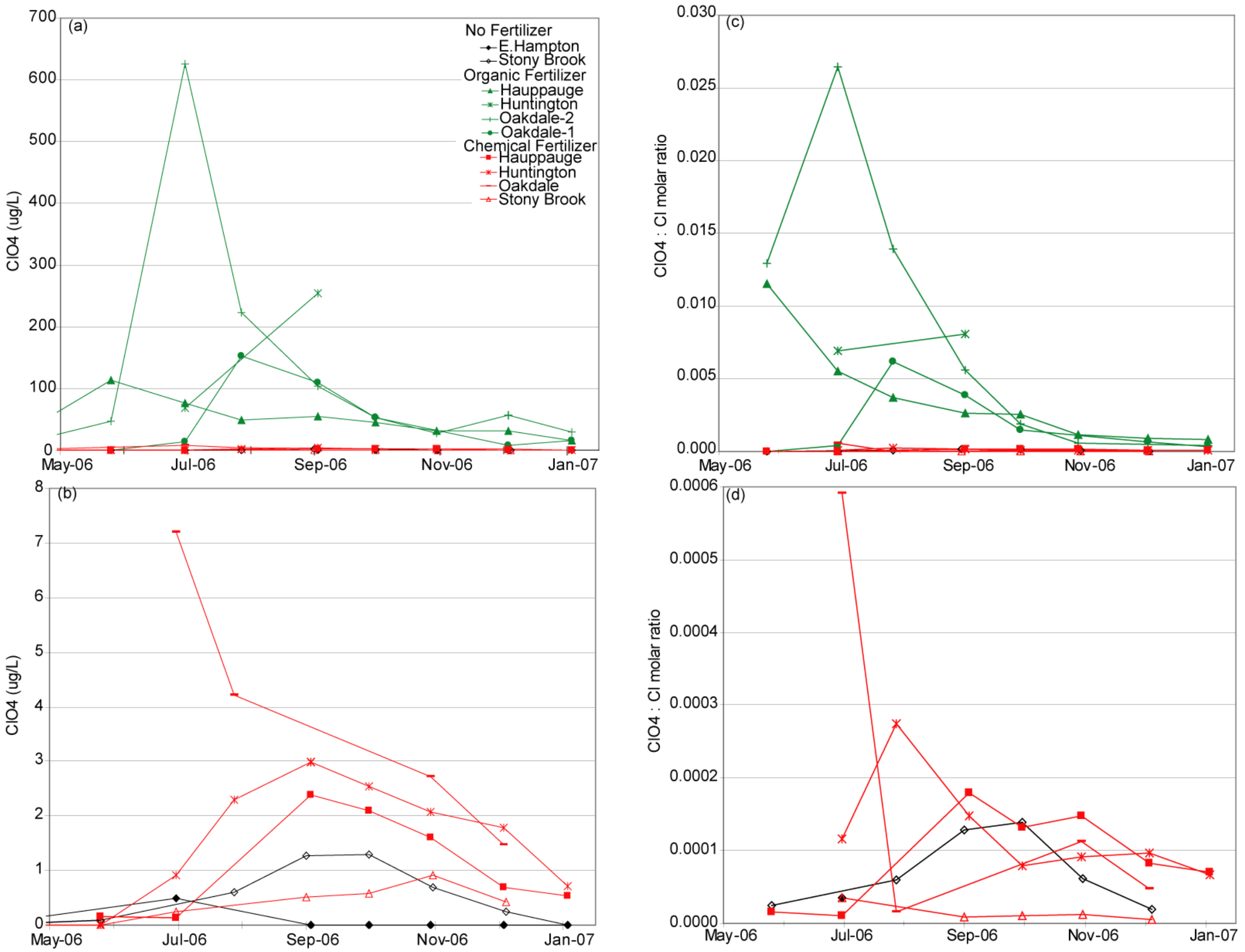

Figure 3. 3. Soil water concentrations at 100 cm from June 2006 through January 2007 (a) ClO_4 for all sites, (b) ClO_4 for sites treated with chemical fertilizer and sites not fertilized (c) ClO_4:Cl ratio for all sites and (d) ClO_4:Cl ratio for sites treated with chemical fertilizer and sites not fertilized.

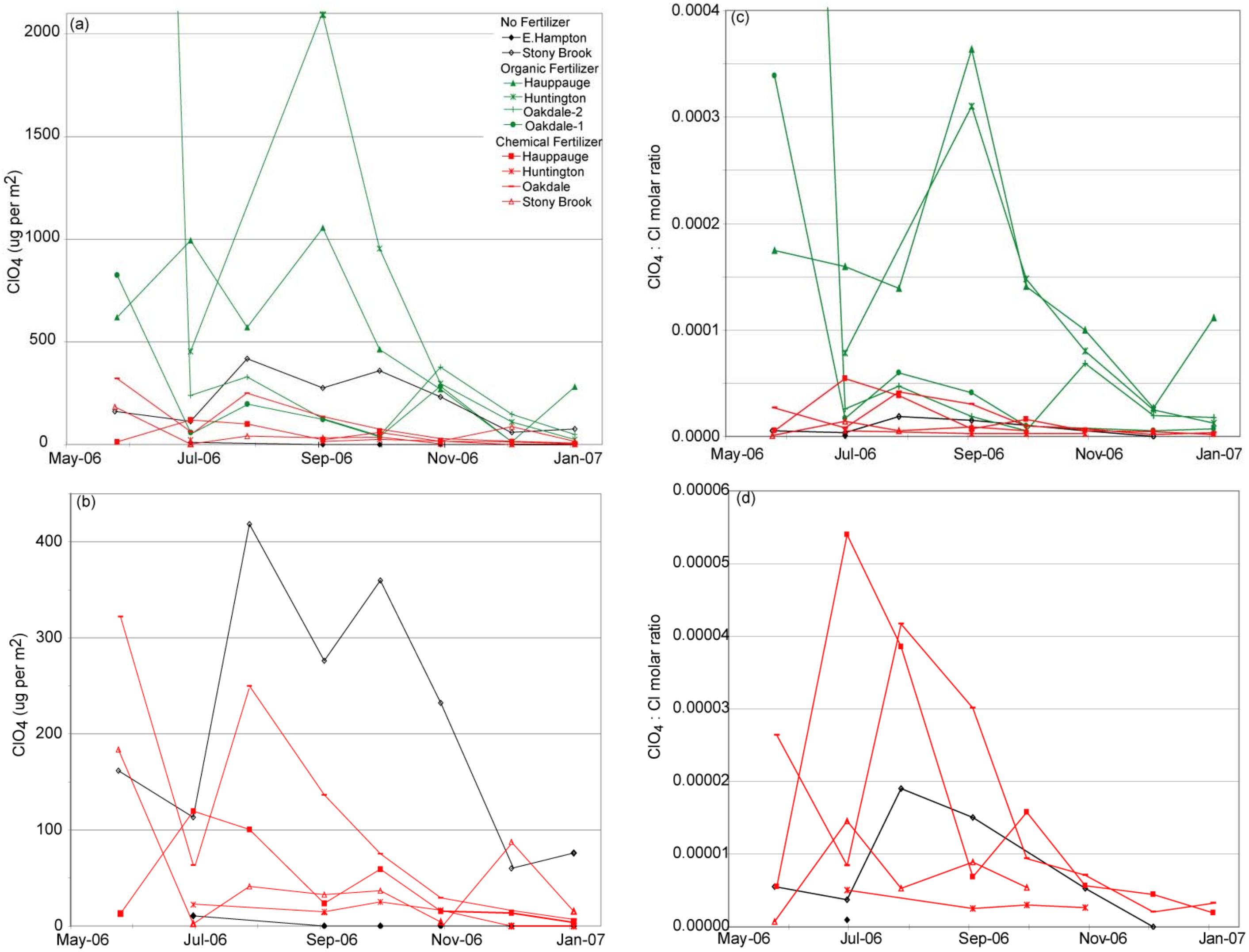

Figure 3. 4. Turfgrass ClO_4 content from June 2006 through January 2007 for (a) all sites and (b) for sites treated with chemical fertilizer and sites not fertilized and ClO_4:Cl molar ratio for (c) all sites and (d) sites treated with chemical fertilizer and sites not fertilized. Outliers not showed Oakdale-2 on 6/1/06 at 11,087 mg per m^2 (a) and 0.0016 (c).

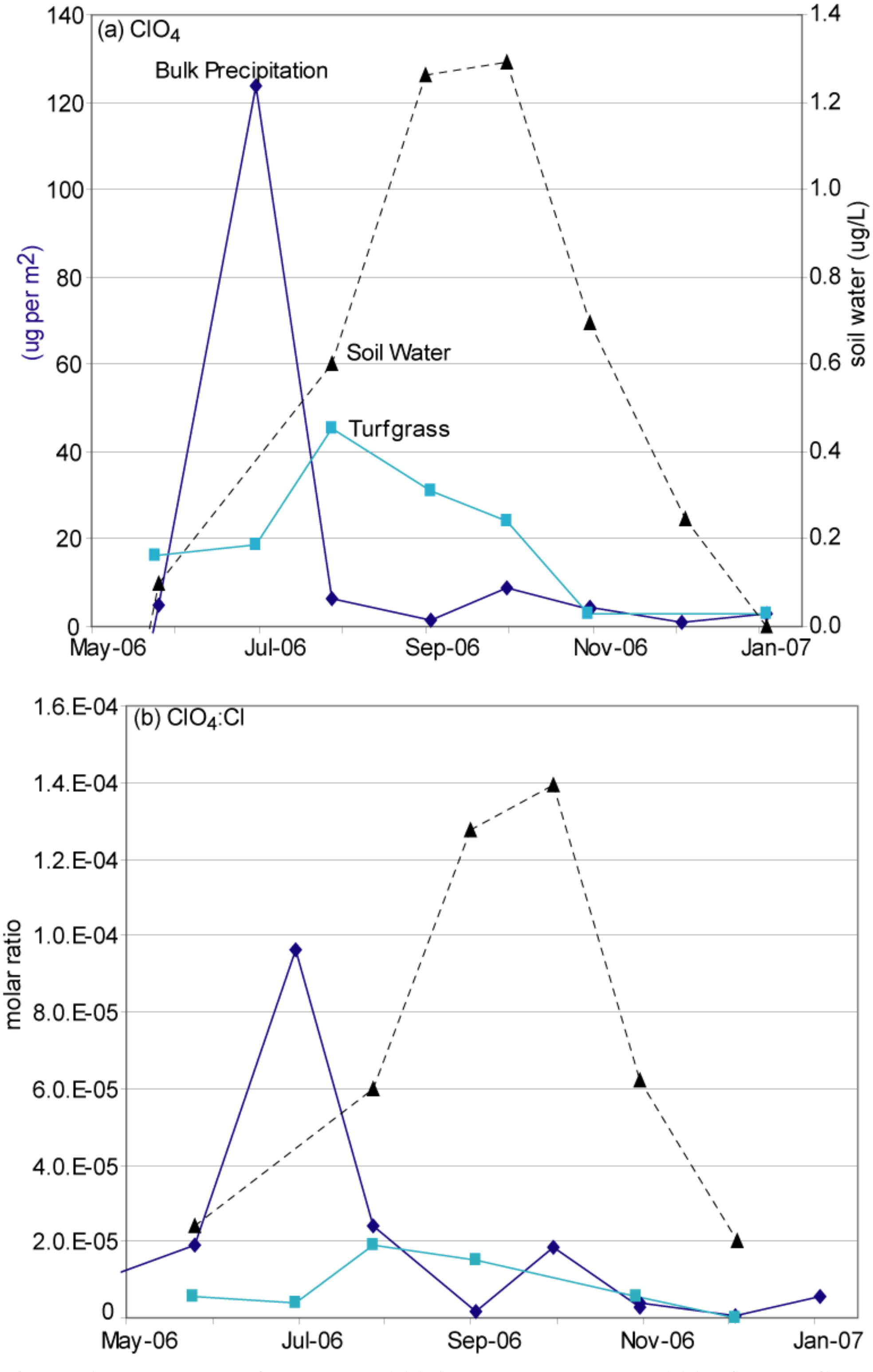

Figure 3. 5. Patterns from June 2006 through January 2007 for the Stony Brook site, not treated with fertilizer for (a) ClO$_4$, (b) ClO$_4$:Cl ratio. Soil water from 100 cm depth.

3.3.2. *Soil core data*

For all three soil cores the concentrations of ClO_4, Cl, N-NO_3 and SO_4 in the surface sample, 5 cm, has a higher concentrations than that at 10 cm (Figure 3. 6). The patterns after 10 cm vary some between the ions and between sites. Chloride concentrations are not conservative with depth (Figure 3. 6 a1, b1, c1), indicating that changes of ion concentrations with depth are likely due to dilution, dispersion, evaporation and variability in the sources of the ions. The N-NO_3 data suggest that there is little to no biodegradation beyond 10 cm depth (Figure 3. 6 a2, b2, c2) and that biodegradation does occur in the surface soils. At the Oakdale-1 site there is increased concentrations of ClO_4 at 20-25 cm, 40 cm and at 90 cm. Similar increases are seen at 40 and 90 cm in Cl and SO_4 concentrations. At the Oakdale-2 site the main increase in ClO_4 concentration is observed around 30 cm. A possible corresponding peak is observed in the Cl profile. The SO_4 profile has a general decreasing trend in concentration with depth. At the Hauppauge site there is an increase in ClO_4 around 70 and 85 cm with corresponding peaks in Cl at those depths. Sulfate also peaks at 85 cm depth. Linear correlations between the ions suggest signification correlation between ClO_4 and N-NO_3 at the Oakdale-1 site and for most ions at the Hauppauge and Oakdale-2 sites (Table 2).

Table 3. 2. Linear R^2 values (95% confidence interval) for soil core concentrations.

Oakdale-1	Cl	N-NO_3	SO_4
ClO_4	0.16	0.62	0.11
Cl	\	0.12	0.40
N-NO_3		\	0.22
Oakdale-2			
ClO_4	0.69	0.97	0.35
Cl	\	0.81	0.83
N-NO_3		\	0.50
Hauppauge			
ClO_4	0.64	0.62	0.62
Cl	\	0.30	0.54
N-NO_3		\	0.75

Any increase in the ClO_4 to Cl ratio from bulk precipitation indicates another source of ClO_4 besides precipitation to the soil cores, since evaporation would not change this ratio. The increased ClO_4 is likely from organic fertilizer and mulched grass, although Cl is also present in these sources. The sites are mowed from April to November. Grass takes a few weeks to breakdown due to the high ligand content. The breakdown increases the source of nutrients available for leaching or uptake by the live

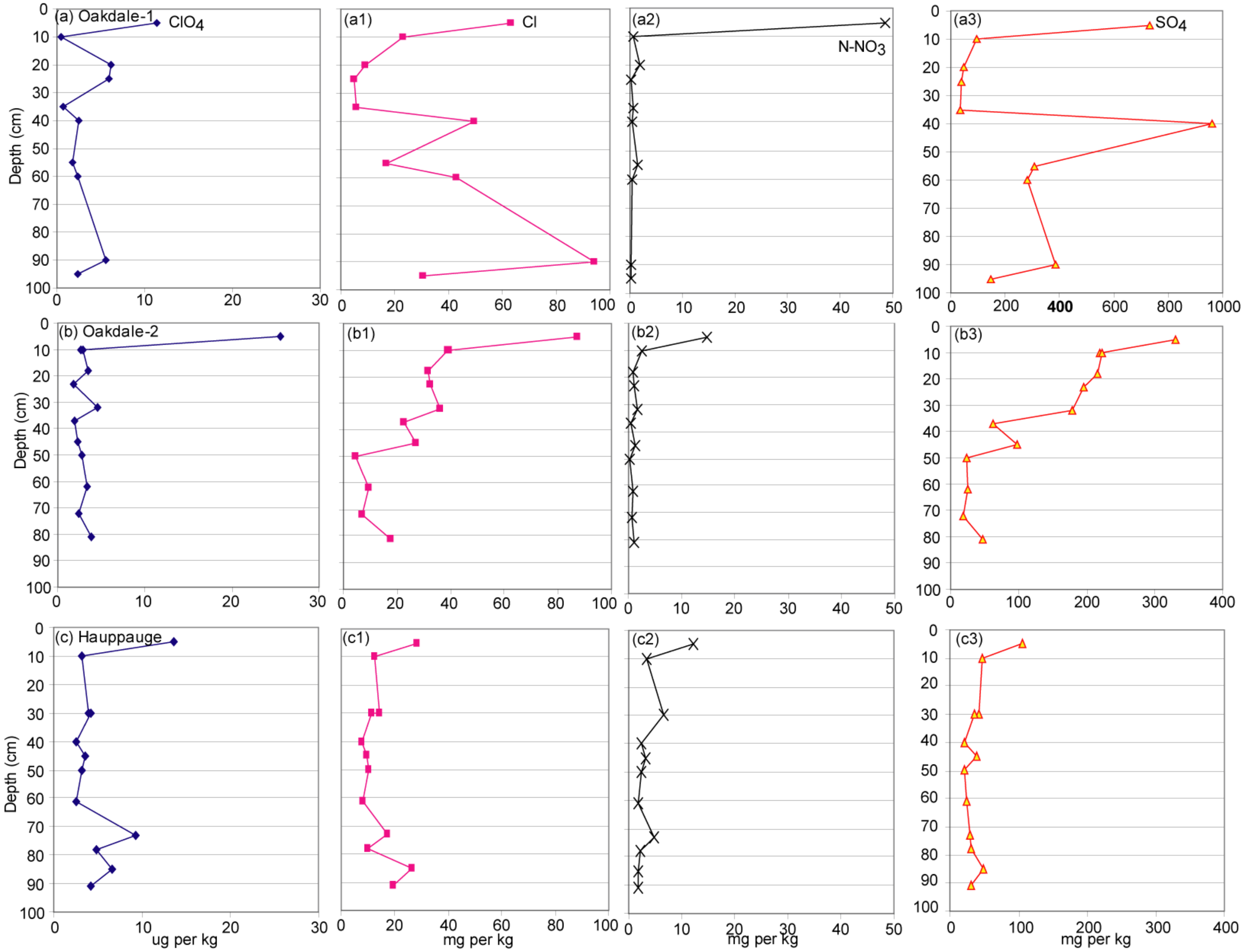

Figure 3. 6. Ion concentrations of soil cores collected from three sites, treated with organic fertilizer, sampled in November 2006. Note the different scale on the x-axis of plot a3.

grass. In fact, it has been shown than 20-30% of turfgrass clipping nitrogen and carbon mineralizes within 7 days after being cut (Shi et al., 2006), with decomposition rates depending on whether the clippings remain on or within the turf canopy, or are transported to the soil surface. The ClO_4 to Cl ratio of the organic fertilizer used in this study is 0.0035. The ratio of the mulched grass is unknown but the ratio of live grass ranges from 0.00001 to 0.00155 from June 2006 to January 2007 at these three sites. The average value is 0.00006 for samples from October 2006 and November 2006 at these three sites. The average value for bulk precipitation in October 2006 and November 2006 at Hauppauge and Oakdale is 0.00001; thus turfgrass, on average, has a higher ratio than bulk precipitation. Increased ratios of ClO_4 to Cl, relative to precipitation, are observed at Oakdale-1 between 20-45 cm, at Oakdale-2 at 50 cm and between 45-80 cm and at Hauppauge for the entire core (Figure 3.7). Soil water samples have higher ClO_4 to Cl ratios than do the soil cores. When the

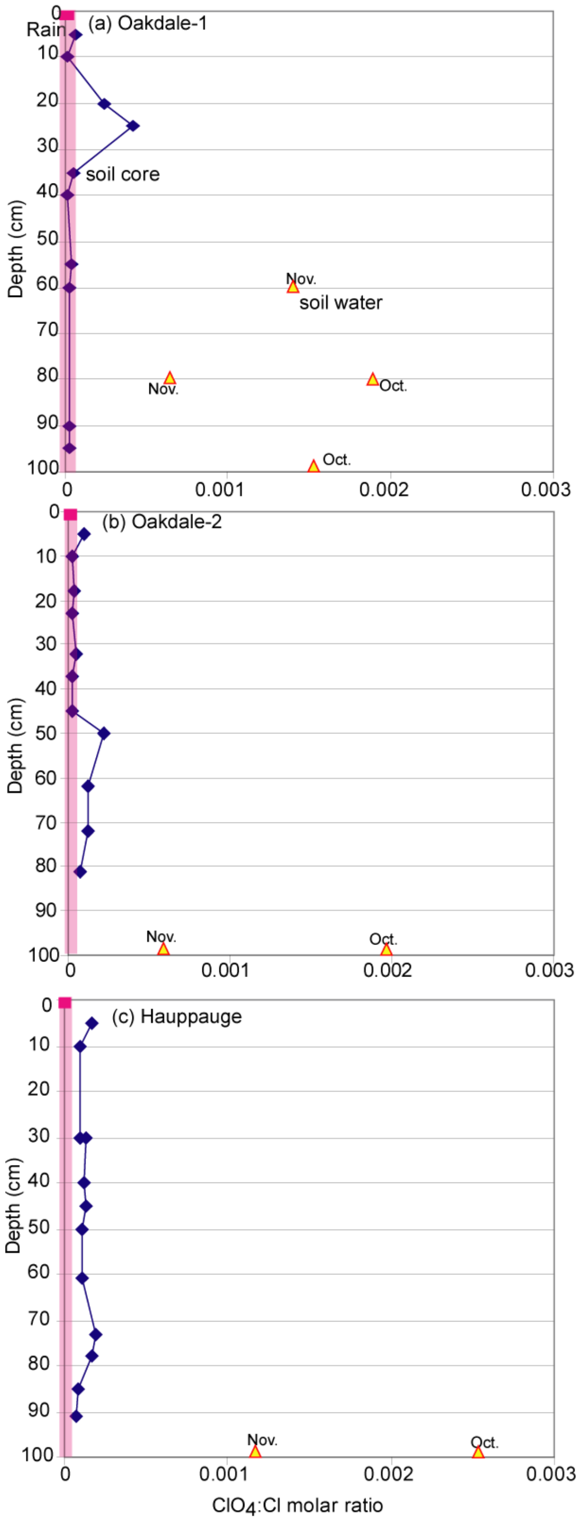

Figure 3. 7. ClO_4 to Cl ratios of soil cores collected from three sites, treated with organic fertilizer, sampled in November 2006, and for monthly soil water samples collected in October 2006 and November 2006.

comparison is available the ClO_4 to Cl ratio is higher in soil water samples collected in October than soil water collected in November.

The peaks observed in ClO_4 to Cl ratios at the Oakdale-1 site and the Oakdale-2 site is likely from the fertilizer applied in October. There is a slight peak in the Hauppauge soil core at 75-80 cm.

3.4 DISCUSSION

The soil water and turfgrass concentrations at the sites treated with chemical fertilizer and those not fertilized are around 2% of the concentrations at the sites treated with organic fertilizer. Concentrations in the lawn environment are dependent on the sources of perchlorate to the system and since the organic fertilizer applied has 9000 μg ClO_4 per kg fertilizer and the concentration of bulk precipitation is less than 3 μg/L (see Chapter 2a) the sites treated with organic fertilizer concentrate and leach more perchlorate. However, the pattern and cycling of perchlorate is similar in all sites. Initially, the turfgrass takes up the additional perchlorate from precipitation in July or from the fertilizer applied in May. The grass is likely taking up ClO_4 via mass flow (Tan et al., 2006) since the $N\text{-}NO_3$ uptake pattern is not similar to ClO_4. Then, that grass is mowed and the clippings are left on the surface to decompose providing an additional source of perchlorate to the lawn environment from May to November. Concentrations of perchlorate in the live grass generally follow the growing cycle of cool season grasses but are also dependent on availability of perchlorate (Jackson et al., 2005). What the grass does not take up eventually leaches in the unsaturated zone, as detected in the soil water 100 cm.

The mistake in fertilizer application at Oakdale chemical and Oakdale-2 organic occurred nine months before the first sample was collected for ClO_4 at Oakdale. This mistake may show that residual perchlorate from the organic fertilizer is still present in soil water at 100 cm up to nine months after application, although perchlorate is also introduced to the system from mulched grass. Perchlorate on soils is not tightly absorbed to the soil particles, and it is unlikely that the perchlorate in a sodium nitrate fertilizer could adsorb to the soil due to high concentrations of other anions (Urbansky and Brown, 2003). It is not certain if the high concentrations at the Oakdale chemical site in August

2006 and November 2006 are from the organic fertilizer as they are less than 1.5 μg/L higher than those at the other sites and additionally the ClO_4 to Cl ratio in the soil water those months are similar to the other sites treated with chemical fertilizer.

Concentrations of ClO_4, Cl and N-NO_3 in the soil cores are linearly correlated. This was not found for the soil water samples. All of the study sites except East Hampton and Hauppauge have a high sand content (60-95% sand) and all of the study sites have high gravel content (1-50% >2mm). As such, water movement through the soil profile should be quick. It is likely that the soil profile from 0-100 cm, in the field, is flushed with rain and irrigation water multiple times per month. Since the soil water samples are a monthly accumulation, relationships between the ions could be complicated due to averaging in the lysimeter.

Soil water concentrations of perchlorate at sites treated with organic fertilizer are a threat to drinking water quality as concentrations are routinely above the state action levels of 5 and 18 μg/L for NY State and above the proposed level by the EPA of 24.5 μg/L. In some states the action level is as low as 1 μg/L and concentrations beneath the sites treated with chemical fertilizer can be greater than that. The perchlorate concentrations in soil water at 100 cm may not be the concentration that enters the groundwater as biodegradation may occur below this depth. Nitrate, however, is a co-contaminant in a lawn environment and present at much higher concentrations than perchlorate. In the presence of relatively high nitrate concentrations the bacteria will preferentially use nitrate as an electron acceptor because growth on nitrate is much faster (Tan et al., 2004a).

3.5. CONCLUSIONS

Urban lawns fertilized with perchlorate containing fertilizers can adversely affect local groundwater quality. It is important to further study the mechanisms of turf uptake and evaluate if lawns fertilized with products containing high concentrations of ClO_4 should have the mowed grass left on the surface to decompose. Additionally a green house study would be prudent identifying which species in the lawns uptake perchlorate, as the lawns in this study are mixed species grasses and other species such as clover. It is possible that a combination of planting certain lawn species that uptake perchlorate and the removal and proper disposal of grass clippings would greatly reduce the amount of perchlorate leaching to groundwater. However, reducing the amount of perchlorate present in fertilizers is likely the easier solution. In fact, Pro Grow, the organic fertilizer used in the study is now manufacturing an organic fertilizer without Chilean nitrate-the main source of perchlorate to this fertilizer.

The results of this study are further complicated when also assessing the impact of nitrate from lawn fertilizers as chemical fertilizers tend to leach more nitrate while organic fertilizers leach more perchlorate. It is clear that lawns can adversely affect groundwater quality and that maintained lawns require time and effort to minimize this affect, time that most home owners, who apply fertilizer, don't wish to invest.

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3.7. SUPPLEMENTAL INFORMATION

Data plots are presented in this section that might be helpful to the reader but are not fully interpreted.

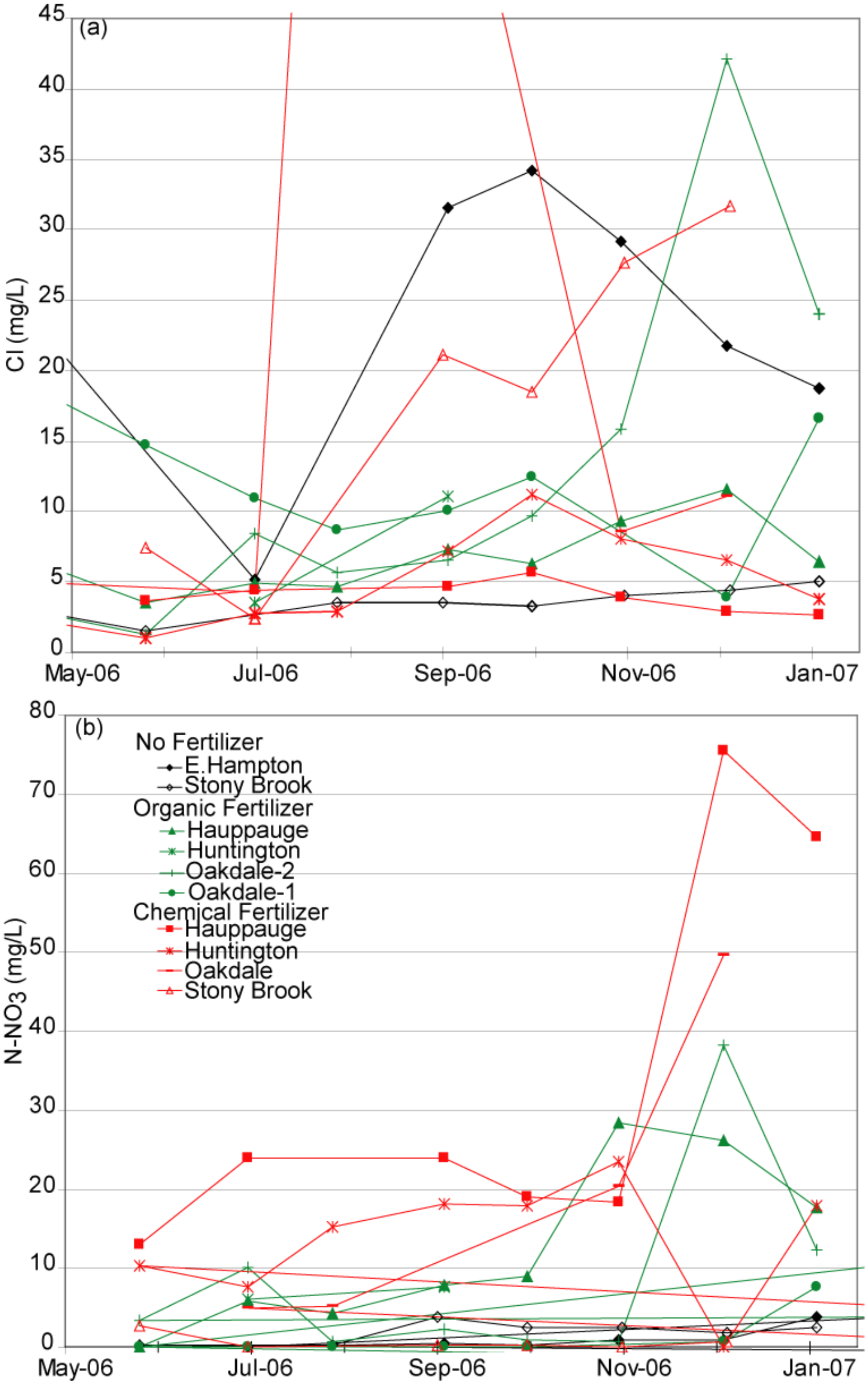

Figure 3. 8. Soil water concentrations of (a) Cl and (b) N-NO_3 for soil water samples collected at 100 cm at all sites. Outlier not showed (a), 97 mg/L.

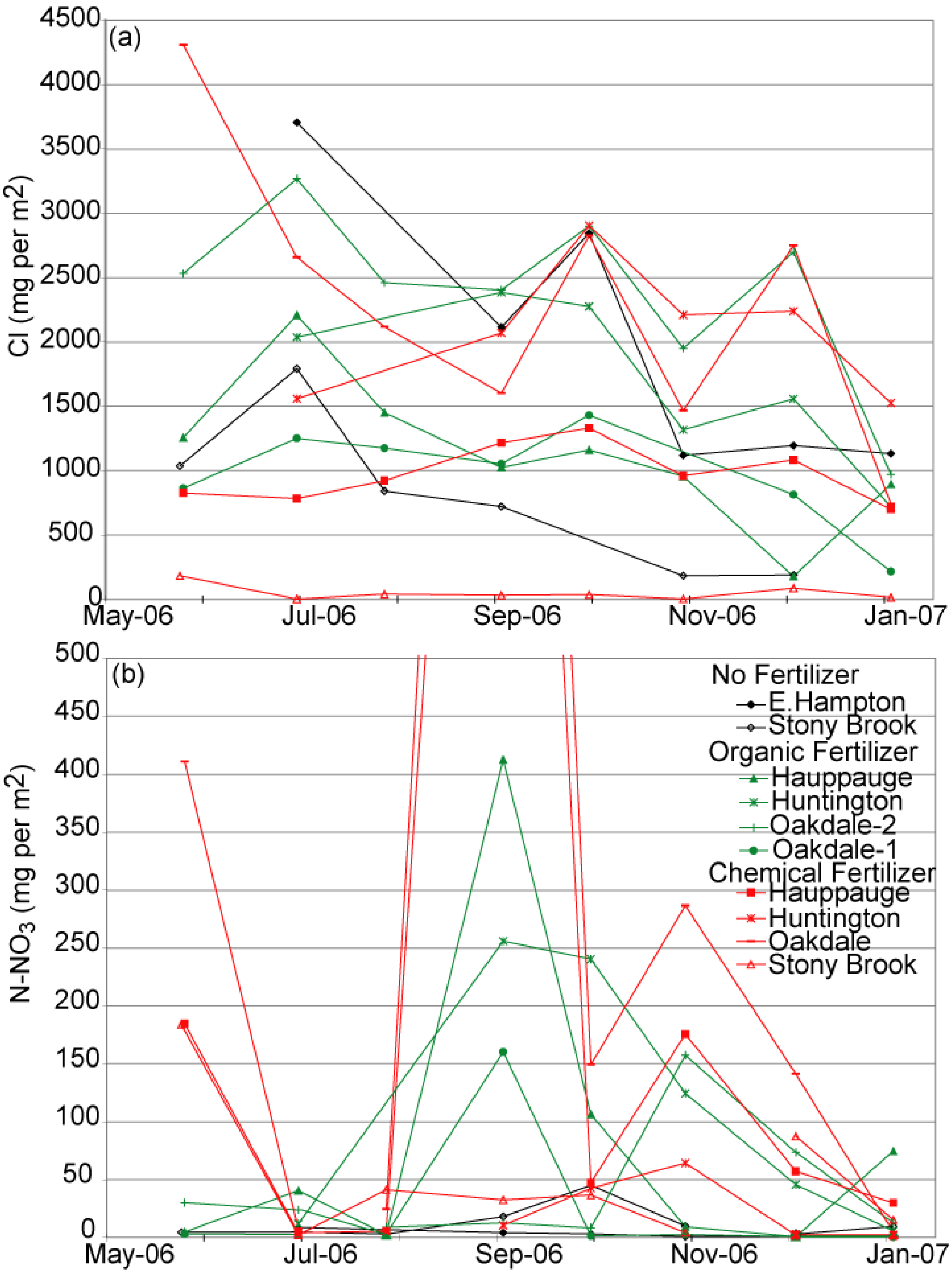

Figure 3. 9. Content of turfgrass samples for (a) Cl and (b) N-NO$_3$ for all plots. Outliers not showed (b) 1489 mg per m^2 at Hauppauge, 1743 mg per m^2 at Oakdale.

For some sites, concentrations of chloride in soil water at 100 cm is relatively constant over the study period, for example, the Stony Brook site that is not fertilized (Figure 3. 8a). Soil water concentrations at other sites peak in August through December. No distinct pattern is observed in turfgrass uptake of Cl, but in general concentrations tend to decrease over the study period (Figure 3. 9a). Concentrations of Cl overlap for the different fertilizer types.

In general, the higher concentrations of N-NO_3 in soil water for the sites are observed late in the year, for the months November, December and January (Figure 3. 8b). Content of nitrate uptake in turfgrass overlap for the sites treated with chemical fertilizer and organic fertilizer, but the highest concentrations are in turfgrass collected from sites treated with chemical fertilizer (Figure 3. 9b). A few general patterns are observed with an initial peak in turfgrass uptake observed in June, and secondary peaks in September and November.

Depth profiles were established at three of the sites (Figure 3.10). Lysimeters within a site are a few meters from each other and spatial variability can complicate interpretation of the data. Variation of perchlorate concentration as a function of depth is not consistent between the three sites or for the duration of the study period. At the Oakdale-1 site treated with organic fertilizer concentration are similar with depth from October through January. From June to August concentrations are highest at 80 cm decreasing with depth. It seems possible that the fertilizer applied at the surface in May is observed in July at 80 cm and then this pulse is observed at 100 cm in August and September. The decrease in peak concentration from 80 to 100 cm could indicate biodegradation. The trend in depth is constant over time at the Oakdale site treated with chemical fertilizer. As a reminder this site was treated, by accident, with organic fertilizer in October 2005. There is a decreasing trend in the data over time at all depths. Concentrations decrease from 60 to 80 cm depth but then increase from 80 cm to 100 and 120 cm in June, July and August. Higher concentrations are observed at 100 cm from June to September with an increase at 120 cm compared to 100 cm in November at the Hauppauge site. There is more clay at Hauppauge than the other sites. It is likely that the breakthrough of perchlorate is not being seen at 120 cm depth until November.

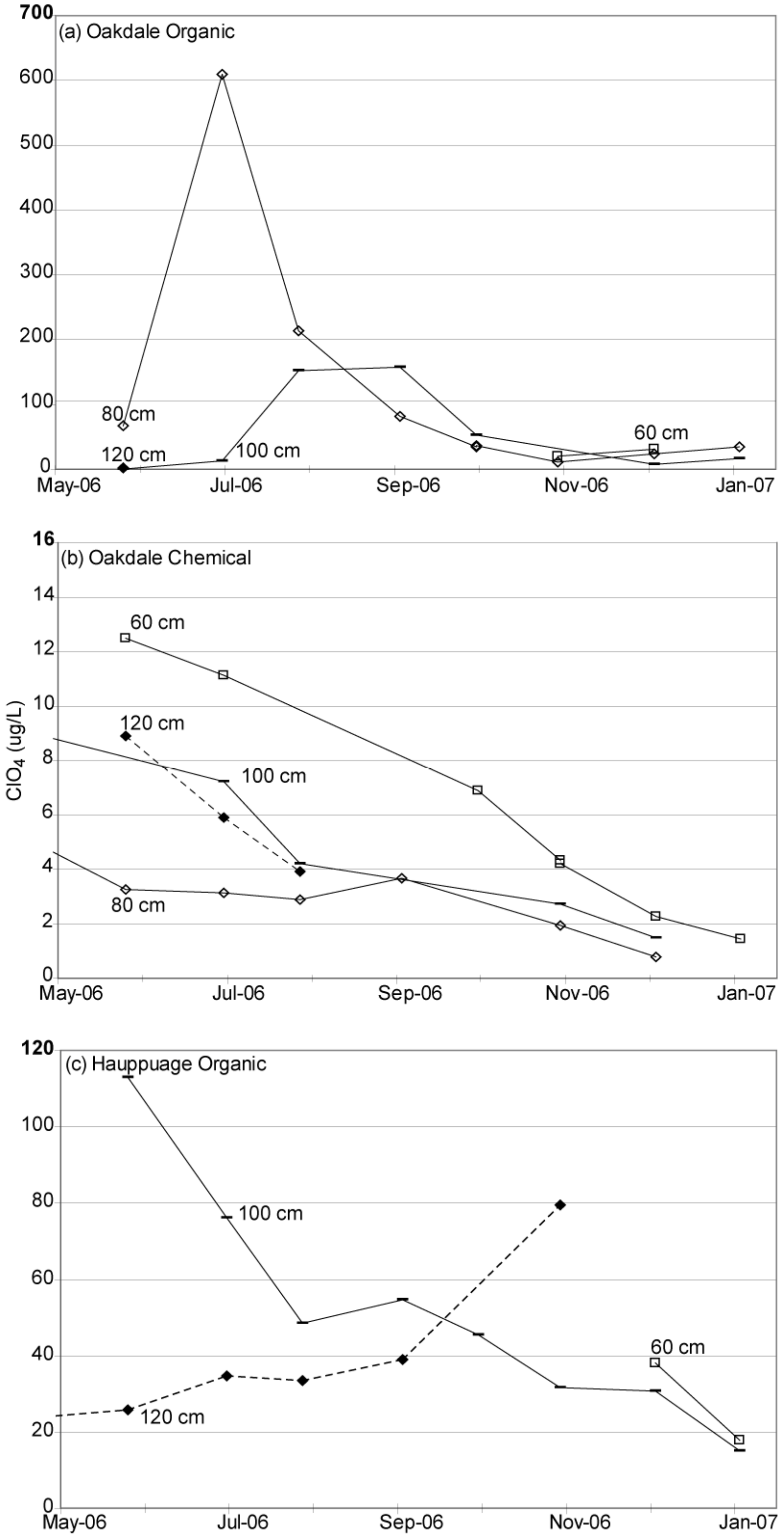

Figure 3. 10. Concentrations of perchlorate as a function of depth for (a) Oakdale-1 organic, (b) Oakdale chemical, fertilizer mistake in May where this site received organic fertilizer instead of chemical and (c) Hauppauge organic. Note the variable axis.

At both the Hauppauge and Huntington locations there is a site treated with chemical fertilizer and a site treated with organic fertilizer. It is beneficial to compare these sites which have little variability in properties besides type of fertilizer, such as lawn species, soil properties, irrigation amount and temperature. Patterns of perchlorate concentrations in soil water collected from 100 cm are different at Hauppauge between the organic site and the chemical site, with the peak concentration occurring earlier in the organic site than the chemical site (Figure 3.11a). However, both sites have an increase early in the study period with decreasing concentrations over time. Turfgrass content at Hauppauge peaks in July at both sites and generally decreases with time with the chemical site having another peak in October and the organic site having an additional peak in September (Figure 3.11b). At Huntington, soil water concentrations were not analyzed for the entire period at the site treated with organic fertilizer, but in July and September the pattern is similar at both sites (Figure 3.11c). The pattern in turfgrass content at Huntington is not similar between sites except at the end of the growing season when content decreases at both sites (Figure 3.11d).

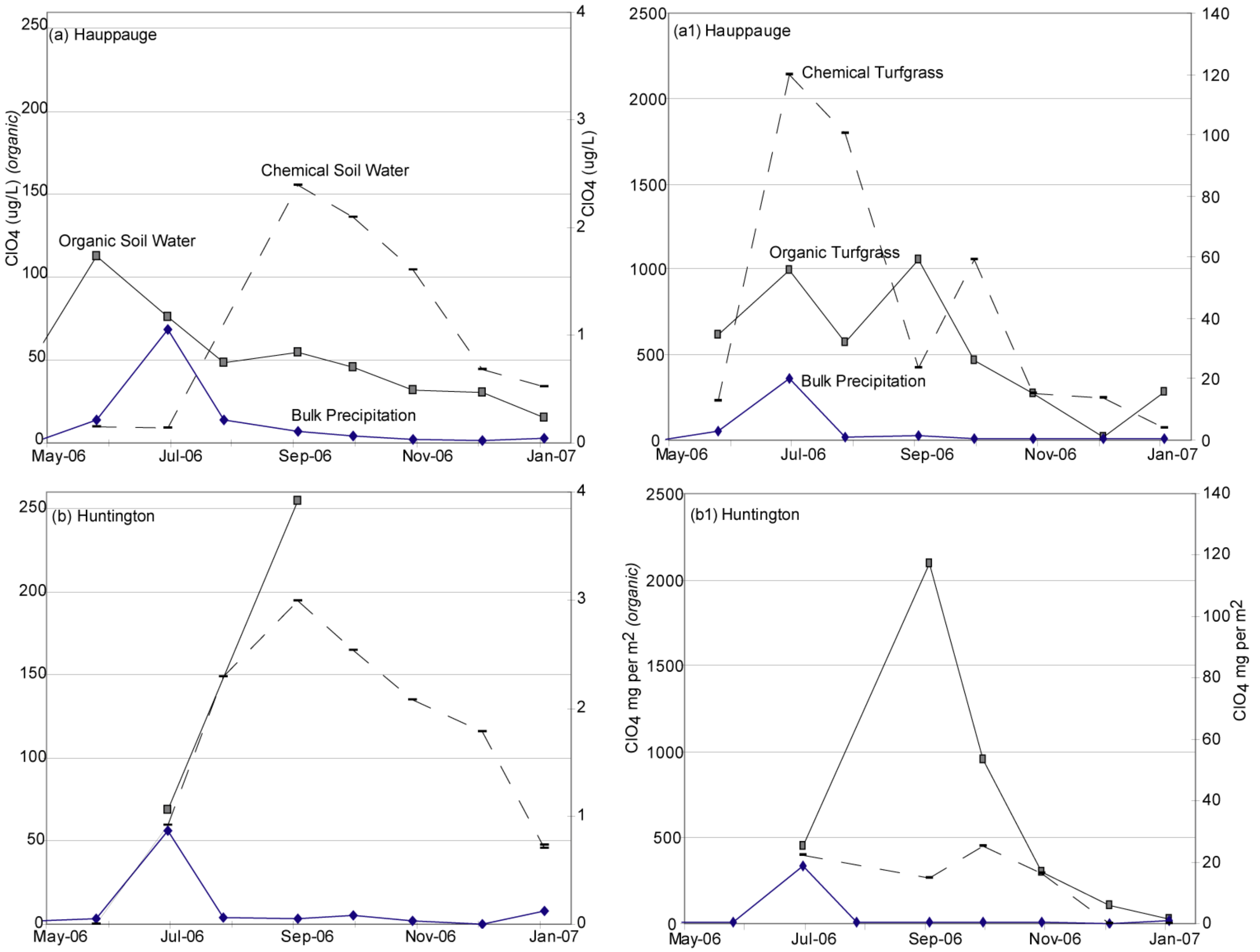

Figure 3. 11. Profile of bulk precipitation, turfgrass content and soil water collected beneath a site that is treated with chemical fertilizer and one which is treated with organic fertilizer at the same study location for (a) Hauppauge, soil water (b) Hauppauge, turfgrass and (c) Huntington, soil water and (d) Huntington, turfgrass.

4. Perchlorate concentrations of sewage from residential septic systems

4.1. INTRODUCTION

Sewage is a nonpoint source of perchlorate to Suffolk County groundwater because: 1) two-thirds of the dwellings in Suffolk County operate on septic systems, which leach sewage to groundwater, 2) up to 8000 µg/L of perchlorate (ClO_4) is present in bleach, and 3) human urine can have up to 21 µg/L.

A study conducted in Massachusetts found a maximum of 390 µg/L in fresh household bleach and up to 8000 µg/L in bleach that was two years old. Bleach used to disinfect drinking water supplies had between 260 and 6750 µg/L (DEP, 2006). The study proposed that sodium hypochlorite breaks down to form perchlorate most probably by the formation of chlorate from hypochlorite and then by the formation of perchlorate from chlorate. The perchlorate concentration in bleach increases with storage duration. The rate of this process appears to increase with the concentration of sodium hypochlorite and storage temperature.

Perchlorate does not appear to be metabolized and is excreted virtually unchanged in the human body (Anbar et al., 1959), with a clearance half-time of roughly 6-8 hours (Greer et al., 2002). Concentrations in human urine suggest that drinking water is not the main source of perchlorate in the human diet because concentrations of perchlorate in urine were higher than the local tap water (Martinelanger, 2006; Valentin-Blasini, 2005). Perchlorate is present in various food sources (U.S.FDA, 2005), where it is hypothesized that plants either concentrated perchlorate from fertilizers or irrigation water.

The U.S. Environmental Protection Agency reports that most standard physical and chemical water or wastewater treatment processes do not remove perchlorate (DTSC, 2004). However, perchlorate reducing bacteria are common in the environment (Coates et al., 1999) and redox conditions of a sewage plume are favorable for perchlorate reduction (Bardiya and Bae, 2005). Reduction of perchlorate in septic systems is probable, as reduction of perchlorate was demonstrated in two septic tanks where the local tap water was greater than 150 μg/L, yet the concentrations in the septic tanks were less than 0.3 μg/L (DEP, 2006).

The objective of this study is to determine the concentration of perchlorate in sewage samples from residential septic systems and to evaluate the impact of sewage derived perchlorate to groundwater in Suffolk County, NY.

4.2. METHODS

Thirty five residential sewage samples were acquired from Suffolk County Department of Public Works. Most septic systems combine a cesspool with a secondary septic tank; however, septic tanks weren't required until the mid 1970's. Sewage samples were centrifuged to separate the solids from the liquid. The supernate was filtered first with a 0.45 μm glass fiber filter and then with a 0.2 μm surfactant-free cellulose acetate (SFCA) filter and collected in untreated, sample rinsed, polypropylene vials. Samples were stored at 4°C until analysis. Initial samples were analyzed by ion chromatography (IC), with a detection limit of 2 μg/L (Wagner et al., 2005). Secondary sets of samples were analyzed using a sequential ion chromatography-mass spectroscopy/mass spectroscopy (IC-MS/MS) technique (Aribi and Sakuma, 2005) with a method detection limit of 0.1 μg/L. The precision determined from replicate analysis was ± 5%. To account for matrix effects in the IC-MS/MS method, all samples were spiked with an oxygen-isotope (^{18}O) labeled ClO_4 internal standard.

One container of household bleach was purchased at a local grocery store in Setauket, NY, from which four samples were prepared for perchlorate analysis by IC-MS/MS. Samples were diluted by 1000 before analyzed to reduce the conductivity, as high conductivity can interfere with the results. Two of the samples were not filtered and two were filtered using 0.2 μm SFCA filters. All samples were stored in untreated, sample rinsed, polypropylene vials at 4°C until analysis. Storage time was the same for all samples.

4.3. RESULTS AND DISCUSSION

4.3.1 Concentrations of perchlorate in bleach and sewage

Concentrations of perchlorate in household bleach are between 380 and 460 µg/L ClO_4 and within the range of samples analyzed elsewhere (DEP, 2006). There was no difference between filtered and unfiltered samples. The average value is 401 ± 4 (standard error) µg/L. The Suffolk County Water Authority uses bleach to disinfect drinking water, however, only a small amount is used and the bleach used has minimal storage time.

The highest concentration of perchlorate in sewage is 258 µg/L, all other samples have less than 10 µg/L (Table 4.1). The samples analyzed by IC-MS/MS, which has a lower detection limit than those analyzed by IC, have an average concentration of 2.2 ± 0.5 µg/L. To my knowledge this is the first data set of raw sewage. Samples from sewage treatment plants in China were analyzed (Shi et al., 2007) yet these samples are digested sludge collected from the final step in wastewater treatment plant (Written communication, Yaqi Cai, 5/20/08) and can not be directly compared with my data. Primary (raw) sludge is the collection of solids from the fresh sewage. This sludge is then processed in one of many ways involving a digestion or decomposition that reduces the volume of sludge, this final sludge is called digested sludge. The concentrations in their study are between 0.6 and 380 µg ClO_4 per kg for 31 samples from facilities that include both residential and industrial sewage from a large geographical range in China (Shi et al., 2007).

4.3.2. Calculations of perchlorate in sewage and groundwater

The expected concentration of perchlorate in sewage from septic systems is estimated as:

$$C_s = \frac{Vol_T * C_T + Vol_B * C_B + Vol_U * C_U}{Vol_{Total}} \qquad (1)$$

Where C is concentration in µg/L ClO_4, Vol is daily discharge volume in liters, T stands for the local tap water, B is for household bleach, U is for urine and S is for sewage. Bulk precipitation has an average concentration of 0.2 µg/L and a maximum concentration of 3 µg/L (Chapter 2a). Few supply wells have concentrations greater than 2 µg/L (Suffolk

Table 4. 1. Concentrations of perchlorate in sewage from residential septic systems.

Date Collected	Lab #	ClO_4 *(µg/L)*	Detection Method
11/9/2005	W40	<2.0	IC
11/9/2005	W41	4.80	IC
11/9/2005	W42	<2.0	IC
11/9/2005	W43	<2.0	IC
11/9/2005	W44	<2.0	IC
11/9/2005	W45	260	IC
11/9/2005	W46	<2.0	IC
11/9/2005	W47	<2.0	IC
11/9/2005	W48	<2.0	IC
11/9/2005	W49	2.20	IC
11/9/2005	W50	<2.0	IC
11/9/2005	W51	<2.0	IC
3/21/2006	W53	2.4	IC-MS/MS
3/21/2006	W54	3.9	IC-MS/MS
3/21/2006	W55	3.4	IC-MS/MS
3/21/2006	W56	3.3	IC-MS/MS
3/21/2006	W57	1.0	IC-MS/MS
3/21/2006	W58	0.68	IC-MS/MS
3/21/2006	W59	4.0	IC-MS/MS
3/21/2006	W60	0.96	IC-MS/MS
3/21/2006	W61	2.20	IC-MS/MS
9/11/2006	W62	3.90	IC-MS/MS
9/11/2006	W63	9.0	IC-MS/MS
9/11/2006	W65	0.60	IC-MS/MS
9/11/2006	W70	2.3	IC-MS/MS
9/11/2006	W71	0.62	IC-MS/MS
9/11/2006	W72	0.13	IC-MS/MS
9/11/2006	W73	0.16	IC-MS/MS
9/11/2006	W74	3.8	IC-MS/MS
9/11/2006	W75	0.35	IC-MS/MS
9/11/2006	W76	5.6	IC-MS/MS
9/11/2006	W77	<0.1	IC-MS/MS
9/11/2006	W78	0.23	IC-MS/MS
9/11/2006	W79	0.11	IC-MS/MS
9/11/2006	W81	1.64	IC-MS/MS

IC=ion chromatograph, MS=mass spectrometer

County Water Authority Water Quality Report, 2007). Concentrations of perchlorate in tap water should then be between 0.2 – 3 μg/L. In fact, perchlorate in 16 supply wells in Western Suffolk County that I analyzed was within this range. Groundwater from wells sourced in open space were <0.05 to 0.1 μg/L and groundwater from wells sourced in low or medium residential density land use ranged from 0.4 to 2.2 μg/L. The volume of tap water (Vol_T) is essentially the total volume (Vol_{Total}), which is estimated to be 900 L per day (Flynn et al., 1969), since the volume of urine and the volume of bleach are small. On average, 1.25 L per person per day is excreted as urine (Wilsenach and van Loosdrecht, 2003). If there are four people in each household then the total contribution is 5 L of urine per septic system per day with a concentration of 21 μg ClO_4 per L urine. The Massachusetts Dept. of Environmental Protection estimates that people use one cup (0.2 L) of bleach per laundry load. We assume one load of laundry per day with concentrations of bleach ranging from 89 to 8000 μg/L. Concentrations of sewage calculated from these assumptions are at 0.3 to 5.2 μg/L. The average value of this study, of 2.2 μg/L, is in the middle of the calculated concentrations. Concentrations greater than 5 μg/L are likely due to higher concentrations in bleach and urine than these estimates or from additional sources of perchlorate to sewage.

The average concentration of groundwater in Suffolk County, influenced by sewage, can be calculated as:

$$C_{gw} = \frac{Vol_S * C_S + Vol_P * C_P}{Vol_{Total}} \qquad (2)$$

Where C is concentration in μg/L ClO_4, Vol is the daily recharge volume in liters, gw stands for groundwater, S for sewage and P for bulk precipitation. Bulk precipitation has an average concentration of 0.2 μg/L (Chapter 2a) and an estimated recharge of 4,900 million liters per day (assumes 50% of precipitation is recharged; (Busciolano, 2004)). Sewage from septic systems discharge 900 L per cesspool per day (Flynn et al., 1969) and since 2/3 of the homes in Suffolk County operate on cesspools (Allee et al., 2001) an estimated 313 million liters per day of sewage is recharged to the groundwater. Using the range in concentrations for sewage, 9 μg/L and 0.1 μg/L, and the average value of bulk precipitation, 0.2 μg/L, groundwater contaminated by sewage and diluted by precipitation would result in concentrations less than 1 μg/L. However, this is an average concentration across Suffolk County. In areas of concentrated residential land use, this estimate will increase. Assuming all dwellings in a given area have a septic system, the estimated yearly average of perchlorate concentrations in groundwater are 0.2 to 1.4 µg/L for low residential density land use (259 dwellings per square km; (CDM, 2003)) and from 0.2-4.1 µg/L for medium residential density land use (1375 dwellings per square km).

4.4. CONCLUSIONS

Perchlorate from sewage will raise the concentration in the groundwater above background levels. Depending on the density of septic systems and the amount of perchlorate reduction by bacteria, the groundwater concentrations may increase to near the NY State advisory level of 5 µg/L. Although microbial reduction was demonstrated in a septic system in Massachusetts it is uncertain if degradation occurs in septic systems in Suffolk County since measured concentrations are within the range of calculated concentrations (DEP, 2006). Future research measuring the sources to a specific cesspool and monitoring the concentrations of ClO_4 in the cesspool and within the plume would aid in answering this question. Mitigation of septic systems in Suffolk County is not likely to occur as sewering older homes are a costly endeavor. The likely way to reduce the perchlorate impact from sewage is to reduce the concentration and volume disposed of for the sources.

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5. Perchlorate and ion chemistry of road runoff

5.1. INTRODUCTION.

Since perchlorate was added to the U.S. Environmental Protection Agency contaminant candidate list in 1998 (EPA, 1998), perchlorate has been the focus of much research and debate. Perchlorate inhibits iodide uptake of the thyroid gland (NRC, 2005), which is of particular concern for the portion of the population with iodide deficiencies. This health concern coupled with the mobility of perchlorate poses a threat to groundwater. Suffolk County, Long Island, NY is particularly sensitive to groundwater contamination as all potable water is derived from the local aquifers. New York State has implemented advisory levels of 18 µg/L ClO_4 for the public notification level and 5 µg/L ClO_4 for the drinking water planning level in groundwater. Advisory levels are as low as 1 µg/L in Massachusetts, Maryland and New Mexico (EPA, 2005).

Perchlorate contamination is commonly associated with rocket fuel propellant or Chilean nitrate fertilizer use; yet, perchlorate is detected in groundwater samples where these two common sources have not been present. In dry regions, atmospheric deposition may account for the unknown perchlorate source (Plummer et al., 2006; Rajagopalan et al., 2006). In temperate regions where natural perchlorate does not concentrate, other sources must be considered. Road safety flares and car air bags are suggested as possible nonpoint sources (GC, 2005). Some air bags contain 110-1000 mg of $KClO_4$ mixed with Zr, Ti and B (Turboflare USA Inc.). Road safety flares are typically composed of (by weight) 75% $Sr(NO_3)_2$, and <10% each of $KClO_4$, S, and a binder (Turboflare USA Inc.). Although some flares do not contain perchlorate, the road flares purchased by Suffolk County Police department have at least “some” perchlorate present (Kenny Harrison, Orion Safety Products, written communication, 2006).

Leaching from a road flare manufacturing plant has contaminated groundwater in Santa Clara Valley, CA (Ruby, 2004). The distribution of perchlorate was generally between 4 and 10 µg/L. Prompted by this contamination event, Silva (2003), measured perchlorate content from unburned, partially burned and burned road flares. He found that unburned road flares contained 3,600 mg of perchlorate per flare, and that fully burned flare residue contained 1.9 mg perchlorate per flare. Based on total flare sales, average cost of a flare, and 3,600 mg of perchlorate per flare, researchers have estimated that 140 tons of perchlorate is used each year for road flares in the continental United States (GC, 2005).

Although road flares have been recognized as a nonpoint source there is relatively little research analyzing their impact on the environment. Dasgupta et al. (2007) suggested that road flares are not a significant source of contamination based on the small portion of perchlorate used for flare production compared to other uses and on the fact that flares are usually allowed to burn to completion. Veeger et al. (2005) usually found less than the detection limit of 4 µg/L perchlorate for water in ditches that collect road runoff where flares had been used in Rhode Island, USA.

Perchlorate concentrations were investigated in road runoff from highways with high incident of traffic accidents on the assumption that road flares are a possible nonpoint source of perchlorate contamination to groundwater. To aid in interpreting the sources of perchlorate to road runoff the concentrations of Br, Cl, I, B, Ca, Na, Mg, K, Sr, NO_2, NH_4, NO_3, and SO_4 were analyzed.

5.2. METHODS

5.2.1. Site locations

Two locations were chosen in Suffolk County, New York (Figure 5.1) to evaluate perchlorate concentrations in road runoff. According to Suffolk County Police Department statistics from January 1999 through December 2000 these sites had the highest incidents of traffic accidents in the Township of Brookhaven. Site 112 is along State Highway 112 (Figure 5.2) between Horse Block Road and Express Drive North, north of the Long Island Expressway (N40°49’39-27” and W72°59’51-33”). There were 237 traffic accidents between January 1999 and December 2000. Seven accidents actually occurred during the sampling period between April 1 and April 16, 2006, yet none of these accidents occurred after dark which was around 7:30 pm this time of year. One accident, on April 6 occurred at 5:45 pm which was classified as a motor vehicle accident with injuries. An accident causing injuries could incur more damage and involve more vehicles, resulting in the use of road flares even though it may not be near dark. The study area covers approximately 0.32 km of roadway. Samples were taken at four stormwater basins at this site. Sampling locations labeled 1 and 2 are at traffic lights and those labeled 3 and 4 are at shopping center entrances (Figure 5.2).

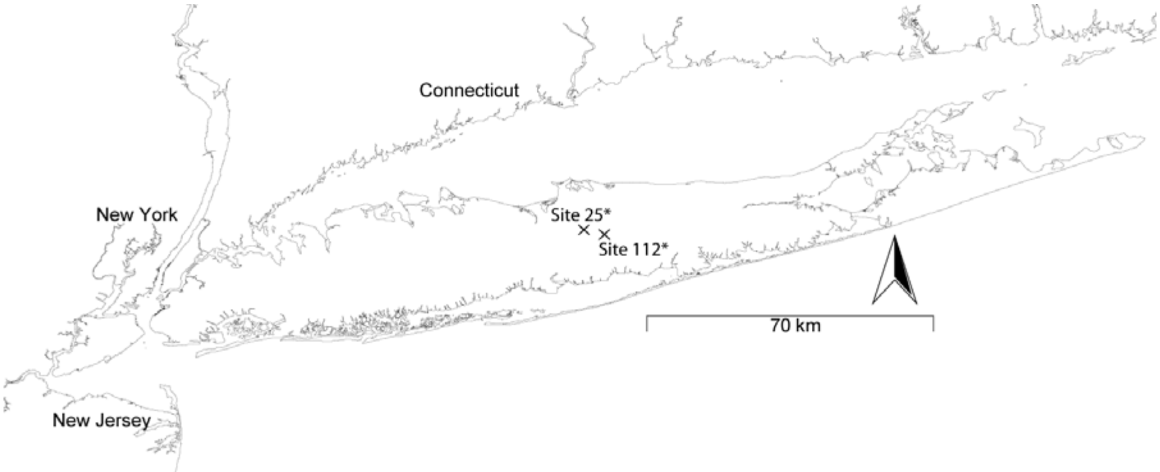

Figure 5. 1. Map of study sites. *See Figures 5.2 and 5.3 for site details.

Site 25 is along State Highway 25 (Figure 5.3) west of Nicolls Road and east of Oak Street (N40°51’39-27” and W73°05’51”-04’3”). There were 430 total accidents from January 1999 through December 2000. Site 25 covers a greater length of roadway (3.9 km) and was the location of more accidents than Site 112. At Site 25, twenty nine accidents occurred during the sampling period. Two after dark accidents included injuries. Five accidents that occurred during the day included injuries. Samples were collected at nine stormwater basins and two recharge basins. Sample 1 was taken at a traffic light for a fire department station and sample locations 2, 4 and 6 are at intersections with traffic lights. Other samples were located at sidewalk curbs (Figure 5.3).

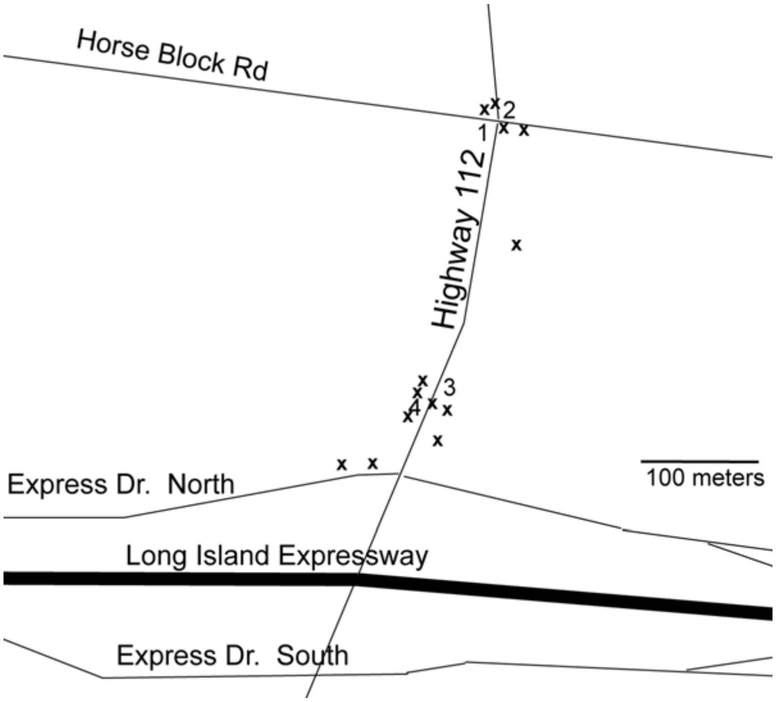

Figure 5. 2. Details of Site 112. An X indicates a stormwater basin that was not sampled. Numbers correspond to sample numbers.

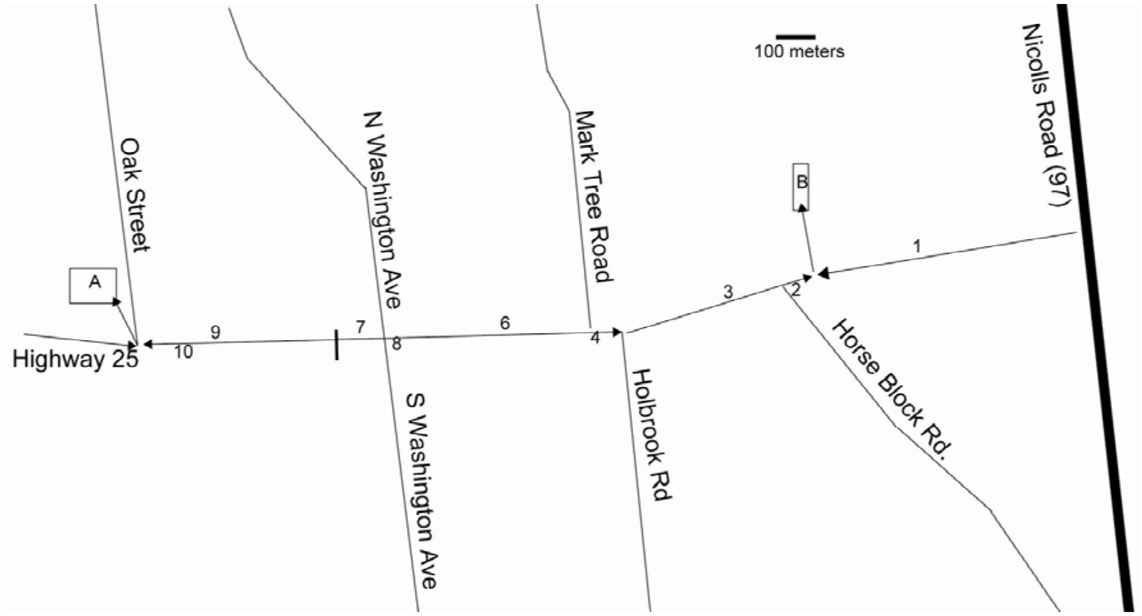

Figure 5. 3. Details of Site 25. Numbers correspond to sample numbers. A and B are recharge basins. The arrows indicate the direction of storm water flow from the stormwater basins.

5.2.2. Sampling

Road runoff samples from stormwater basins and recharge basins were collected after five different rain events during April, 2006. NALGENE© stormwater samplers (cat. nos. 1100-1000) were installed in four stormwater basins (grates) at Site 112 and at nine stormwater basins at Site 25. These samplers allowed collection of the "first flush" of runoff. The samplers fill and seal off after one liter is collected. The samplers were hung beneath stormwater grates. Some grates had impeded flow due to sand build up near the grate. We did our best to remove this sand. We found the best method to determine placement of the stormwater samplers was to go out during a rain event and observe the direction of stormwater flow.

Two recharge basins which receive water from Highway 25 were also sampled (Figure 5.3). These basins both had standing water at all sampling events. Residence times of recharge basins can vary from a few hours to months, with the average residence time for basins on Long Island being 4 days in wet periods and 20 days with no wet precipitation (Aronson and Seaburn, 1974). We did not calculate residence time at these basins since we weren't able to quantify the stormwater inputs or the depth of the basin. The surface water near the inflow pipe of the basins was sampled with each collection of the stormwater samplers. Samplers 9 and 10 drain into recharge basin A and samplers 1-8, drain into recharge basin B (Figure 5.3).

The sample bottles were picked up within 24 hours after each rain event, and taken directly back to the lab where they were filtered with a 0.2µm surfactant-free cellulose acetate (SFCA) filter for perchlorate analysis and a 0.45µm glass fiber filter for major ion analysis and stored in sample rinsed polypropylene sample bottles at 4ºC until analysis. Perchlorate was analyzed using a sequential ion chromatography-mass spectroscopy/mass spectroscopy (IC-MS/MS) technique (Aribi and Sakuma, 2005) with a method detection limit of 0.1 µg/L. To account for matrix effects, all samples were spiked with an oxygen-isotope (^{18}O) labeled ClO_4 internal standard. The precision determined from replicate analysis was ±5%.

The ions, B, Br, I, Ca, Mg, Na, K and Sr were analyzed by Activations Laboratory using ion coupled plasma mass spectrometry. Detection limits were as follows: B 1 µg/L, Br 3 µg/L, I 1 µg/L, Ca 700 µg/L, Mg 2 µg/L, Na 5 µg/L, K 30 µg/L, Sr 0.04 µg/L. Most samples were above the 35 mg/L maximum limit for Na, and a few were above the 20 mg/L maximum limit for Ca and Mg, and the 200 μg/L maximum limit for Sr. Samples above the maximum limit for Sr, Na, Ca and Mg were reanalyzed by direct couple plasma optical emission spectroscopy in the Department of Geosciences at Stony Brook University. The anions Cl, N-NO_3, PO_4 and SO_4, were analyzed in the Marine Science Research Center at Stony Brook University, using a Lachat's QuickChem8500 Flow Injection Analysis System. Detection limits are 0.1 mg/L for N-NO_3 and PO_4, and 1 mg/L for SO_4 and Cl. The precision for these analyses is 10%.

A total of one hundred and fifteen samples containing both wet and dry (i.e. bulk) deposition were collected monthly for 20 months between November 30, 2005 and July 5, 2007 at six locations in Suffolk County, NY. Samples were processed with the same protocol as the stormwater samples.

Road salt samples from the Stony Brook University storehouse and from one Suffolk County Highway storehouse were analyzed for perchlorate. According to the New York State Procurement Service Group salt in Suffolk County is purchased from the International Salt Co. which reports that their salt is >98.5% pure NaCl (www.ogs.state.ny.us/purchase/). Approximately 5g of road salt was dissolved into 50 mL of deionized water, filtered with a 0.2μm SFCA filter and stored at 4ºC until analysis. The Cl content of the Stony Brook University sample was measured with an automated potentiametric titration producing silver chloride (AgCl) using a CMT 10 Chloride Titrator by the Marine Science Research Center at Stony Brook. From this concentration the concentrations of the other elements could be estimated using ion to chloride mass ratios from the literature (Granato, 1996; Panno, 2005).

5.3. RESULTS

The average concentrations of the stormwater basins and the recharge basins are greater than the average concentrations of bulk precipitation (Table 5.1) for all ions except N-NO_3, which measure similar concentrations as precipitation in the recharge basins but not in the stormwater basins. The average ion concentrations of stormwater basins between Site 112 and Site 25 do not differ by more than the standard error of the mean for all ions except for B, N-NO_2 and N-NO_3, with Site 112 measuring higher average values and for Br, with Site 25 measuring a higher average value (Table 5.1). The average values of all stormwater basins are higher than the recharge basin averages except for Cl, Na and Sr where the values for the recharge basins are greater.

Perchlorate is not correlated ($R^2<0.5$, 95% confidence interval) with any of the ions for water from all stormwater basins (Table 5.2). At Site 112 perchlorate concentrations in stormwater basins are positively correlated with N-NO_2, N-NO_3, Ca, Mg, SO_4, Sr and B. Perchlorate concentrations of water collected at the stormwater basins of Site 25 are correlated with N-NO_2 and Sr. Perchlorate concentrations of water collected from the recharge basins are positively correlated with Cl, Na, Mg, Sr and I.

Table 5. 1. Average ion concentrations of stormwater basins, recharge basins and bulk precipitation.

	N-NO_2 *mg/L*	**N-NH_4** *mg/L*	**N-NO_3** *mg/L*	**ClO_4** *µg/L*	**Cl** *mg/L*	**SO_4** *mg/L*	**Na** *mg/L*	**Mg** *mg/L*	**K** *mg/L*	**Ca** *mg/L*	**I** *µg/L*	**Br** *µg/L*	**Sr** *µg/L*	**B** *µg/L*
Site 112-stormwater basins (14)														
Avg.	0.41	1.3	2.2	2.5	156	46	101	1.6	4.9	17	11	49	64	231
SE	0.22	0.4	0.5	0.9	42	13	24	0.4	1.6	5	2	12	12	101
Site 25-stormwater basins (19)														
Avg.	0.07	2.0	1.2	2.0	160	38	101	2.5	3.0	25	12	92	60	98
SE	0.02	0.5	0.3	0.9	37	8	20	0. 7	0.5	10	2	23	13	15
All stormwater basins (33)														
Avg.	0.21	1.8	1.6	2.2	158	41	101	2.1	3.8	21	11	73	62	153
SE	0.09	0.3	0.35	0.7	27	7	15	0.4	0.8	6	1	14	9	44
Both recharge basins at Site 25 (10)														
Avg.	0.02	0.49	0.29	3.0	306	8.3	182	1.4	1.3	8.6	4.6	38	91	54
SE	0.00	0.25	0.04	0.9	38	1.2	15	0.1	0.1	0.6	0.2	4	8	6
Bulk Precipitation (115)														
Avg.	<0.1	0.16	0.25	0.20	3.6	2.6	2.3	0.28	0.6	0.5	6.7	9.1	3.5	26
SE	ND	0.05	0.03	0.04	0.3	0.2	0.2	0.02	0.1	0.1	1.1	0.5	0.3	3

SE is the standard error of the average (Avg.). The number in parenthesis next to the sample group is the number of samples collected, not all samples could be analyzed for all ions. Samples below detection were treated as a zero value and values above detection were not included in the calculations.

There is little research available to identify the major and minor ions in auto exhaust and other roadway sources of contamination as most research has been concerned with heavy metal contamination or hydrocarbons. A paper that mentioned mass percent of Cl, K, Ca, Br, Sr, Mg, Na, Cl, NO_3 and SO_4 of exhaust from catalyst and non catalyst automobiles, paved road dust, brake dust and tire dust (Hildemann et al., 1991) was insufficiently detailed to be able to calculate concentrations of the ions. However, the mass ratios aid in determining sources of contamination to road runoff (Figures 5.4). The Cl to Br mass ratio (mg/mg) of catalyst automobiles is 61, for non-catalytic automobiles it is 0.3, paved road dust and tire dust are both 30 while bake dust is 38. The mass ratio lines of the auto and road sources are not similar to those of the stormwater or recharge basin samples (Figure 5.4b). Road salt Cl to Br ratios in the literature range from 250,000 to 2,000 (Granato, 1996). Most samples lie within this range (Figure 5.3b). The samples at Site 25 show positive linear correlations between Br and Cl concentrations in both the stormwater basins (R^2, 0.85) and in the recharge basins (R^2, 0.70).

Table 5. 2 Linear correlations (R^2 values) of the ions with perchlorate for stormwater basins and recharge basin samples.

	All stormwater basins	Site-112 stormwater basins	Site-25 storm water basins	All recharge basins
N-NO_2	0.37	**0.89**	**0.47**	0.26
N-NH_4	0.09	0.25	0.08	0.00
N-NO_3	0.39	**0.64**	0.28	0.12
Cl	0.14	0.18	0.12	**0.65**
SO_4	0.27	**0.66**	0.10	0.00
Na	0.14	0.34	0.05	**0.51**
Mg	0.08	**0.52**	0.03	**0.47**
K	0.11	0.22	0.06	0.02
Ca	0.08	**0.80**	0.02	0.38
I	0.22	0.33	0.16	**0.55**
Br	0.02	0.39	0.00	0.44
Sr	**0.50**	**0.81**	**0.46**	**0.61**
B	0.30	**0.83**	0.04	0.04

The Na to Cl mass ratio of catalyst and non-catalyst automobiles is 0.6, paved road dust is 1, tire dust is 1.1 and brake dust is near zero. Road salt Na to Cl mass ratios range from 0.5 to 0.7 (Granato, 1996). The samples show a slightly different relationship with Na than with Br with tire dust, road dust and auto exhaust in addition to road salt influencing the Na concentrations (Figure 5.3a). All samples show positive linear correlations between Na and Cl with an R^2 of 0.96 in the stormwater basins at Site 112, an R^2 of 0.88 in the stormwater basins at Site 25 and a R^2 of 0.80 in the recharge basins.

The road salt collected from campus and the county stockpiles contain 64 and 7.8 μg ClO_4 per kg solid respectively. New York State uses an annual average of 10,300 kg road salt per lane-km (U.S. Dept. of Transportation, 1991). The New York State Department of Transportation requires application of 63-76 kg salt per lane-km per storm. There are four lanes on both Highway 112 and Highway 25, two in each direction. At Site 112 road salting could account for 640-6204 μg ClO_4 per event for the entire study area. Site 25 could receive 7800-75,600 μg ClO_4 per event for the entire study area due to road salting. There was 3.8 inches of snow during March (Weather Underground, www.wunderground.com/). Although snow was not reported during our study period salting could have been extensive in anticipation of a large storm. Residue of road salt was still visible on the roadways during our study period.

I measured perchlorate in two salt samples and therefore do not have a good estimate of the average concentration as trace element concentration is likely variable in salt deposits. The mass ratios for the perchlorate content in the campus sample were plotted since there is a corresponding Cl concentration for this sample. The Cl content is 562,672 mg per kg. From the Cl content and the Cl to Br mass ratio we can estimate the Br content of the salt. Only a few samples fall near the Br to ClO_4 mass ratio line for road salt (Figures 5.5a). Bromide and perchlorate and not linearly correlated and likely do not share similar sources (Table 5.2).

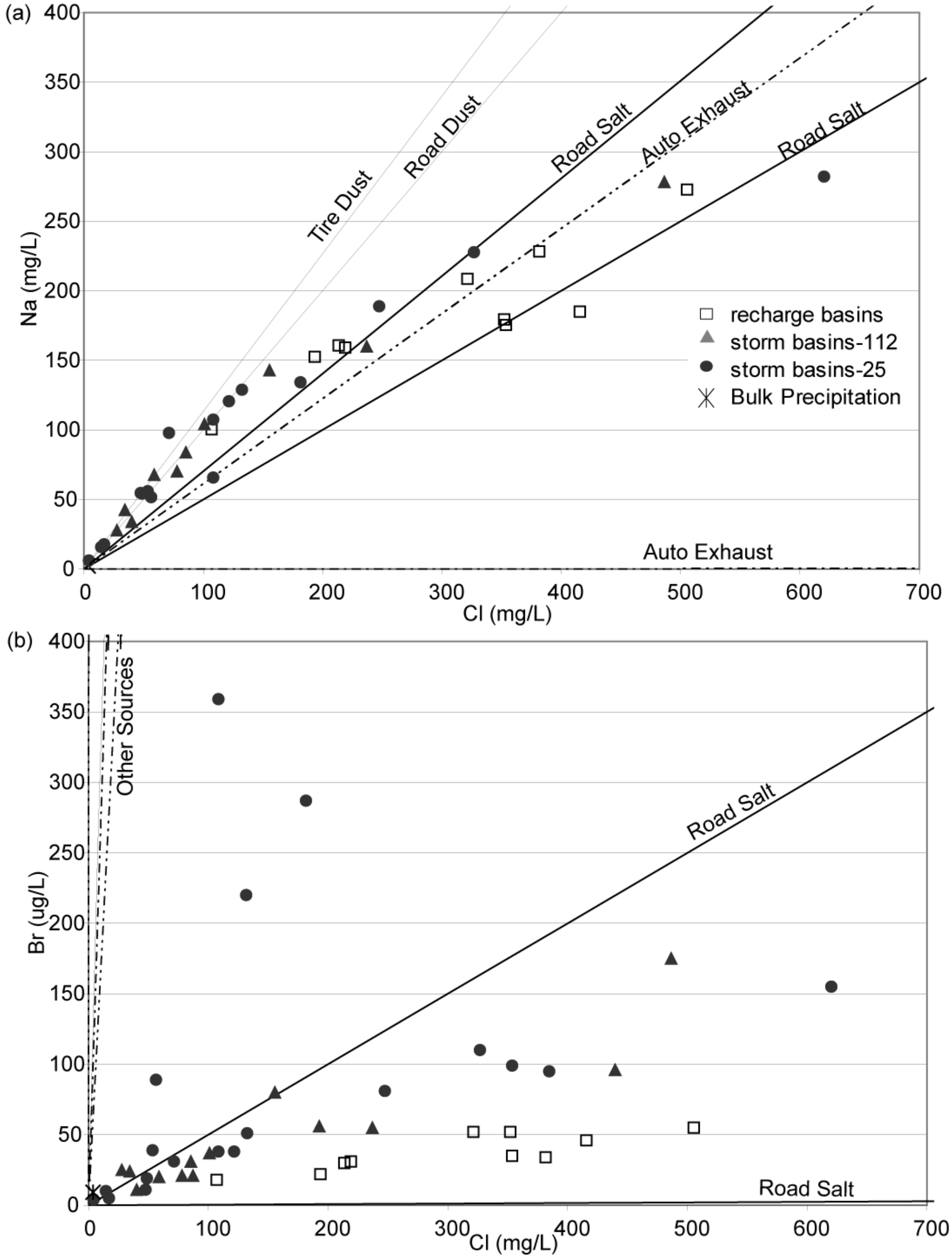

Figure 5. 4. Chloride concentrations plotted verses (a) Na and (b) Br. Bulk precipitation is plotted as an average value. Mass ratio lines are plotted next to the name of the source.

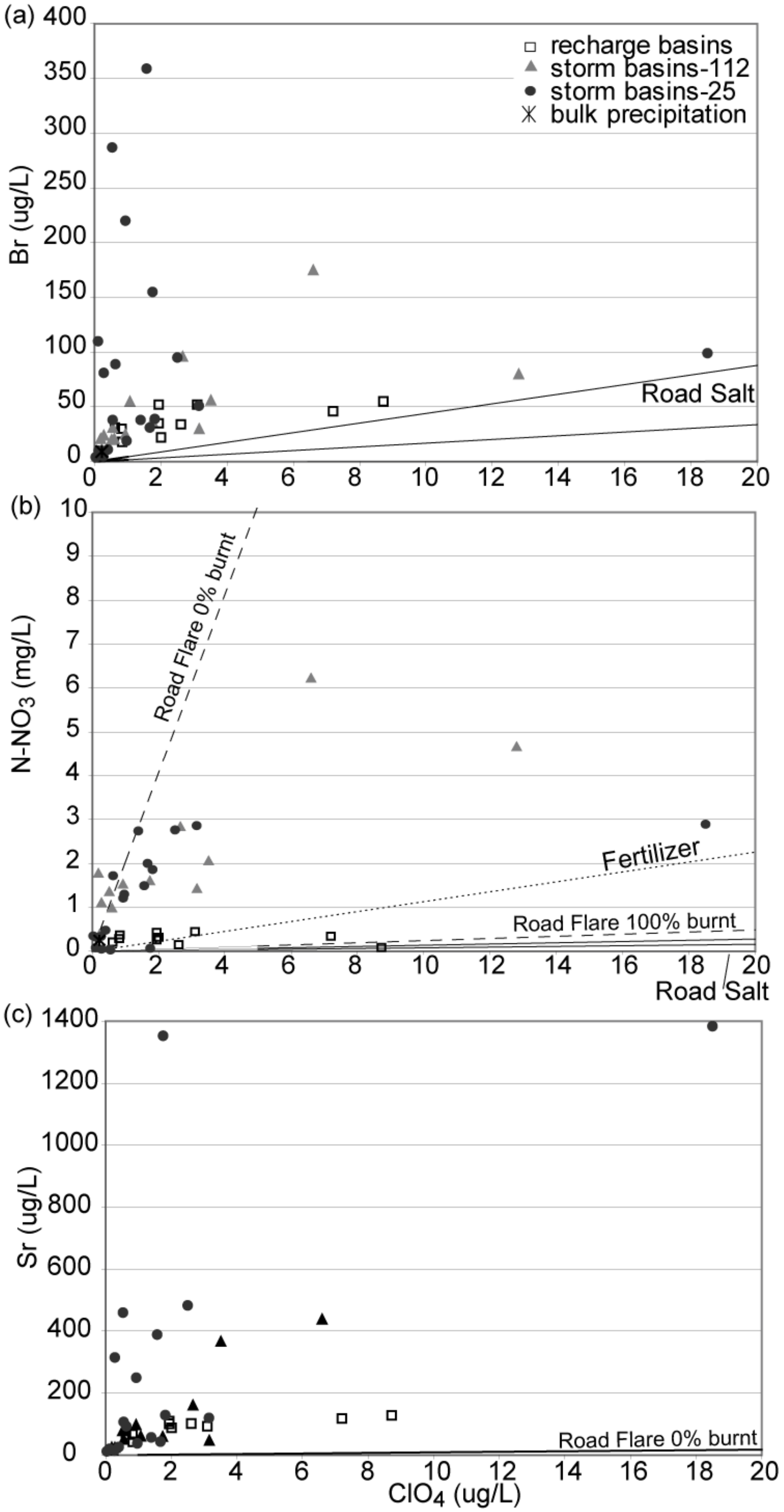

Figure 5. 5. Perchlorate concentrations plotted verses (a) Br, (b) N-NO$_3$ and (c) Sr. Bulk precipitation is plotted as an average value. Mass ration lines are plotted next to the name of the source. Linear correlations of the ions to ClO$_4$ is presented in Table 5.2.

Silva (2003) measured both perchlorate and nitrate concentrations in road flares and the relationship between the two ions may distinguish road flare use. The solution which the road flares were quenched in measured 130 ug/L ClO_4 and 14 mg/L NO_3 or a N-NO_3 to ClO_4 mass ratio of 24 (mg/mg) for a 100% burnt flare. An unburned road flare has a mass ratio of 2. The stormwater samples appear to be highly influenced by flares which have not been burnt to completion (Figure 5.5b). Perchlorate and nitrate are present in some organic fertilizers. The N-NO_3 to ClO_4 mass ratio for Bulldog Soda, which is sodium nitrate derived solely from mined Chilean caliches, is 113 (Collette et al., 2003). This is the main source of perchlorate in organic fertilizers but it is conceivable that this ratio will vary depending on the fertilizer. The road salt mass ratios are 8 and 14 based on the Cl content and the reported Cl to NO_3 ratio in the literature (Granato, 1996). Most samples fall above the mass ratio lines of fertilizer, road salt and 100% burnt road flares, with the recharge basins showing the most influence by these sources. Fertilizer may have been used during the study period since some products recommend an early to late spring fertilizer application (February to June). Nitrate is only correlated with perchlorate in the stormwater basins at Site-112 (Table 5.2).

Strontium and perchlorate are highly correlated (Table 5.2) in all sample locations. The road flare Sr to ClO_4 mass ratio for an unburned flare is based on the molar mass of the composition of road flare, a value calculated as 0.82 (Figure 5.5c). As perchlorate is used up in the flare this ratio will increase. It is possible that the storm water sample concentrations of Sr and ClO_4 are influenced by road flares which were not burnt to completion.

5.4. DISCUSION

On average, the stormwater and recharge basin samples are contaminated since the average values are higher than precipitation (Table 5.1). Increases compared to precipitation can not be accounted for due to evaporation in the stormwater basins, although this is a possible cause for increases in ions in the recharge basins. In addition, dilution in the recharge basins may explain why concentrations of ions are lower in the recharge basins compared to the stormwater basins, as the samples from the stormwater basins only receive a first flush of runoff from the highways. The concentrations of the first flush of runoff to stormwater basins should be more contaminated in intense rain events where contaminants can be cleansed from the highways (Vaze and Chiew, 2002). However, since our samples do not capture the full rain event when runoff is greater than the volume of the sampler (one liter) we can not make inferences based on rain volume. Furthermore, concentrations in the recharge basins are more of a site average as stormwater basin sample localized contamination near each basin. The difference in ion concentrations between sites maybe due to variability in ion sources which is also evident by the variability in correlations between the ions and perchlorate (Table 5.2).

Major sources of contamination to stormwater are auto exhaust, road deicers, wear and tear of automobiles and brake pad wear (Breault and Granato, 2000). Auto exhaust contains B, Br, Ca, Mg, Na, N, K and Sr. Dust from brake pads contains Mg, Cl, and Ca. Bromide is present in fuel. Nitrogen can be present in roadside fertilizers. Road flares contain mostly K, Sr, NO_3 and ClO_4, however most of the NO_3 and ClO_4 should be consumed during use. Deicers are mostly Cl, Na and Ca with impurities of Br, SO_4, B, Mg, N, K and Sr, as well as perchlorate as concluded in this study. None of the ions measured in this study are specific to any one roadway source, however, concentrations of the ions and ratios of the ions may provide signatures of the various sources.

Road salt appears to be the most likely source of Na, Cl and Br during our study period (Figure 5.4). It is probable that ClO_4 is present in part due to road salt since some samples fall near the road salt mass ratios for Br to ClO_4 (Figures 5.5a). There is no linear correlation with ClO_4 and Cl, Br or Na in the stormwater basins indicating they do not share similar sources, yet there is a correlation in the recharge basins indicating some of the perchlorate maybe present from road salt (Table 5.2).

It is probable that perchlorate in storm water is from road flares although it is perplexing that the mass ratios of N-NO_3 to ClO_4 and Sr to ClO_4 indicate that the flare influences is mostly from unburned flares.

5.6. CONCLUSIONS

I have presented possible sources of perchlorate to road runoff in areas with high incidents of traffic accidents, which include road salt and road flare use. This is the first study to document concentrations in road runoff waters. In Suffolk County, NY, as well as other areas which direct road runoff for groundwater recharge, the concentrations measured in this study are of concern for groundwater quality. While the average concentration presented here is below the NY state drinking water planning level of 5 ug/L, individual samples are above this level. As a result, we have to be concerned about the risk of concentrations of perchlorate in groundwater increasing to above the New York State planning level and above the potential EPA drinking water standard.

Further studies of sources of perchlorate to road runoff are essential to reduce the impact of perchlorate in drinking water as most runoff eventually reaches the groundwater. Two conceivable methods come to mind. One would be an isotopic study of δ^{35}Cl and Δ^{17}O isotopes in recharge basins, yet milligrams of ClO_4 are needed for analysis and stormwater basins do not yield those quantities per sampling event. Recharge basins, however, should be able to provide enough sample for analysis. The limitation of isotopes is that they may only determine if the perchlorate is anthropogenic or natural. Another approach would be to carefully monitor an area of roadway and do a mass balance study quantifying the sources to the road. Any difference in stormwater concentrations could be due to sources which were thought not to contain perchlorate.

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6. Nitrate leaching beneath fertilized turfgrass sites

6.1. INTRODUCTION

Fertilizer practices of turfgrass lawns by homeowners and commercial landscapers can influence groundwater quality (Baier and Rykbost, 1976; Flipse and Bonner, 1985; Flipse et al., 1984; Kimmel, 1984; Porter, 1980). Nitrogen is an essential nutrient needed for turfgrass growth with nitrate being the preferred form for the plant and also the species which leaches most readily from the soil profile to the groundwater aquifer. Quantifying and understanding nitrate leaching from lawn fertilizer is essential to keep concentrations in groundwater below the U.S. Environmental Protection Agency drinking water standard of 10 mg/L nitrate as nitrogen ($N\text{-}NO_3$).

Although results from investigations elsewhere assist in understanding properties that affect nitrate leaching beneath turfgrass (Petrovic, 1990), it is exceedingly important to examine local conditions to determine the impact of turfgrass practices to local groundwater. This is especially important in Suffolk County, Long Island, NY, where all potable water is derived from the local groundwater aquifers and the potential for nitrate leaching to the groundwater is large due to fast infiltration rates of the sandy soils, a large volume of infiltration from rain and irrigation sprinklers each year, and the popularity of turfgrass in landscaping of homes, business complexes and parks. In Suffolk County, 25% of the land was classified as lawns, i.e. turfgrass, from a 1970's land survey (Koppelman, 1978). The Suffolk County Water Authority estimates 30% (~73 billion liters annually) of the yearly water consumption in Suffolk County is for the purpose of irrigation. An estimated 50% of the 112.2 cm of precipitation received each year infiltrates to the groundwater (Busciolano, 2004). Yet few field studies have been conducted to determine nitrate leaching beneath turfgrass on Long Island (Porter, 1980, Schuchman, 2001).

Porter (1978 and 1980), conducted a field survey to evaluate the impact of lawn fertilizer to groundwater in urban areas of Nassau and Suffolk County, NY. The sites received ammonium nitrate-nitrogen fertilizer, a fertilizer not commonly used anymore as concerns for the environment have move towards slow release forms of nitrogen. The fertilizer was applied at rates of 0, 48, 97 and 146 kg N/ha. The maximum nitrogen concentration in soil water was in the shallow samplers, 10.1 cm, with decreased concentrations at 50.8 cm. For the site not fertilized, the maximum nitrogen concentration was 9.8 mg N per L dry soil (Porter, 1978). At the site fertilized with 48 kg N/ha the maximum concentration was 13.2 mg/L. At the site fertilized with 97 kg N/ha the maximum concentration was 22.5 mg/L. At the site fertilized at 146 kg N/ha the maximum concentration was 16.7 mg/L. The maximum concentrations are above the EPA drinking water standard but the study found that at depth concentrations decreased to values between 2.1 and 6.1 mg/L.

Fertilizers applied to recreational lawns are estimated to contribute 29-35% of the nitrogen load to Long Island groundwater depending on the extent of nitrogen losses (Porter, 1978). More recently, Councilman Steve Levy was quoted as stating that "Fertilizers account for 56 percent of nitrogen pollution emanating from residential properties (in Suffolk County)" however; it is unclear what data his estimate is based upon (http://www.co.suffolk.ny.us/).

Guillard and Koop (2004) state that "more studies are needed to determine the fate and transport of N-NO_3 applied to turf in urban or suburban settings." In his review, Petrovic (1993), indicates a need for long term (>5 years) studies on slow release nitrogen fertilizers and for more leaching studies using different sources of nitrogen. My study addresses these concerns, as a four year study measuring nitrate concentrations beneath urban lawns that are fertilized with organic fertilizer, chemical fertilizer, no fertilizer and a forested site. The goal of this study is to gain a basic understanding of potential nitrate concentrations leaching into Suffolk County groundwater. Soil water nitrate concentrations were collected below the turfgrass root zone, from ceramic suction lysimeters at depths of 100 cm and 120 or 150 cm, from a diverse set of study sites located throughout Suffolk County. When studying nitrate leaching below maintained turfgrass sites it is ideal to control and keep site properties constant except for one to determine its effect on nitrate leaching. Although this approach aids in understanding nitrate leaching, it does not represent the natural environment. My approach was to investigate lawns in Suffolk County, NY with diverse site characteristics and fertilizer practices which enabled us to study natural conditions.

In this chapter I will attempt to answer three main questions

(1) Is there a difference between N-NO_3 concentrations in soil water collected at 100 cm between sites that are treated with organic fertilizer, chemical fertilizer or no fertilizer?

(2) How does soil water N-NO_3 concentrations change with depth, from 100 cm to 120 or 150 cm?

(3) What is the impact of maintained lawns to the N-NO_3 concentrations in groundwater?

6.2. METHODS

6.2.1. Site Installation

Ceramic suction lysimeters (from Soilmoisture Equipment Corp. and Campbell Scientific Inc.) were installed at 100 cm and 120 or 150 cm below the soil surface at six locations in Suffolk County (Figure 6.1). All sites have a lysimeter at 100 cm but not all sites have one at a deeper depth. A 15 cm diameter hole was dug to 5 cm below the desired depth using a hand auger and a post-hole digger. A larger hole was then dug around the borehole to a depth of 20 cm to fit a plastic sprinkler box, which covers and encloses the unit beneath grade. Silica sand or <2 mm local sandy soil was used as a filter media to surround the lysimeter suction cup over a span of approximately 20 cm. The hole was then backfilled with local, less than 2 mm soil and compacted to 20 cm below the surface where a 5 cm layer of bentonite was placed to inhibit water flow directly down the hole. The remaining hole was then filled partially with native soil, the sprinkler box was installed and room was left to access the tubing of the lysimeter (Munster, 2004; Schuchman, 2001).

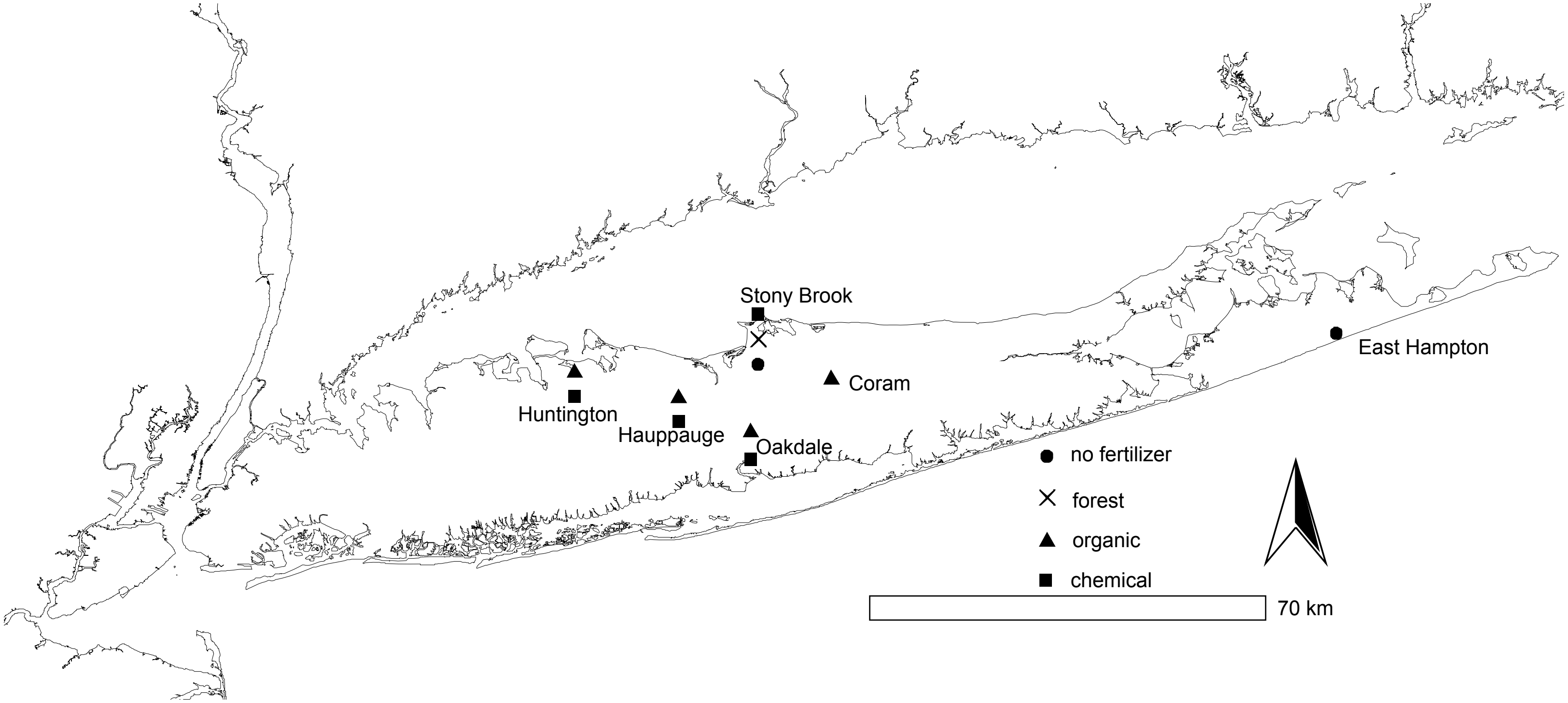

Figure 6. 1. Map of study locations indicating the study sites at each location. All locations have precipitation gauges.

Table 6. 1. Year of site installations.

Location	2003	2004	2005	2006
Stony Brook	No fertilizer[1] Chemical[1]*	No fertilizer Chemical* Forest	No fertilizer Chemical* Forest	No fertilizer Chemical* Forest
East Hampton	Organic	Organic	No fertilizer[2]	No fertilizer
Coram	Organic	Organic	Organic	Organic
Oakdale	Organic* Chemical[1]*	Organic* Chemical*	Organic (2)[3] Chemical*	Organic (2) Chemical*
Hauppauge	Organic*	Organic*	Organic* Chemical	Organic* Chemical
Huntington	Organic	Organic	Organic Chemical	Organic Chemical

*Has a lysimeter at 120 or 150 cm in addition to 100 cm [1] Indicates the site was established by Schuchman (2001) before 2003. [2] No new lysimeter was installed, instead the lawn maintenance changed. [3] An additional organic site was established with only a 100 cm lysimeter.

The study locations have developed over time, with multiple sites at most locations (Table 6.1). We refer to the sites by their treatment type. The two types of fertilizer treatments are called organic or chemical (see details below) and the sites that receive no fertilizer are called as such, no fertilizer or forest.

6.2.2. Study Site Descriptions

Sites were chosen to represent a variety of locations in Suffolk County (Figure 6.1). The lawns vary in size and the lysimeters are at least 5 m from the nearest tree or building and at least 1.5 m from each other. The Stony Brook chemical site is a small rectangular site, 7 by 5 meters, in the middle of a larger rectangular lawn that is 675 m^2 and is the location of the Stony Brook site which is not fertilized. The forest site at Stony Brook is 15 meters from the lawn and is a small forest roughly 2420 m^2. The East Hampton site is approximately 465 m^2. The Coram site is approximately 39 m^2, situated among other landscaping plants. The Oakdale organic site is in a 510 m^2 circular lawn surrounded by a parking lot and roads. About 30 meters away is the Oakdale chemical site and an additional organic site. The chemical site is rectangular, 665 m^2, and directly adjacent to the organic site which is 225 m^2. The Hauppauge organic site is 215 m^2 and separated by a few large trees from the chemical site which is 250 m^2. The Huntington organic site is 280 m^2 directly adjacent to the chemical site which is 330 m^2.

The species of turfgrass at our study sites is unknown, except at the Stony Brook chemical site which was established with a blend of fescue and bluegrass made by Dura-Sod, as recommended by the manufacturer for the Long Island area (Schuchman, 2001). Some sites are not 100% turfgrass but include clover, crabgrass, dandelion, moss, and other non-turf plants. Most sites look similar except the two at Huntington, which are high density turf lawns mostly free of other plants.

6.2.3. Fertilizer Treatments

Organic sites were maintained by an organic landscaper until 2005, when staff at the Suffolk County Water Authority (SCWA) took over treatment. The organic landscaper combined compost, lime, and granular fertilizers (manufactured by Healthy Turf and Progrow). The organic fertilizers were composed of natural sulfate of potash, phosphate rock, colloidal phosphate, oyster meal, kelpmeal, greensand, vegetable and animal protein meals, natural nitrate of soda, compost, and dried whey. Application frequency was dependent on the needs of the soil. Manure was not used. The nitrogen content of the compost is unknown. Healthy Turf was applied at a rate of 30 kg N/ha (Figure 6.2). When SCWA took over in 2005 treatment became scheduled and only Progrow was applied at a rate of 20 kg N/ha, the same rate the landscapers applied, as directed by the instructions on the fertilizer bag.

The chemical site at Oakdale was fertilized by staff at the SCWA with different varieties of Scotts brand fertilizer according to recommendations on the Scotts website. Application rates varied from 55-75 kg N/ha (Figure 6.2). Scotts Fertilizers are 9-30% urea N, 1-10% water soluble N and about 1% water insoluble N. Lesco brand chemical fertilizer was applied by the author at the Stony Brook site at an application rate of 35 or 50 kg N/ha. This fertilizer is 9-18% urea N. An error occurred during the fall application in October 2005 such that the Oakdale chemical site received organic fertilizer while the Oakdale-2 organic site received chemical fertilizer.

All sites except Stony Brook were watered with an automatic sprinkler system twice per week providing infiltration of 3.8-5.1 cm per week in accordance with the recommendations on the SCWA web site (www.scwa.com, Oral communication Michael DeBlasi, SCWA, August 2004). All sites are mowed between April and November and the clippings are not removed.

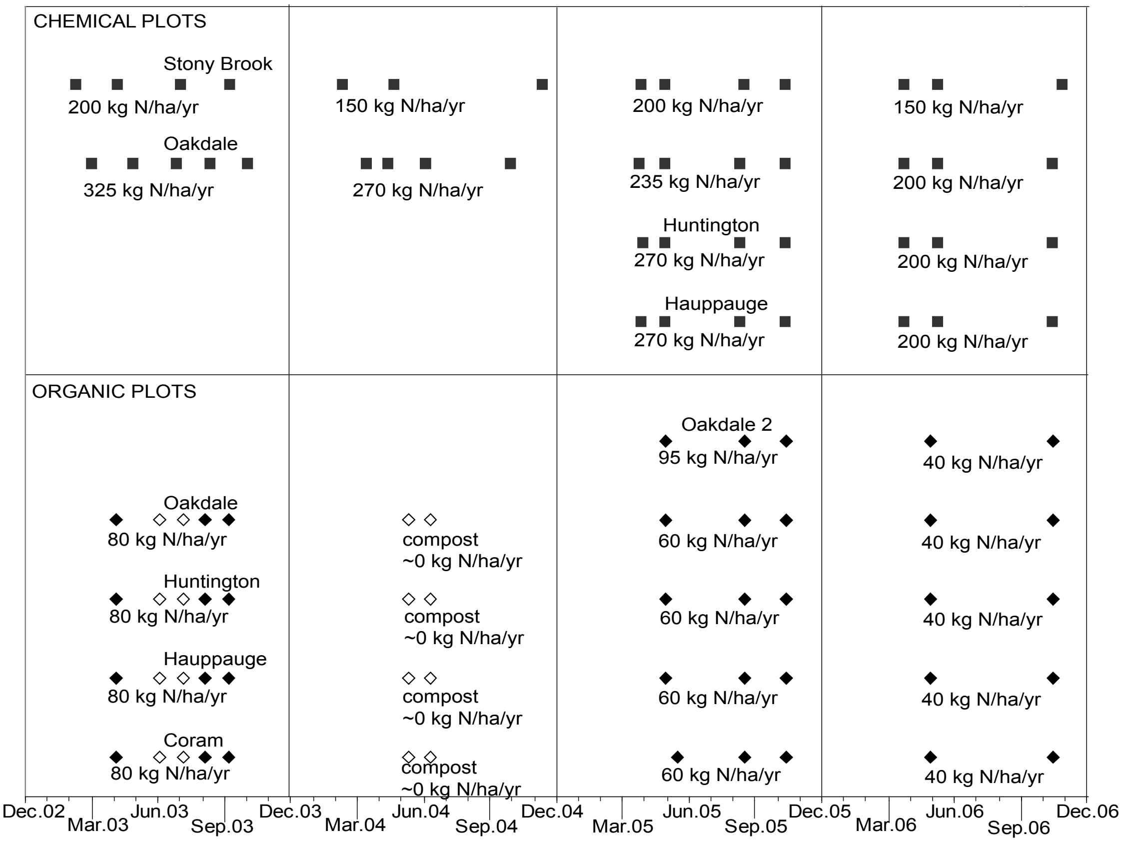

Figure 6. 2. Fertilizer timing and yearly nitrogen application rates.

6.2.4. Sampling

Soil water samples from lysimeters were acquired monthly, filtered in the field, stored in acid-rinsed polypropylene bottles and, once in the laboratory, frozen (-10ºC) until analyzed. On average 250 mL were collected but sample volume ranged from 5 to 450 mL. Concentrations of N-NO_2, NH_4 and N-NO_3 were analyzed at the Marine Sciences Research Center at Stony Brook University on a Lachat's QuickChem8500 Flow Injection Analysis System using Lachat's Method 10-107-04-1-J. Five to ten milliliters of sample are needed for analysis. These analyses have an uncertainty of 5% determined by anonymous standards and duplicate analysis. Detection limits were 0.1 mg/L for all ions. Nitrite and ammonium were rarely detected in the soil water samples. A representative sample was randomly chosen and analyzed thirteen times for $N\text{-}NO_3$ between September 2003 and January 2007. The sample was not acidified and stored at 4ºC. Results of the analysis is 1.2 mg/L ± 0.1 (1σ; 9%).

Statistical calculations were performed using the program Minitab. One-way, Analysis of Variance (ANOVA, unstacked) Turkey tests, with a 95% confidence interval, is a way to test the equality of three or more means at one time by using variance. The Mann-Whitney test was used to compare populations. This test assumes the sample populations are not normally distributed, and test if the means of two populations are equal or if one population is greater than the other. A sigma value less than 0.05 (95% confidence interval) is a significant result and the hypothesis can be accepted.

6.3. RESULTS

Monthly nitrogen as nitrate ($N\text{-}NO_3$) concentrations in soil water collected at 100 cm varies throughout the study period (Figure 6.3). Concentrations vary between years (Figure 6.4), between sites (Figure 6.5), and between fertilizer treatments (Figure 6.6). Figure 6.3 demonstrates the variability observed throughout the study period however, it is difficult to discern trends in the data. As such, most of the data presented in this chapter will focus on average concentrations, as averages are statistically reliable, help simplify the more than four hundred data points, and clear trends can be observed with averages that are difficult to observe with hundreds of individual data points.

The relationship of average soil water $N\text{-}NO_3$ concentrations between treatment types vary among the years of the study (Figure 6.4). In 2003 the average concentrations between all treatments are not significantly different (ANOVA, $p<0.05$). In 2005 and 2006 the average concentrations are statistically similar for the sites treated with chemical fertilizer and the sites treated with organic fertilizer. In 2004 and for the combined years (2003 through 2006) average concentrations for the sites treated with chemical fertilizer are statistically higher than the sites treated with organic fertilizer. In 2004 the sites treated with organic fertilizer and those not fertilized have statistically similar average concentrations. In 2005, 2006, and the combined years, the sites not fertilized and the forest site have statistically similar average concentrations.

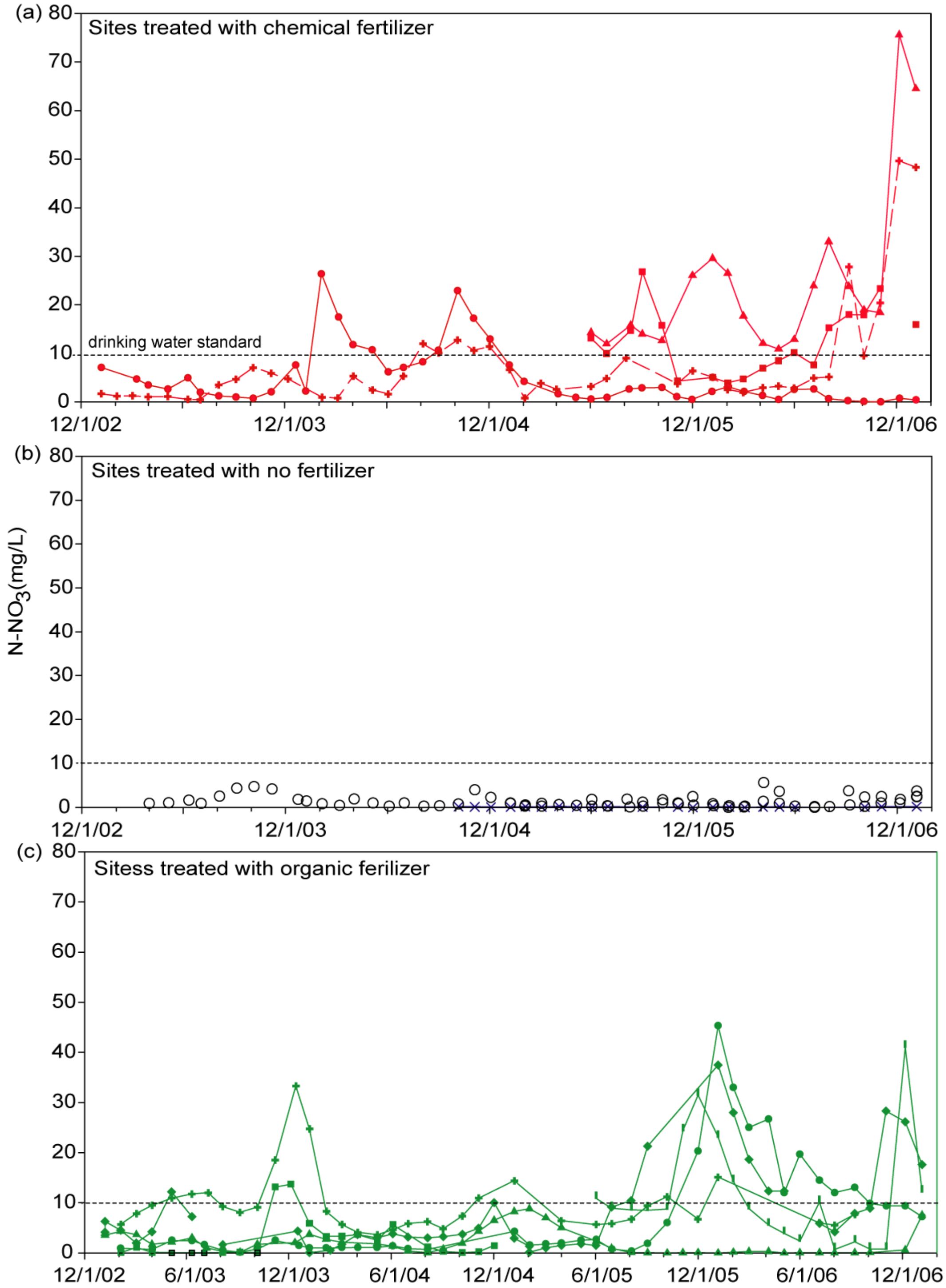

Figure 6. 3. Monthly N-NO_3 concentrations of soil water collected at 100 cm at sites treated with (a) chemical fertilizer, (b) no fertilizer and beneath the forest (blue x-symbols) and (c) organic fertilizer. The EPA drinking water standard is 10 mg/L represented as a dashed horizontal line.

Although the sites treated with chemical fertilizer leach, on average, more nitrate than the sites treated with organic fertilizer this difference may be due to differences in site properties and not a function of fertilizer treatment, as average soil water N-NO_3 concentrations vary between sites, even between sites treated with the same type of fertilizer (Figure 6.5). To test this hypothesis soil water N-NO_3 concentrations at 100 cm, for sites treated with different fertilizer at the same location, are compared to minimize variability that could be due to differences in the study location. The data show that concentrations or patterns of concentrations are, at times, similar between fertilizer treatments (Figure 6.6). The sites at Hauppauge are similar from July 2005 through May 2006 with a statistically higher average concentration at the chemical site than the organic site (Mann-Whitney, $p=0.033$, Figure 6.6a). At Huntington concentrations are higher beneath the chemical site than the organic site from June 2005 through October 2005 and in August 2006 to the end of the study period (although samples weren't continuously collected, Figure 6.6b). While the average concentration at the chemical site is higher than the organic site the difference is not statistically significant ($p=0.060$). At Oakdale, the organic site measures higher concentrations in October 2005 through March 2006, while the chemical site measures higher concentrations in September 2006 through January 2007 (Figure 6.6c). The average values between these sites are similar.

Average N-NO_3 concentrations, grouped according to fertilizer treatment, vary among the years of the study, except for the forest site (Table 6.2). The sites treated with chemical fertilizer are statistically similar for all years except 2003, which has the lowest average concentration of 3.1 mg/L. The average concentration of the sites treated with organic fertilizer is statistically similar for all years except 2006, when the average nearly doubles. Yearly averages can vary between years within a given site, although most averages are not statistically different between years (Table 6.3). At the Stony Brook site that is not fertilized the average concentration for 2003, 2.4 mg/L, is statistically higher than the other years. For the Stony Brook chemical site the average N-NO_3 concentration for 2004, 13 mg/L, is statistically higher than the other years of the study. At the Coram organic site, the Hauppauge organic site and the Oakdale organic site the average concentration in 2006 is statistically different than the rest of the years.

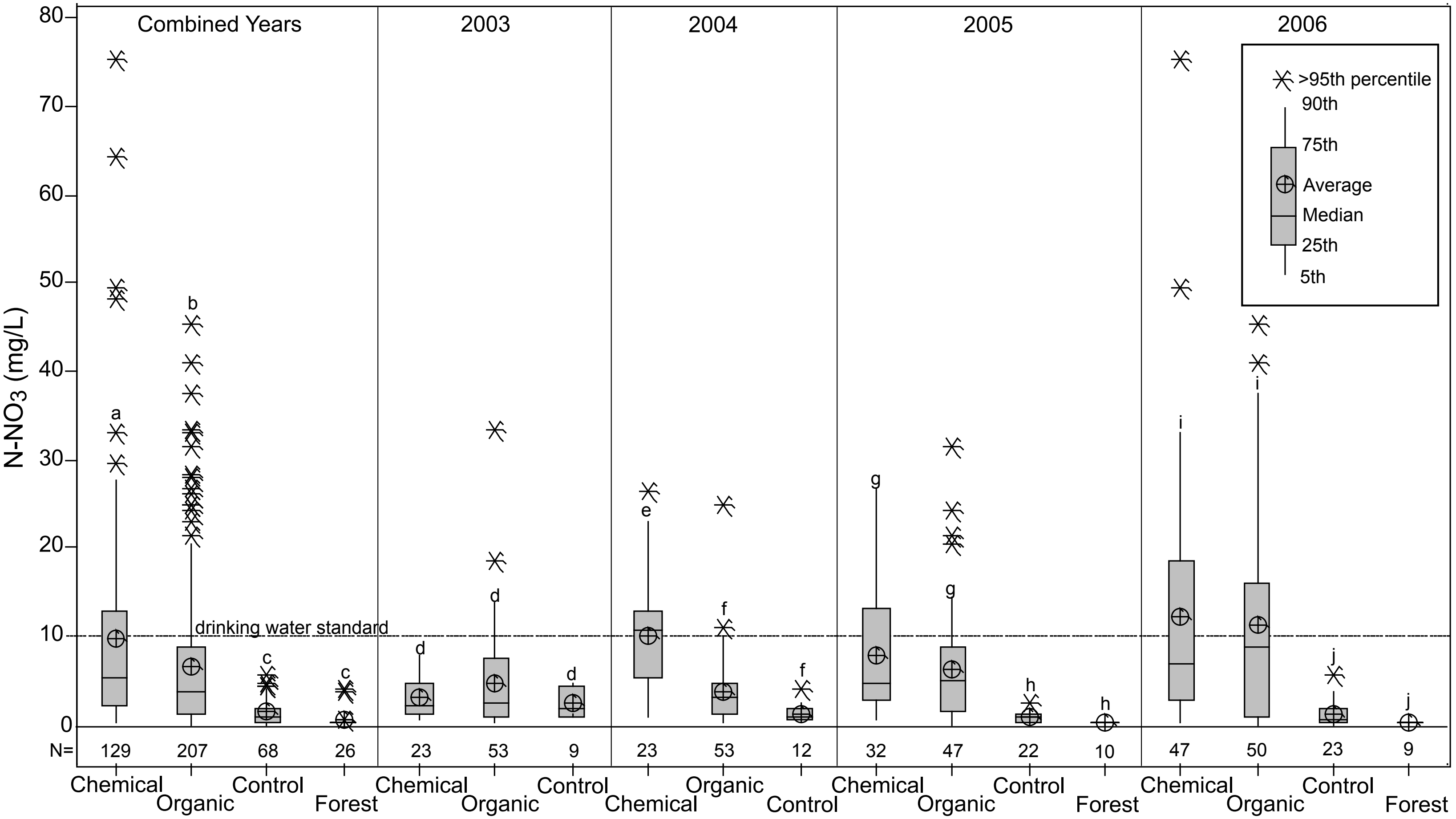

Figure 6. 4. Box plot of yearly soil water N-NO$_3$ concentrations at 100 cm. Averages of boxes within a given year that share a letter (a through j) are not significantly different according to an unstacked ANOVA Turkey test ($p < 0.05$). Refer to Table 6.2 for relationships of each fertilizer treatments between years. The EPA drinking water standard of 10 mg/L is represented by the dashed horizontal line.

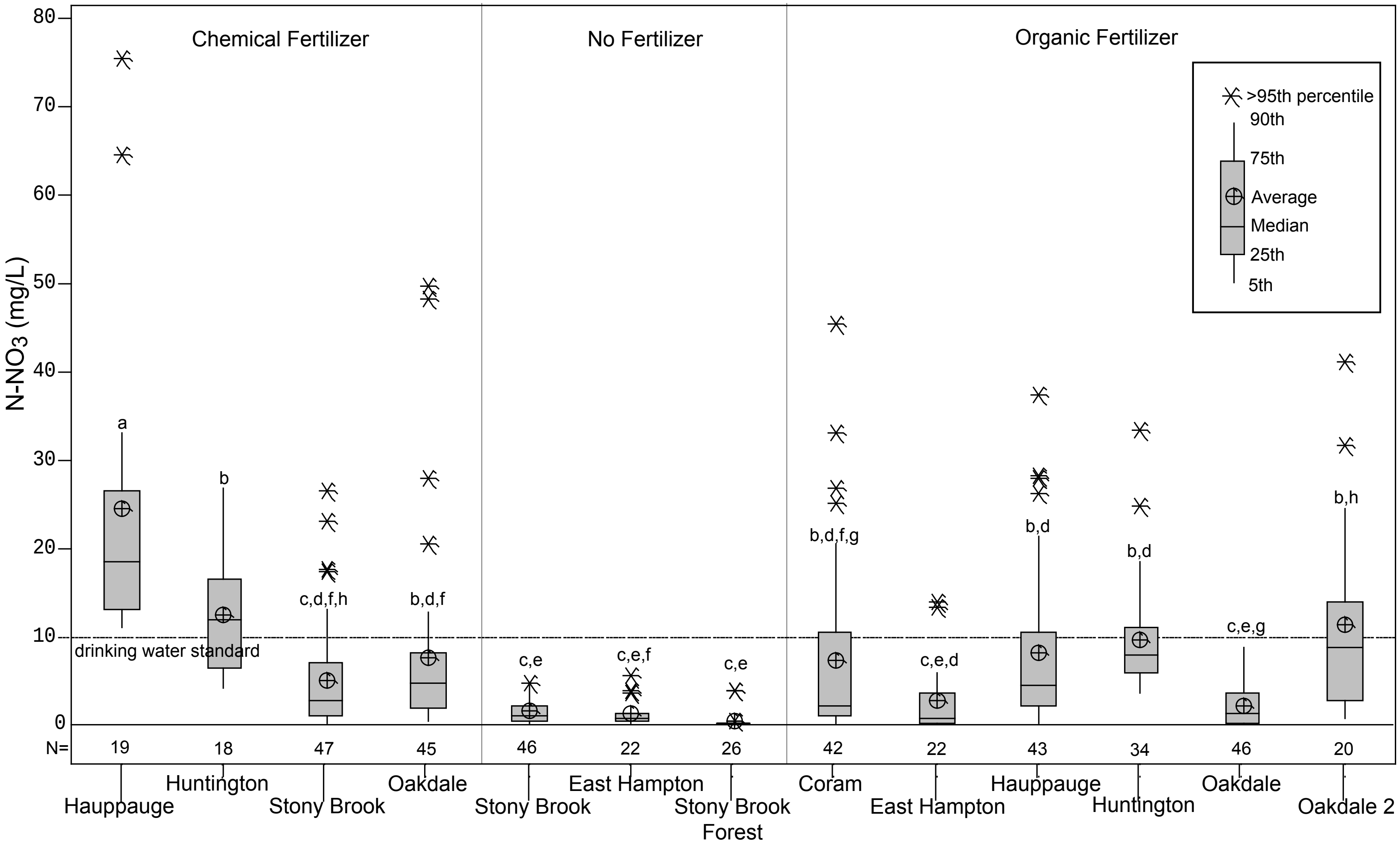

Figure 6. 5. Box plot of soil water $N-NO_3$ concentrations at 100 cm for each site for the combined years. Averages of boxes that share a letter (a through h) are not significantly different according to an unstacked ANOVA Turkey test ($p < 0.05$). The EPA drinking water standard of 10 mg/L is represented by the dashed horizontal line.

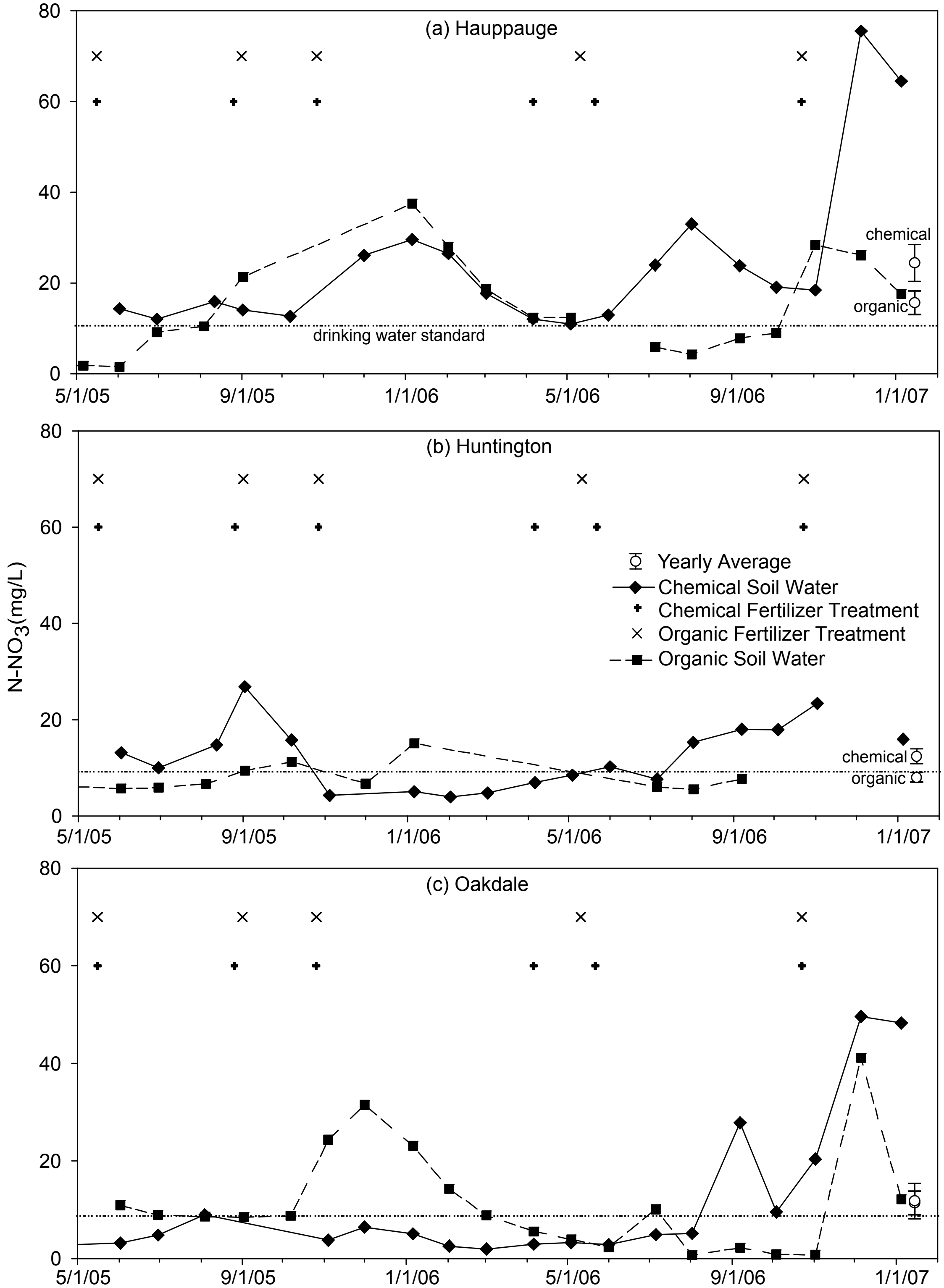

Figure 6. 6. Soil water N-NO$_3$ concentrations collected at 100 cm for three locations that have both a site treated with chemical fertilizer and one treated with organic fertilizer at (a) Hauppauge, (b) Huntington and (c) Oakdale. Error bars are standard error of the mean. The EPA drinking water standard is 10 mg/L, represented by the dashed horizontal line.

Table 6. 2. Yearly average soil water N-NO_3 concentrations at 100 cm and for bulk precipitation.

Year	Avg.	SE	N	Max.
	Chemical			
Combined[ab]	9.7	1	129	76
2003[b]	3.1	0.5	23	7.6
2004[a]	9.9	1.4	23	26
2005[a]	7.7	1.3	32	27
2006[a]	12	2	47	76
	Organic			
Combined[c]	6.5	0.6	207	45
2003[c]	4.8	0.8	53	33
2004[c]	3.6	0.5	53	25
2005[c]	6.3	1.0	47	32
2006[d]	11	2	50	45
	No Fertilizer			
Combined[ef]	1.3	0.2	68	5.6
2003[f]	2.4	0.5	9	4.7
2004[ef]	1.2	0.3	12	4
2005[e]	0.83	0.13	22	2.4
2006[ef]	1.2	0.3	23	5.6
	Forest			
Combined[g]	0.40	0.20	26	3.9
2005[g]	0.11	0.02	10	0.26
2006[g]	0.07	0.02	9	0.14
	Bulk Precipitation			
2005[1]-2007	0.44	0.12	121	13

[1] May 2005. Values for bulk precipitation are total inorganic nitrogen. Average N-NO_3 concentrations of years, within a given treatment, that share a letter (a through g) are not significantly different according to an unstacked ANOVA Turkey test ($p < 0.05$)

Table 6. 3. Yearly average soil water N-NO$_3$ concentrations at 100 cm for each site.

Year	Site	Treatment	Avg.	SE	N	Max.
Combined	Stony Brook^{a}	forest	0.40	0.20	26	3.9
2005	Stony Brook^{a}	forest	0.11	0.02	10	0.26
2006	Stony Brook^{a}	forest	0.08	0.02	10	0.16
Combined	East Hampton^{b}	no fertilizer	1.1	0.3	22	5.6
2005	East Hampton^{b}	no fertilizer	0.83	0.19	10	1.89
2006	East Hampton^{b}	no fertilizer	1.2	0.5	11	5.6
Combined	Stony Brook^{cd}	no fertilizer	1.4	0.2	46	4.7
2003	Stony Brook^{c}	no fertilizer	2.4	0.5	9	4.7
2004	Stony Brook^{cd}	no fertilizer	1.2	0.3	12	4.0
2005	Stony Brook^{cd}	no fertilizer	0.82	0.20	12	2.4
2006	Stony Brook^{cd}	no fertilizer	1.1	0.3	12	3.7
Combined	Hauppauge^{e}	chemical	24	4	19	76
2005	Hauppauge^{e}	chemical	16	2	6	26
2006	Hauppauge^{e}	chemical	28	6	13	76
Combined	Huntington^{e}	chemical	12	1.6	18	27
2005	Huntington^{e}	chemical	14	3	6	27
2006	Huntington^{e}	chemical	12	2	12	23
Combined	Oakdale^{f}	chemical	7.4	1.6	45	50
2003	Oakdale^{f}	chemical	2.8	0.7	12	7.1
2004	Oakdale^{f}	chemical	6.7	1.4	11	13
2005	Oakdale^{f}	chemical	4.6	0.8	9	9.0
2006	Oakdale^{f}	chemical	11	4	12	50
Combined	Stony Brook^{g}	chemical	5.0	0.9	47	26
2003	Stony Brook^{g}	chemical	3.4	0.7	11	7.6
2004	Stony Brook^{h}	chemical	13	2	12	27
2005	Stony Brook^{g}	chemical	2.4	0.6	11	7.6
2006	Stony Brook^{g}	chemical	1.4	0.3	12	3.1
Combined	Coram^{i}	organic	7.2	1.6	42	45
2003	Coram^{i}	organic	1.4	0.3	10	2.5
2004	Coram^{i}	organic	1.6	0.6	9	5.9
2005	Coram^{i}	organic	4.0	1.7	11	20
2006	Coram^{j}	organic	19	3	12	45
Combined	East Hampton^{k}	organic	2.6	0.9	22	14
2003	East Hampton^{k}	organic	2.6	1.6	11	14
2004	East Hampton^{k}	organic	2.2	0.6	10	5.7
Combined	Hauppauge^{l}	organic	8.0	1.3	43	37
2003	Hauppauge^{l}	organic	5.2	1.1	9	12
2004	Hauppauge^{l}	organic	3.4	0.7	12	10
2005	Hauppauge^{l}	organic	5.1	2.1	10	21
2006	Hauppauge^{m}	organic	17	3	11	37
Combined	Huntington^{n}	organic	9.5	1.0	34	33
2003	Huntington^{n}	organic	12	2.3	11	33
2004	Huntington^{n}	organic	7.8	1.8	11	25
2005	Huntington^{n}	organic	8.3	1.1	8	14
2006	Huntington^{n}	organic	8.6	2.2	4	15
Combined	Oakdale^{mn}	organic	2.1	0.4	46	8.8
2003	Oakdale^{mn}	organic	2.3	0.4	12	4.3
2004	Oakdale^{mn}	organic	2.3	0.6	11	6.5
2005	Oakdale^{m}	organic	3.0	1.1	11	8.8
2006	Oakdale^{n}	organic	0.13	0.05	11	0.58
Combined	Oakdale 2^{o}	organic	11	2	20	41
2005	Oakdale 2^{o}	organic	15	4	7	32
2006	Oakdale 2^{o}	organic	9.5	3.5	12	41

Average N-NO$_3$ concentrations of years, within a given site, that share a letter (a through o) are not significantly different according to an unstacked ANOVA Turkey test ($p < 0.05$).

Average $N\text{-}NO_3$ concentrations vary between months (Figure 6.7). For the sites not treated with fertilizer the highest averages are observed in April and September through December. The highest average concentration of bulk precipitation is in April, a value of 0.86 mg/L. Average concentrations for the fertilized sites follow a similar pattern with each other, with overlapping values throughout the year except for August through October. This pattern differs from the not fertilized sites for most of the months except January, February, and March. Between August and October the average concentrations for the sites treated with chemical fertilizer increase while the average of the sites treated with organic fertilizer remain constant. These months are when average concentrations deviate most between the chemical sites and the organic sites. Average concentrations near or above the drinking water standard are observed in January, November, and December for both the chemical sites and the organic sites. The average concentrations of the sites treated with chemical fertilizer in August, September, and October are also above the drinking water standard.

Soil water $N\text{-}NO_3$ concentrations vary between soil water collected at 100 cm and that collected at 120 or 150 cm. The combined average concentration for the Stony Brook chemical site at 100 cm is significantly greater than the average concentration at 150 cm (Mann-Whitney Test, $p=0.018$). The other study sites, Oakdale chemical, Hauppauge organic and Oakdale organic, have statistically equal concentrations at 100 cm and 120 cm.

There is a 36% probability that soil water collected at 100 cm beneath a lawn treated with organic fertilizer will reach or surpass the drinking water standard of 10 mg/L, while a lawn treated with chemical fertilizer has a 50% chance (Figure 6.8a). However, in the deeper soil water samples (those collected at 120 or 150 cm) the probability decreases and becomes similar for both types of fertilizer treatment. This value is 25% (Figure 6.8b). Soil water collected beneath lawns that are not fertilized will likely not reach the drinking water standard (Figure 6.8a).

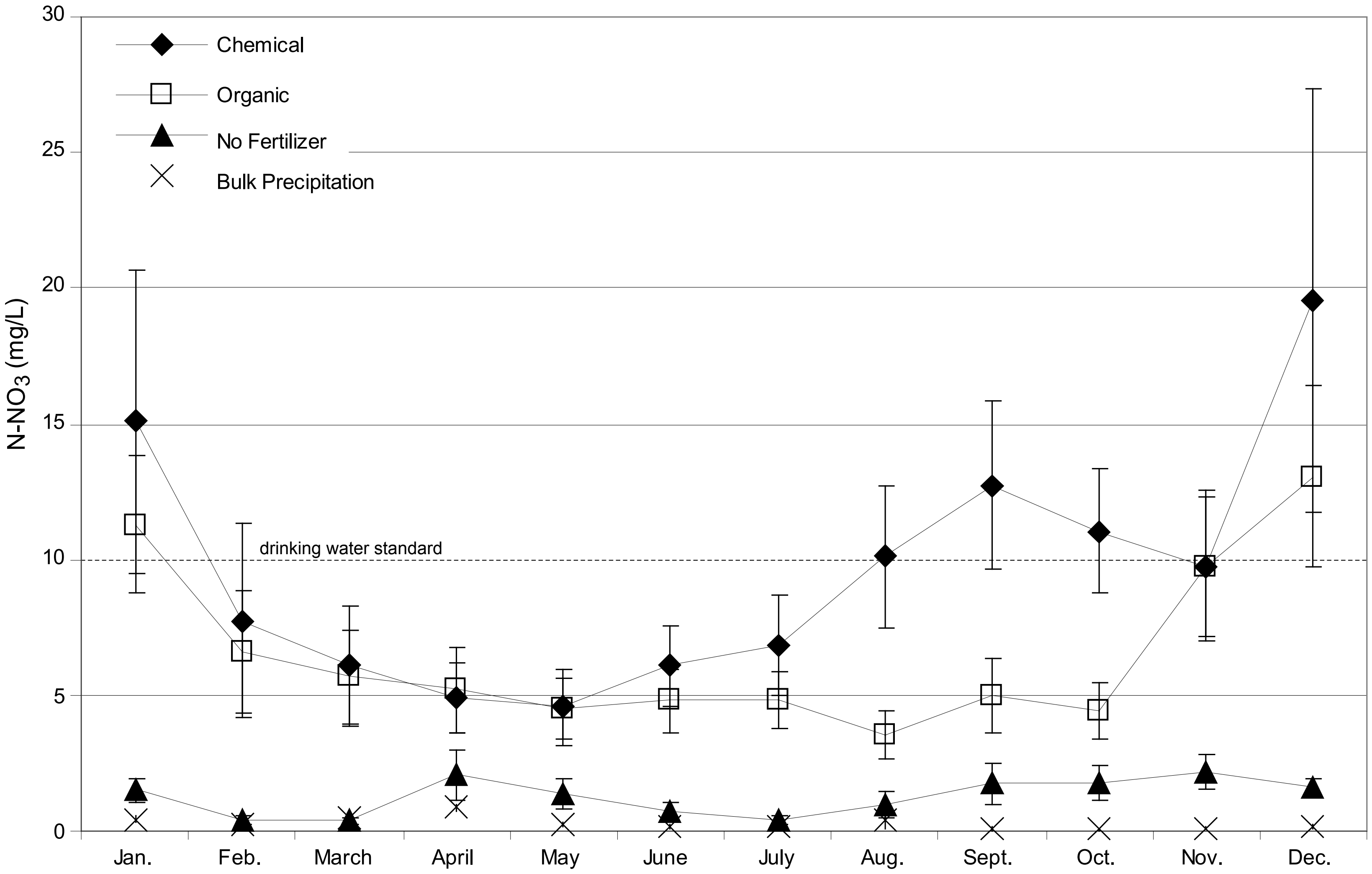

Figure 6. 7. Monthly average N-NO$_3$ concentrations of soil water collected at 100 cm from the combined years, and for bulk precipitation collected from May 2005 to January 2007. Error bars are standard error of the mean. The EPA drinking water standard is 10 mg/L, represented by the dashed horizontal line.

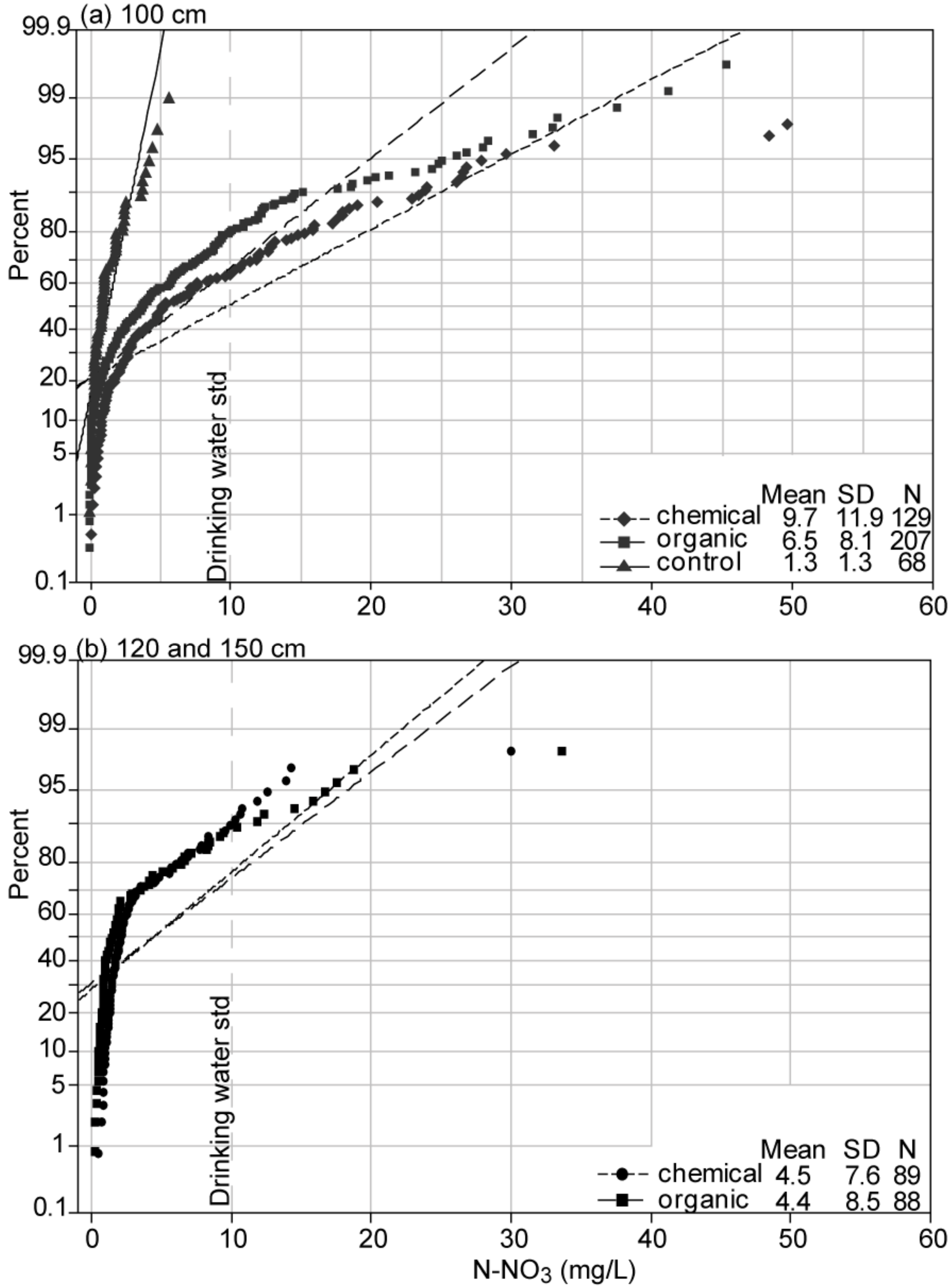

Figure 6. 8. Probability plot ($p < 0.005$) of soil water N-NO_3 concentrations (a) for the 100 cm samples and (b) for the 120 and 150 cm samples.

6.4 DISCUSSION

Concentrations of N-NO_3 in soil water leachate beneath fertilized turf are commonly less than 5 mg/L (Petrovic, 1990). However, a few studies find concentrations in the leachate can reach 40 mg/L, values comparable with concentrations in this study (Frank et al., 2006; Guillard and Kopp, 2004). The concentrations in this study may be higher than those in other studies because the lawns are mixed species. Erickson et. al. (2001) found that on recently established plots (<1 year old) that those with mixed species leached ten times more nitrate than did areas with homogenous grass.

There is a difference in soil water N-NO_3 concentrations at 100 cm, on average, between different fertilizer treatments (Figure 6.4) however, there is also variability between sites that receive the same type of fertilizer (Figure 6.5). This variability could be due to variable moisture and temperature differences from year to year, although concentrations at a given site do not vary much between years (Table 6.3). More likely the variability is due to difference in soil and hydrologic properties (Munster et. al., 2006).

Higher soil water average N-NO_3 concentrations under the sites treated with chemical fertilizer than those treated with organic fertilizer (Figure 6.4) could be due to higher rates of applied nitrogen at the sites treated with chemical fertilizer (Figure 6.2), although there is no direct relationship between yearly application rate and average concentrations. When following manufacturers' instructions there will be more applied N on a lawn fertilized with chemical fertilizer than with organic fertilizer. Despite the elevated inputs of nitrogen at sites treated with chemical fertilizer, the sites treated with organic fertilizer leached similar concentrations in 2005 and 2006 (Figure 6.4). This same pattern was observed when comparing sites of different fertilizer treatments at the same location (Figure 6.6). This implies that even when soil and hydrologic properties are relatively constant sites fertilized with organic fertilizer can leach similar concentrations of nitrate as chemical sites even though inputs of nitrogen are less at the organic sites.

The Oakdale sites suggest that a change in fertilizer treatment may affect soil water leaching concentrations. This site was incorrectly fertilized in October 2005 where the chemical site received organic fertilizer and the organic site received chemical fertilizer. After this treatment there is an increase in the nitrate concentrations measured beneath the organic site. In addition these sites, unlike the other two locations with both a chemical and an organic site, have no difference in the average values between sites at the end of the study period, possibly owing to the overlap of fertilizer treatments (Figure 6.6).

A study relating nitrate leaching with fall fertilizer application on the 15th of September, October, November or December, of the same year, found that mean nitrate mass collected in percolate water was linearly related to the date of fertilizer application, with higher losses for later application dates; yet, improved turf color and density was not different for fertilizer treatments made between October and December (Mangiafico and Guillard, 2006). Therefore, recommendations to apply fertilizer in mid to late November in southern New England may not be compatible with water quality goals. In October 2007, Suffolk County voters passed legislation that will prevent turf fertilizer from being applied from November 1 through April 1.While this law can prevent excess nitrate leaching from lawns which were previously fertilized during these months, if the yearly application rate is reduced, the procedure would not change the outcome of the results presented in this study since none of the sites were fertilized during these months. Using slow release nitrogen as fertilizer delays the leaching of nitrate in the subsurface. Studies found that 15-26% of nitrogen applied as fertilizer were present as organic soil nitrogen within four months to four years after application, with additional nitrogen stored in the thatch layer (Starr and Deroo, 1981; Watson, 1987; Webster and Dowdell, 1986).

Variability in monthly average concentrations between sites treated with chemical fertilizer and sites treated with organic fertilizer in August, September, and October is likely due to the higher rates of chemical fertilizer applied yearly which, during the warm wet months of August, September, and October are mobilized by mineralization and infiltration (Petrovic, 1990). Most of the aquifer recharge in Suffolk County, NY occurs in the cool season, October through March (Busciolano, 2004). Average concentrations of the fertilized sites in this study, in December and January, are above the EPA drinking water standard (Figure 6.8), and since most of this nitrate will leach to the groundwater the quality of groundwater will be adversely affected.

The data indicate that the best treatment to reduce the impact of nitrate leaching from lawns and reaching the groundwater is to not fertilize at all. However, there is likely a reduction of nitrate concentrations reported at 100 cm and in the concentrations reaching the groundwater, since the probability of reaching the drinking water standard decreases by 25% from 100 cm to 120/150 cm at the sites treated with chemical fertilizer and by 14% at the sites treated with organic fertilizer. At the deeper depth there is no difference between sites treated with organic and chemical fertilizers. Additionally, at three of the four sites where soil water N-NO_3 concentrations were measured at both 100 and 120/150 cm, there was no difference in average concentrations with depth. No fertilizer is still the best solution as the lawns not fertilized have a low likelihood of even reaching the drinking water standard and <0.5% of reaching 5 mg/L.

6.5 CONCLUSIONS

On average, concentrations of soil water N-NO_3 collected at 100 cm beneath lawns treated with chemical fertilizer is statistically higher than soil water collected beneath lawns treated with organic fertilizer or no fertilizer. Though, it is striking that nitrate concentrations of soil water collected beneath lawns treated with organic fertilizer are also routinely above the EPA drinking water standard of 10 mg/L even though these sites receive less than 1/3 the amount of nitrogen as the lawns treated with chemical fertilizer. The impact of lawn fertilizer to the local groundwater is still uncertain as concentrations of nitrate will likely decrease with depth before influencing groundwater quality, thus more research is needed on this aspect. However, the detection of soil water concentrations between 10 to 80 mg/L is large enough to warrant concern for groundwater quality, especially during the months of high recharge.

Ideally fertilizer would be applied based on the need of the lawns. These needs are highly variable and to determine these needs require more time and effort than most home owners wish to invest. Additionally application rates tend to favor error on the side of excess instead on the side of caution further increasing the amount of nitrate leaching to groundwater.

6.6. REFERENCES

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7. Conclusions

Sewage from septic systems, road runoff from highways and leaching from fertilized lawns are possible nonpoint sources of perchlorate (ClO_4) contamination in urban settings to groundwater.

Perchlorate concentrations of bulk precipitation are between 0.2 to 3 μg/L ClO_4, with the highest concentrations impacted by atmospheric fallout from firework displays. Bulk precipitation content is predominantly influenced by sea spray with minor components (<16%) of anthropogenic contamination and terrestrial dust. The average soil water concentrations of perchlorate, collected at 100 cm, beneath lawns treated with organic fertilizer is 90 μg/L which is 45 times higher than concentrations beneath lawns treated with chemical fertilizer or lawns that were not fertilized. However, on average, concentrations of soil water N-NO_3 collected at 100 cm beneath lawns treated with chemical fertilizer is statistically higher than soil water collected beneath lawns treated with organic fertilizer or no fertilizer. Though, it is striking that nitrate concentrations of soil water collected beneath lawns treated with organic fertilizer are also routinely above the EPA drinking water standard of 10 mg/L even though these sites receive less than 1/3 the amount of nitrogen as the lawns treated with chemical fertilizer.

Perchlorate concentrations in sewage range from below detection (0.1 μg/L) to 260 μg/L, with an average concentrations of 2.2 μg/L. Perchlorate from sewage will likely raise the concentration in the groundwater above natural levels and depending on the density of septic systems and the amount of perchlorate reduction by bacteria, the groundwater concentrations may increase to near or above the NY State advisory level of 5 μg/L. Road runoff collected in catch basins and recharge basins have, on average, 3 μg/L ClO_4 and 2 mg/L Total Inorganic N (nitrate and ammonium). In areas where road runoff directly recharges to groundwater, the concentrations from these areas are of concern for groundwater quality. While the average concentration, 3 μg/L, is below the NY state drinking water planning level, some samples are above this level at concentrations as high as 18 μg/L. As a result, we have to be concerned about the risk of concentrations of perchlorate in groundwater increasing to above the New York State planning level. As in most studies the data presented here is not conclusive and more research is needed to fully understand the sources of perchlorate in urban areas.

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Appendix 1. Major ion chemistry of perchlorate and nitrate sources

As part of my master's thesis I measured the ion chemistry of the major nonpoint sources of nitrate in residential land use. This included nitrate, phosphate, sulfate, chloride, sodium, potassium, calcium, magnesium, boron, bromide and fluoride concentrations in sewage from septic systems, public sewage treatment plants and soil water collected beneath turfgrass plots managed one of three ways (chemical fertilizer, organic fertilizer and no fertilizer). This data was limited in sample quantity, lacked precipitation concentrations and insufficient detection limits prevented the use of boron, bromide, fluoride and phosphate as geochemical tracers. In addition a miscommunication with Suffolk County Public Works prevented detailed nitrogen analysis of the initial sewage samples. Due to these issues the major ion chemistry of nitrate sources was continued as part of my dissertation work. In addition to nitrate sources I also examined the chemistry of perchlorate sources in residential land use.

In this appendix is presented the analysis for

1. forty nine sewage samples from septic systems
2. twenty one sewage samples from sewage treatment plants
3. precipitation samples collected monthly at eight sites in Suffolk County from November 2005 through July 2007
4. soil water samples, totally almost 300 samples, collected at 60, 80, 100 and 120 cm between January 2003 and January 2007, from sites managed with chemical fertilizer, organic fertilizer, no fertilizer or from beneath a forest site
5. storm water samples (n=33) and samples from recharge basins (n=13) collected after five precipitation events in April 2006.

Samples were analyzed for perchlorate, nitrate, ammonium, organic nitrogen, sulfate, chloride, bromide, iodide, strontium, boron, sodium, magnesium, potassium and calcium. No method section or interpretation of the data will be presented here as each of these sources have been examined in other chapters of this thesis.

Table Explanation:

ND	not determined
NA	not applicable
<	less than detection limit, this value sometimes varies among an individual ion and is listed when known
>	greater than the maximum detection
STP	sewage treatment plant
Dry	a particular type of bucket sampler for dry precipitation (ref)
CO	Coram
EH	East Hampton
HA	Hauppauge
HU	Huntington
OA	Oakdale
SB	Stony Brook
c	chemical fertilizer site
n	no fertilizer site
o	organic fertilizer site
f	forest site

Sample lysimeters and rain gauges were identified using the following protocol;

> XXx.depth, where the first two capital letters identify the site and the third letter, which is lowercase, identifies the type of site. The depth is listed in centimeters or if the sampler is a rain gauge the word “rain” replaces depth.

Some samples are composite samples. These can be identified by the date column. If a word is listed instead of a numerical date then the sample is a composite for the season listed.

Ion concentrations of sewage

Date Collected	Lab #	Type	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Sr ug/L	Br ug/L	I ug/L	TKN mg N/L	ClO_4 ug/L	B ug/L	Cl mg/L	SO_4 mg/L	PO_4 mg/L
11/9/2005	W39	cesspool	92.50	7.21	15.90	32.00	151	230	220	ND	ND	ND	ND	ND	ND
11/9/2005	W40	cesspool	277.00	6.76	18.50	42.00	133	160	260	40.82	<	459	256.10	85.20	1.30
11/9/2005	W41	cesspool	259.00	5.26	16.60	16.00	50	90	250	42.30	4.80	634	322.00	12.00	40.80
11/9/2005	W42	cesspool	111.00	3.67	9.00	15.00	54	150	170	25.67	<	208	125.80	10.50	8.70
11/9/2005	W43	cesspool	89.60	7.54	17.70	34.00	161	250	240	38.52	<	392	117.40	4.70	2.80
11/9/2005	W44	cesspool	183.00	4.94	15.90	23.00	86	150	170	41.54	<	305	237.60	9.40	19.10
11/9/2005	W45	cesspool	132.00	3.30	13.70	21.00	90	60	<10	44.95	257.50	136	183.80	3.60	3.40
11/9/2005	W46	cesspool	88.20	2.58	22.50	<7	16	120	90	29.00	<	168	109.50	9.90	47.10
11/9/2005	W47	cesspool	82.20	4.30	15.10	23.00	66	290	<10	44.96	<	205	105.80	5.60	2.60
11/9/2005	W48	cesspool	117.00	12.90	25.20	45.00	166	460	210	54.00	<	300	163.10	9.20	19.00
11/9/2005	W49	cesspool	196.00	5.21	14.90	22.00	66	220	150	23.30	2.20	569	274.70	5.60	22.70
11/9/2005	W50	cesspool	60.40	3.30	8.40	17.00	54	60	<10	45.52	<	128	86.10	22.90	6.20
11/9/2005	W51	cesspool	126.00	4.94	16.60	16.00	61	210	1080	60.00	<	397	133.50	8.10	26.40
3/21/2006	W53	cesspool	104.00	7.40	22.00	29.52	150	<300	200	47.38	2.44	493	107.74	42.90	7.59
3/21/2006	W54	cesspool	192.00	4.50	24.00	3.32	48	300	<100	45.36	3.89	455	203.93	27.00	7.03
3/21/2006	W55	cesspool	118.00	6.40	20.00	25.74	80	<300	<100	57.96	3.42	304	152.68	60.30	7.11
3/21/2006	W56	cesspool	118.00	8.30	33.00	15.51	87	<300	<100	ND	3.25	168	123.07	15.00	9.12
3/21/2006	W57	cesspool	122.00	3.80	13.00	12.79	66	<300	<100	38.64	1.04	205	131.67	12.70	4.48
3/21/2006	W58	cesspool	85.00	6.70	24.00	14.17	202	<300	100	78.83	0.68	155	100.28	76.10	8.21
3/21/2006	W59	cesspool	129.00	5.30	26.00	6.61	42	<300	<100	108.29	4.01	171	130.87	35.90	7.09
3/21/2006	W60	cesspool	66.60	11.20	18.00	34.21	173	<300	100	50.98	0.96	552	62.70	42.00	7.92
3/21/2006	W61	cesspool	111.00	3.80	31.00	13.11	47	<300	<100	57.01	2.20	178	93.85	13.70	6.56
9/11/2006	W62	cesspool	149.00	9.00	35.00	21.35	94	<300	300	78.83	3.90	573	156.23	31.50	9.40

Date Collected	Lab #	Type	Na	Mg	K	Ca	Sr	Br	I	TKN	ClO_4	B	Cl	SO_4	PO_4
9/11/2006	W63	cesspool	96.50	4.40	17.00	18.10	86	<300	<100	37.51	9.01	110	106.36	31.90	6.92
9/11/2006	W64	cesspool	128.00	5.90	15.00	14.37	63	<300	100	ND	ND	ND	153.56	37.30	7.95
9/11/2006	W65	cesspool	78.20	6.30	29.00	<7	77	<300	<100	86.59	0.60	461	97.67	31.60	7.10
9/11/2006	W70	cesspool	117.00	4.90	11.70	9.00	75	70	40	30.17	2.25		58.30	14.00	4.34
9/11/2006	W71	cesspool	63.20	5.65	22.90	20.00	53	100	30	95.82	0.62	407	59.80	15.70	14.20
9/11/2006	W72	cesspool	88.60	6.00	33.40	45.60	279	2040	50	58.02	0.13	436	214.00	12.30	6.40
9/11/2006	W73	cesspool	65.30	5.41	23.10	37.30	150	100	30	77.42	0.16	240	84.30	26.00	9.83
9/11/2006	W74	cesspool	105.00	5.48	13.70	22.70	104	100	<10	47.00	3.80	304	130.00	13.30	7.64
9/11/2006	W75	cesspool	42.00	4.02	9.00	15.00	47	50	<10	31.31	0.35	545	48.70	11.60	2.17
9/11/2006	W76	cesspool	191.00	3.62	18.90	<7	77	180	20	85.12	5.56	ND	277.00	40.60	14.50
9/11/2006	W77	cesspool	44.50	4.96	17.30	19.00	72	90	<10	53.64	<0.1	539	56.10	18.00	7.09
9/11/2006	W78	cesspool	120.00	7.30	20.70	22.10	92	200	<10	80.72	0.23	252	173.00	15.90	12.40
9/11/2006	W79	cesspool	58.10	2.64	11.10	15.00	122	140	10	38.72	0.11	551	67.50	19.00	4.33
9/11/2006	W81	cesspool	227.00	6.51	36.50	21.20	110	170	<10	92.53	1.64	189	312.00	45.70	14.40
1/31/2003	W3	cesspool	250.30	6.77	36.85	7.70	ND	ND	ND	ND	ND	737	201.08	29.11	91.58
1/31/2003	W4	cesspool	40.55	7.23	10.40	19.52	ND	ND	ND	ND	ND	202	55.70	8.96	30.29
1/31/2003	W5	cesspool	83.39	4.43	16.23	8.63	ND	ND	ND	ND	ND	153	65.19	7.60	15.85
1/31/2003	W6	cesspool	103.20	5.08	23.29	31.26	ND	ND	ND	ND	ND	434	164.31	15.93	13.70
1/31/2003	W7	cesspool	38.94	5.40	10.85	19.39	ND	ND	ND	ND	ND	223	44.45	1.64	25.26
1/31/2003	W8	cesspool	161.50	8.20	21.14	19.41	ND	ND	ND	ND	ND	576	67.69	30.66	29.84
5/14/2003	W9	cesspool	41.28	7.74	18.36	47.49	ND	ND	ND	ND	ND	311	42.23	3.73	15.27
5/14/2003	W10	cesspool	82.72	3.86	16.81	6.03	ND	ND	ND	ND	ND	208	72.46	5.66	10.66
5/14/2003	W11	cesspool	39.33	5.28	13.98	5.59	ND	ND	ND	ND	ND	430	48.47	5.89	26.88
5/17/2003	W12	cesspool	294.80	5.69	251.50	32.69	ND	ND	ND	ND	ND	229	1410.74	288.14	204.0
5/17/2003	W13	cesspool	52.48	9.64	19.17	44.26	ND	ND	ND	ND	ND	429	83.39	9.01	37.75

Date Collected	Lab #	Type	Na	Mg	K	Ca	Sr	Br	I	TKN	ClO_4	B	Cl	SO_4	PO_4
5/21/2003	W14	cesspool	87.27	6.51	25.36	20.81	ND	ND	ND	ND	ND	173	25.64	183.75	0.05
9/26/2003	W15	STP	41.82	6.15	7.67	17.67	ND	ND	ND	ND	ND	131	45.98	36.89	9.11
9/26/2003	W16	STP	28.84	1.23	7.01	7.37	ND	ND	ND	ND	ND	403	20.69	11.13	6.96
9/26/2003	W17	STP	38.06	5.97	10.43	23.42	ND	ND	ND	ND	ND	586	45.06	15.31	11.55
9/26/2003	W18	STP	42.40	4.11	10.72	21.74	ND	ND	ND	ND	ND	198	59.11	18.68	16.15
9/25/2003	W19	STP	37.90	4.51	10.05	22.62	ND	ND	ND	ND	ND	282	45.13	18.86	10.90
9/25/2003	W20	STP	28.14	8.31	7.90	28.16	ND	ND	ND	ND	ND	329	42.61	22.32	5.21
9/25/2003	W21	STP	36.70	4.10	9.47	32.48	ND	ND	ND	ND	ND	494	41.97	16.11	9.05
9/26/2003	W22	STP	47.76	4.83	8.55	22.50	ND	ND	ND	ND	ND	182	44.89	6.78	15.37
9/25/2003	W23	STP	49.24	3.61	16.21	18.44	ND	ND	ND	ND	ND	249	58.97	12.87	14.27
9/26/2003	W24	STP	41.69	6.88	9.81	32.23	ND	ND	ND	ND	ND	1306	48.78	34.07	2.75
9/26/2003	W25	STP	43.04	4.74	19.18	27.97	ND	ND	ND	ND	ND	191	64.49	10.19	10.80
9/26/2003	W26	STP	42.38	3.19	15.71	19.38	ND	ND	ND	ND	ND	176	57.46	11.82	14.83
9/25/2003	W27	STP	51.69	4.78	18.16	20.87	ND	ND	ND	ND	ND	408	73.73	21.26	13.75
9/25/2003	W28	STP	26.88	4.43	7.87	17.62	ND	ND	ND	ND	ND	297	29.51	22.01	8.46
9/25/2003	W29	STP	55.74	4.13	7.44	18.24	ND	ND	ND	ND	ND	185	70.49	19.51	9.26
9/25/2003	W30	STP	148.30	2.80	9.36	22.37	ND	ND	ND	ND	ND	112	32.81	365.49	5.79
9/26/2003	W31	STP	29.11	3.38	9.90	19.02	ND	ND	ND	ND	ND	176	38.69	9.06	10.89
9/25/2003	W32	STP	26.41	3.63	6.02	16.62	ND	ND	ND	ND	ND	147	39.42	17.79	9.39
9/26/2003	W33	STP	49.75	5.77	10.76	21.07	ND	ND	ND	ND	ND	319	31.49	21.94	10.11
9/25/2003	W34	STP	66.82	7.49	19.93	53.55	ND	ND	ND	ND	ND	214	102.41	6.50	47.37
9/25/2003	W35	STP	58.90	22.43	36.46	0.12	ND	ND	ND	ND	ND	120	11.57	2.30	51.15

Ion concentrations of bulk precipitation.

Date Collected	Lab #	Sampler	Vol. Collected *mm*	pH	Na *ug/L*	Mg *ug/L*	K *ug/L*	Ca *ug/L*	Sr *ug/L*	Br *ug/L*	I *ug/L*	N-NO$_3$ *mg/L*	N-NH$_4$ *mg/L*	ClO$_4$ *ug/L*	B *ug/L*	Cl *mg/L*	SO$_4$ *mg/L*	PO$_4$ *mg/L*
9/7/2006	1005	Dry*	5870mL	ND	1400	195	160	< 700	3	14	4	0.55	<0	0.090	7	2.86	5.22	0.02
10/4/2006	1030	Dry*	2935mL	5.0	1030	178	160	< 700	4	12	3	0.49	<0	0.059	< 3	2.67	4.11	0.02
11/3/2006	1056	Dry*	6750mL	4.7	1250	170	130	< 700	2	11	3	0.37	<0	0.020	6	2.75	4.37	0.02
12/6/2006	1079	Dry*	4865mL	4.7	2340	336	150	< 700	2	16	3	0.36	<0	0.016	7	4.26	4.88	0.02
1/5/2007	1111	Dry*	4300mL	5.0	1020	145	110	< 700	2	10	3	0.50	0.08	0.019	3	ND	ND	0.81
2/7/2007	1133	Dry*	1625mL	5.0	2370	214	150	< 700	3	15	22	1.18	0.36	0.069	10	3.33	ND	ND
3/7/2007	1150	Dry*	3550mL	4.7	767	79	100	< 700	1	5	9	<0.1	0.18	0.017	7	4.14	ND	ND
4/4/2007	1166	Dry*	1560mL	5.0	4740	601	330	1400	10	37	62	1.49	0.72	0.105	12	9.16	21.20	ND
5/2/2007	1194	Dry*	4002mL	5.0	2700	366	170	< 700	5	22	42	0.53	0.33	0.055	7	5.22	5.80	ND
6/8/2007	1231	Dry*	1676mL	5.0	1300	355	690	1300	6	13	26	1.09	0.41	0.471	13	3.08	10.11	ND
7/5/2007	1248	Dry*	1400mL	5.0	ND	ND	ND	ND	ND	ND	ND	2.17	0.62	3.240	ND	5.07	15.60	ND
12/1/2005	785	CO.rain	104.4	4.7	1340	217	2070	< 700	2	7	2	0.00	0.13	0.358	70	1.74	2.39	<0.01
1/6/2006	817	CO.rain	not recorded	4.4	782	125	80	< 700	1	5	2	0.27	<0.01	0.017	<3	0.84	0.54	<0.01
2/2/2006	841	CO.rain	118.2	4.7	1820	204	170	< 700	2	10	3	0.20	<0.01	0.024	57	ND	ND	ND
3/2/2006	833a	CO.rain	48.0	5.0	2350	242	570	800	2	10	4	0.39	0.17	0.044	77	2.29	1.13	<0.01
4/6/2006	871	CO.rain	33.6	4.0	2710	360	290	1400	7	8	4	0.82	0.38	0.124	20	7.65	6.07	0.16
5/4/2006	897	CO.rain	162.8	4.0	688	126	150	< 700	2	7	2	0.04	<0.01	0.020	12	ND	ND	ND
6/1/2006	923	CO.rain	139.8	4.5	672	86	430	< 700	2	4	2	0.02	<0.01	0.030	ND	0.85	1.36	<0.01
7/6/2006	951	CO.rain	165.0	4.5	695	95	420	< 700	4	4	3	0.02	0.01	1.800	28	1.49	1.92	0.02
8/2/2006	975	CO.rain	34.3	4.7	1530	371	2620	1100	4	6	6	ND	<0.01	2.410	41	2.34	7.37	0.03
9/7/2006	1002	CO.rain	167.8	4.7	1540	273	240	1100	5	8	6	0.00	<0.01	0.740	ND	3.01	4.66	0.02
10/4/2006	1022	CO.rain	80.8	4.7	1640	422	160	2200	8	7	4	0.00	<0.01	0.068	8	3.02	2.88	0.02
11/2/2006	1031	CO.rain	134.2	4.7	1560	239	300	< 700	3	9	2	0.08	<0.01	0.034	5	3.15	<1	0.01
12/6/2006	1081	CO.rain	149.0	4.7	1450	177	180	< 700	2	8	2	0.02	<0.01	0.062	14	2.68	1.52	0.02
1/5/2007	1104	CO.rain	91.8	4.4	693	121	90	< 700	2	6	2	0.19	<0.01	0.395	ND	2.11	2.19	0.02
2/1/2007	1131	CO.rain	10.0	ND	2100	127	200	< 700	2	6	8	0.60	0.40	0.178	8	3.64	2.91	ND
3/7/2007	1145	CO.rain	not recorded	ND	2900	152	200	< 700	2	8	14	0.25	<0.01	0.033	30	5.08	2.32	ND
12/1/2005	783	EH.rain	96.6	4.7	1640	244	1250	< 700	2	9	2	0.00	0.12	0.033	19	1.99	<1	<0.01
1/6/2006	814	EH.rain	128.0	4.7	4180	511	2450	< 700	3	24	3	0.21	0.13	0.024	ND	6.15	1.61	0.89
2/2/2006	837	EH.rain	60.4	4.7	3500	372	1240	< 700	2	19	3	0.22	0.21	0.037	10	5.33	1.08	<0.01
3/2/2006	834a	EH.rain	480mL	5.3	5570	460	690	< 700	3	20	3	0.30	0.12	0.202	250	5.86	1.97	<0.01
4/6/2006	873	EH.rain	15.0	4.7	4980	614	420	1600	6	16	5	0.53	<0.01	0.089	ND	7.80	5.30	0.05

Date	**Lab #**	**Sampler**	**Vol. Collected**	**pH**	**Na**	**Mg**	**K**	**Ca**	**Sr**	**Br**	**I**	**N-NO$_3$**	**N-NH$_4$**	**ClO$_4$**	**B**	**Cl**	**SO$_4$**	**PO$_4$**
5/4/2006	896	EH.rain	59.4	5.0	3590	504	330	800	5	20	3	0.05	<0.01	0.030	46	ND	ND	ND
7/6/2006	950	EH.rain	31.6	5.0	714	75	480	< 700	2	<3	5	0.00	<0.01	0.060	26	1.94	2.27	0.01
8/1/2006	974	EH.rain	not recorded	8.8	3250	599	640	1400	9	17	28	ND	ND	0.151	30	ND	ND	ND
9/7/2006	1000	EH.rain	126.0	4.7	3070	416	1100	800	4	20	3	0.04	0.24	0.030	ND	5.49	3.43	0.21
10/4/2006	1020	EH.rain	71.2	4.7	1520	234	1120	< 700	2	10	3	0.02	<0.01	0.022	15	3.16	2.19	0.02
11/2/2006	1034	EH.rain	90.4	4.4	5200	675	2280	< 700	4	33	2	0.00	<0.01	0.010	6	8.80	<1	0.05
12/6/2006	1080	EH.rain	121.8	4.7	2770	337	1240	< 700	2	15	2	0.00	<0.01	0.026	8	4.76	1.71	0.02
1/5/2007	1103	EH.rain	62.2	4.7	2390	302	460	< 700	2	14	2	0.18	<0.01	0.016	12	4.43	<1	0.01
5/6/2005	591	HA.rain	115.8	5-	672	135	80	< 700	2	8	<1	0.35	0.12	ND	ND	3.07	1.83	ND
11/4/2005	746	HA.rain	full	4.7	1030	116	150	< 700	1	4	2	0.01	0.12	<0.005	12	1.16	0.46	<0.01
12/1/2005	770	HA.rain	97.0	4.5	1090	183	180	< 700	2	7	2	0.20	0.12	0.049	31	1.24	1.04	<0.01
1/6/2006	794	HA.rain	158.0	4.0	779	113	110	< 700	1	5	2	0.27	0.04	0.029	<3	0.88	0.63	<0.01
2/2/2006	818	HA.rain	94.8	5.0	1850	207	160	< 700	2	8	3	0.21	0.01	0.023	19	2.72	0.88	<0.01
3/2/2006	836a	HA.rain	33.6	5.3	3960	311	350	1100	4	10	5	0.47	0.15	0.182	4	3.92	2.29	<0.01
4/6/2006	856	HA.rain	40.0	4.7	1640	345	210	1500	5	7	4	0.69	0.24	<0.005	<3	2.06	3.26	<0.01
5/4/2006	876	HA.rain	116.0	4.7	1020	154	300	< 700	2	8	2	0.23	<0.01	0.020	87	ND	ND	ND
6/1/2006	904	HA.rain	129.0	4.5	1150	152	1970	< 700	2	5	3	0.05	4.12	0.210	31	1.13	4.58	0.28
7/6/2006	931	HA.rain	187.8	4.5	564	140	480	< 700	3	<3	<1	0.04	<0.01	1.050	45	1.53	3.83	0.01
8/2/2006	958	HA.rain	54.4	4.0	425	126	380	< 700	3	3	1	0.04	<0.01	0.210	ND	1.84	<1	0.05
9/7/2006	987	HA.rain	128.4	4.7	986	343	3060	< 700	3	7	3	0.00	0.03	0.110	19	2.36	0.06	0.09
10/4/2006	1006	HA.rain	60.8	4.0	922	164	1380	< 700	3	6	3	0.01	<0.01	0.060	11	2.44	3.27	0.01
11/2/2006	1048	HA.rain	188.0	4.4	1090	183	780	< 700	2	8	2	0.00	<0.01	0.031	7	2.70	2.16	0.02
12/6/2006	1077	HA.rain	129.0	5.0	1770	158	110	< 700	2	7	2	ND	<0.01	0.022	14	2.50	1.18	0.02
1/5/2007	1086	HA.rain	88.2	4.4	1010	148	200	< 700	2	7	2	0.20	<0.01	0.038	18	2.18	2.09	0.01
2/7/2007	1127	HA.rain	53.4	4.7	1700	156	170	< 700	3	6	8	0.39	0.18	0.050	9	3.80	ND	ND
3/7/2007	1147	HA.rain	103.8	5.0	1620	159	170	< 700	3	7	13	0.24	0.02	0.422	23	2.70	2.58	ND
4/4/2007	1151	HA.rain	475mL	4.7	2310	176	180	< 700	2	7	15	0.43	0.12	0.015	17	3.72	3.46	ND
5/2/2007	1174	HA.rain	1500mL	4.0	2670	217	590	< 700	2	11	15	0.62	<0.01	<0.005	36	2.49	2.13	ND
6/8/2007	1214	HA.rain	89.0	6.5	820	326	1620	1000	3	3	11	0.01	<0.01	<0.005	28	3.28	3.78	ND
7/5/2007	1233	HA.rain	70.0	4.5	ND	ND	ND	ND	ND	ND	ND	0.35	2.71	2.780	ND	1.26	4.12	ND
11/4/2005	748	HU.rain	full	4.7	1990	250	360	< 700	2	9	2	0.36	0.14	<0.005	15	3.26	0.91	<0.01
12/1/2005	774	HU.rain	115.2	4.7	1120	184	200	< 700	3	6	3	0.49	0.17	0.132	15	1.45	0.97	<0.01
1/6/2006	801	HU.rain	134.0	4.4	981	240	80	800	3	5	3	0.30	0.10	0.025	ND	0.98	1.04	<0.01
2/2/2006	824	HU.rain	80.2	4.7	2550	281	250	800	3	9	3	0.31	0.09	0.028	15	3.55	2.14	<0.01
3/2/2006	837a	HU.rain	33.0	5.3	3100	301	440	1100	4	9	4	0.60	0.41	0.270	7	2.40	2.40	<0.01

Date	Lab #	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO_3	N-NH_4	ClO_4	B	Cl	SO_4	PO_4
4/6/2006	861	HU.rain	33.8	5.0	8850	592	660	2500	10	11	5	1.23	0.54	<0.005	88	6.20	5.09	<0.01
5/4/2006	882	HU.rain	150.0	4.7	579	152	200	< 700	2	6	2	0.00	0.94	0.030	49	ND	ND	nd
6/1/2006	908	HU.rain	105.8	5.0	573	250	1040	< 700	3	5	3	0.09	0.85	0.050	22	1.16	2.33	<0.01
7/6/2006	937	HU.rain	212.6	4.5	955	150	480	< 700	3	4	1	ND	<0.01	0.870	37	2.18	1.07	0.01
8/2/2006	964	HU.rain	48.2	4.7	853	398	2480	1200	6	6	2	0.00	<0.01	0.062	78	2.46	6.92	0.16
9/7/2006	989	HU.rain	109.0	4.7	1140	266	540	700	4	8	3	0.00	<0.01	0.050	13	2.25	4.26	0.02
10/4/2006	1009	HU.rain	39.8	4.7	1830	294	290	900	4	8	3	0.05	<0.01	0.080	46	2.37	2.02	0.02
11/2/2006	1045	HU.rain	140.2	4.4	714	161	180	< 700	2	6	1	0.02	<0.01	0.026	8	2.10	2.17	0.02
12/6/2006	1076	HU.rain	164.0	4.7	1300	167	170	< 700	2	8	2	0.02	<0.01	ND	9	2.57	1.35	0.02
1/5/2007	1092	HU.rain	77.8	4.7	780	136	210	< 700	2	6	2	1.38	<0.01	0.121	11	1.94	1.25	0.02
2/7/2007	1129	HU.rain	62.8	4.7	3760	175	190	< 700	2	6	7	0.66	0.44	0.056	7	2.88	ND	ND
3/7/2007	1148	HU.rain	132.6	5.0	4160	186	180	< 700	2	7	14	0.26	0.42	0.069	28	7.09	2.97	ND
4/4/2007	1155	HU.rain	65.8	4.4	3180	309	240	900	4	11	18	0.35	0.72	0.036	23	5.43	4.56	ND
5/2/2007	1175	HU.rain	165.4	4.7	1410	238	1310	< 700	2	10	16	0.08	<0.01	<0.005	24	2.45	3.51	ND
6/8/2007	1216	HU.rain	75.0	4.7	1050	398	1310	800	3	5	6	0.02	<0.01	0.062	71	4.14	ND	ND
7/5/2007	1235	HU.rain	58.0	4.7	1460	456	2070	1100	4	5	14	0.00	<0.01	0.743	42	2.29	6.83	ND
5/6/2005	596	OA.rain	82.0	5-	1780	291	470	900	4	16	13	0.55	0.13	ND	ND	2.60	2.81	ND
11/4/2005	758	OA.rain	180.2	4.7	1750	268	130	800	2	7	3	0.00	0.12	<0.005	15	2.09	0.62	<0.01
12/1/2005	779	OA.rain	77.2	4.7	1830	310	290	700	3	10	3	0.42	0.21	0.077	14	2.40	1.54	<0.01
1/6/2006	805	OA.rain	82.0	4.4	2960	244	110	< 700	3	7	3	0.41	0.11	0.063	ND	3.97	1.32	<0.01
2/2/2006	832	OA.rain	87.8	4-	5350	329	120	< 700	3	13	93	0.26	0.07	0.036	11	7.65	1.21	<0.01
3/2/2006	835a	OA.rain	30.0	5.3	10500	518	350	1700	6	13	5	0.78	0.66	0.116	4	17.72	3.63	<0.01
4/6/2006	867	OA.rain	29.8	4.7	9920	500	540	1900	8	11	5	0.96	0.41	0.071	70	16.46	5.14	<0.01
5/4/2006	890	OA.rain	102.2	4.7	1190	240	250	700	3	9	3	0.21	<0.01	0.090	32	ND	ND	ND
6/1/2006	916	OA.rain	104.2	5.0	2170	579	450	2900	9	8	2	ND	ND	0.120	13	2.10	2.32	<0.01
6/1/2006	916	OA.rain	104.2	5.0	2220	552	420	2900	9	8	1	0.16	<0.01	0.120	ND	2.27	<1	<0.01
7/6/2006	938	OA.rain	209.4	4.5	541	99	290	< 700	3	4	1	0.02	<0.01	0.170	9	1.79	2.67	0.02
7/6/2006	938	OA.rain	209.4	4.5	519	98	250	< 700	2	4	1	0.03	<0.01	<0.1	ND	1.64	4.33	0.01
8/2/2006	969	OA.rain	67.8	4.4	3340	356	2470	700	8	6	3	ND	<0.01	0.100	42	ND	ND	ND
9/7/2006	996	OA.rain	109.0	4.7	1650	369	1320	700	4	10	4	ND	<0.01	0.130	8	3.46	7.35	0.12
10/4/2006	1016	OA.rain	66.4	4.0	1250	291	260	1000	7	7	2	0.02	<0.01	0.172	7	2.76	2.85	0.02
11/2/2006	1043	OA.rain	138.8	4.7	3990	695	720	1400	7	26	1	0.20	<0.01	0.129	9	7.38	3.95	0.02
12/6/2006	1072	OA.rain	60.0	4.7	2470	406	290	< 700	5	13	2	0.00	<0.01	0.061	8	4.46	2.55	0.01
1/5/2007	1098	OA.rain	59.4	4.7	1760	290	350	< 700	3	11	3	1.13	<0.01	0.051	14	3.29	2.55	0.02
2/7/2007	1128	OA.rain	380mL	4.7	3960	299	240	900	3	9	9	0.44	0.40	0.046	9	2.78	ND	ND

Date	Lab #	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	N-NH$_4$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
3/7/2007	1146	OA.rain	61.7	5.0	8790	259	180	800	3	10	17	0.48	0.26	0.185	23	15.20	3.27	ND
4/4/2007	1162	OA.rain	25.0	4.4	11900	523	280	1600	6	12	30	0.81	0.45	0.092	20	20.20	5.33	ND
5/2/2007	1183	OA.rain	108.0	4.7	1990	281	530	< 700	3	13	17	0.21	<0.01	0.116	32	3.25	3.13	ND
6/8/2007	1227	OA.rain	84.0	5.5	6310	1690	1130	10200	31	21	25	0.02	<0.01	0.201	24	8.56	6.73	ND
7/5/2007	1240	OA.rain	75.0	5.3	6840	921	960	4700	13	22	22	0.04	<0.01	0.492	26	4.32	4.94	ND
11/3/2005	742	SB.rain	full	4.7	1960	442	440	< 700	2	11	2	0.02	0.12	<0.005	9	3.02	1.37	<0.01
11/30/2005	769	SB.rain	102.0	4.5	1390	220	670	< 700	3	8	2	0.02	0.12	ND	26	3.98	2.64	<0.01
1/5/2006	787	SB.rain	168.4	4.7	935	114	180	< 700	1	5	3	0.22	0.01	0.020	28	ND	ND	ND
2/3/2006	847	SB.rain	115.0	4.7	2100	229	210	< 700	2	10	5	0.33	0.01	0.036	15	2.56	0.79	<0.01
3/2/2006	842a	SB.rain	27.8	4.7	1980	188	460	< 700	2	8	2	0.50	0.07	0.117	3	1.95	2.45	<0.01
4/5/2006	853	SB.rain	28.4	4.7	1690	232	260	800	4	8	4	0.91	0.04	0.018	25	1.82	2.61	<0.01
6/1/2006	929	SB.rain	163.8	5.0	610	68	210	< 700	1	4	1	0.04	0.31	0.030	18	0.55	1.38	<0.01
7/6/2006	957	SB.rain	153.0	4.5	688	86	180	< 700	1	5	2	0.03	<0.01	0.790	18	2.91	3.78	0.01
8/2/2006	981	SB.rain	41.0	4.7	1380	177	630	< 700	4	7	2	0.17	<0.01	0.150	21	2.19	5.62	0.02
9/7/2006	1004	SB.rain	141.9	4.7	867	107	160	< 700	2	8	3	0.11	<0.01	0.010	4	2.07	3.03	0.02
10/4/2006	1029	SB.rain	86.0	4.7	761	86	230	< 700	2	5	2	0.04	<0.01	0.102	18	1.96	2.61	0.01
11/3/2006	1054	SB.rain	196.8	4.7	816	106	140	< 700	1	7	2	0.14	<0.01	0.021	14	2.44	2.56	0.01
11/3/2006	1055	SB.rain	196.8	4.7	832	104	130	< 700	1	7	2	0.10	<0.01	0.022	ND	2.06	1.52	0.01
12/6/2006	1078	SB.rain	147.8	4.7	1740	198	190	< 700	1	9	2	0.07	<0.01	0.005	14	2.98	0.67	0.02
1/5/2007	1110	SB.rain	98.0	4.7	973	101	240	< 700	1	6	2	0.25	<0.01	0.029	15	1.85	2.34	0.02
2/7/2007	1132	SB.rain	325mL	4.7	1610	178	280	< 700	3	8	8	0.57	0.16	0.035	8	3.80	ND	ND
3/7/2007	1149	SB.rain	94.4	5.0	1660	145	200	< 700	2	8	14	0.23	<0.01	0.629	35	3.89	ND	ND
4/4/2007	1165	SB.rain	37.0	4.7	1880	272	190	< 700	3	13	26	0.69	0.11	0.988	16	3.50	3.77	ND
5/2/2007	1191	SB.rain	1025.0	4.4	2060	280	200	< 700	2	16	60	0.19	0.04	0.204	8	2.91	1.88	ND
6/8/2007	1230	SB.rain	77.0	5.0	2670	165	490	< 700	2	9	16	0.02	<0.01	0.314	66	3.77	2.21	ND
7/5/2007	1247	SB.rain	not recorded	4.4	1230	134	350	< 700	2	7	11	0.35	0.07	1.300	60	1.40	ND	ND

Ion concentration of soil water samples

Date Collected	Lab #	Sampler	Vol. Collected mL	pH	Na mg/L	Mg mg/L	K mg/L	Ca mg/L	Sr ug/L	Br ug/L	I ug/L	N-NO_3 mg/L	ClO_4 ug/L	B ug/L	Cl mg/L	SO_4 mg/L	PO_4 mg/L
6/1/2006	907	HAc.100	100	7.5	23.20	61.84	4.53	16.53	186	21	7	12.90	0.15	ND	3.60	55.90	0.02
7/6/2006	930	HAc.100	100	7.5	25.90	79.29	5.84	>20	> 200	25	6	23.94	0.14	ND	4.36	52.80	0.03
9/7/2006	985	HAc.100	100	7.0	22.80	>20	5.95	>20	178	36	12	23.80	2.39	ND	4.71	40.90	0.03
10/4/2006	1008	HAc.100	100	7.7	22.40	>20	5.56	>20	184	39	13	18.99	2.10	ND	5.62	39.30	0.03
11/2/2006	1049	HAc.100	200	6.8	20.90	>20	5.63	>20	182	31	10	18.40	1.61	370	3.87	58.00	0.03
12/6/2006	1059	HAc.100	170	6.8	27.20	>20	10.60	>20	> 200	35	12	75.60	0.68	307	2.91	117.00	0.03
1/5/2007	1089	HAc.100	100	7.4	23.40	>20	8.50	>20	> 200	34	10	64.50	0.53	ND	2.65	91.60	0.03
4/6/2006	862	HUc.100	320	6.0	15.60	8.72	2.84	>20	106	14	5	6.97	ND	< 3	3.07	8.93	<0.01
6/1/2006	909	HUc.100	250	6.5	19.40	11.40	4.20	28.03	151	20	3	10.20	ND	12	1.03	27.50	<0.01
7/6/2006	935	HUc.100	300	6.0	27.40	10.20	4.70	>20	144	21	3	7.64	0.92	25	2.81	22.00	0.02
8/2/2006	963	HUc.100	200	6.1	27.50	14.00	5.30	>20	185	51	6	15.27	2.29	37	2.95	19.70	0.01
9/7/2006	990	HUc.100	250	7.1	28.20	14.30	6.03	>20	> 200	89	8	18.00	2.99	35	7.13	24.10	0.02
10/4/2006	1010	HUc.100	280	6.5	25.20	12.50	4.86	>20	187	46	6	17.94	2.53	27	11.20	20.30	0.02
11/2/2006	1044	HUc.100	200	6.5	25.30	17.20	5.03	>20	> 200	47	5	23.40	2.08	21	8.04	27.50	0.04
12/6/2006	1074	HUc.100	300	6.5	19.40	>20	4.52	>20	> 200	30	3	nd	1.78	18	6.54	60.90	0.01
1/5/2007	1090	HUc.100	300	6.5	12.70	14.40	3.58	>20	179	21	3	17.81	0.71	ND	3.71	28.40	0.02
1/5/2007	1090	HUc.100	300	6.5	11.70	12.70	3.38	>20	166	22	4	14.10	0.73	11	3.71	27.70	0.02
Jan-03	13	SBc.100	NA	NA	12.35	27.99	3.14	75.41	ND	ND	ND	0.17	ND	365	4.05	19.49	0.05
SUMMER 03	122	SBc.100	NA	NA	3.36	39.00	1.96	56.18	ND	ND	ND	2.21	ND	514	5.69	80.79	1.34
FALL 03	219	SBc.100	NA	NA	4.15	49.12	2.65	56.54	ND	ND	ND	0.78	ND	620	3.76	83.05	0.05
6/1/2006	925	SBc.100	200	7.0	4.67	34.62	5.73	31.57	> 200	11	2	2.60	<0.1	154	7.41	6.91	0.30
7/6/2006	953	SBc.100	100	7.5	4.13	10.00	3.56	>20	> 200	6	2	0.00	0.24	ND	2.37	3.48	0.05
9/5/2006	982	SBc.100	225	7.0	>35	>20	10.90	>20	177	17	4	0.30	0.52	185	21.10	12.60	0.50
10/4/2006	1024	SBc.100	220	6.5	>35	>20	15.40	>20	> 200	19	4	0.14	0.58	165	18.50	15.60	0.67
11/3/2006	1050	SBc.100	150	7.1	>35	>20	14.70	>20	> 200	22	3	0.06	0.92	ND	27.60	21.10	0.69
12/7/2006	1084	SBc.100	350	6.5	>35	>20	11.60	>20	> 200	19	2	0.73	0.42	130	31.70	13.70	0.65
Jan-03	10	SCWA 1	NA	NA	69.98	69.20	4.25	38.19	ND	ND	ND	1.33	ND	1283	10.07	25.76	0.05
SUMMER 03	107	SCWA 1	NA	NA	15.03	35.83	1.50	52.70	ND	ND	ND	0.05	ND	208	1.00	85.84	1.51
SUMMER 03	171	SCWA 1	NA	NA	12.56	56.85	2.40	97.47	ND	ND	ND	59.63	ND	1303	19.20	88.10	0.05
FALL 03	209	SCWA 1	NA	NA	48.23	80.79	4.43	51.11	ND	ND	ND	6.68	ND	602	6.19	87.80	2.54
11/4/2005	753	SCWA 1	250	7.0	9.47	30.07	4.73	36.25	175	33	21	2.48	<0.1	100	4.01	11.50	7.76

Date	Lab	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	$N\text{-}NO_3$	ClO_4	B	Cl	SO_4	PO_4
6/1/2006	913	SCWA 1	120	7.5	9.62	55.16	5.32	33.03	> 200	19	6	1.53	8.90	ND	2.42	10.40	0.63
7/6/2006	943	SCWA 1	110	7.5	11.10	>20	6.49	>20	> 200	27	6	nd	5.90	ND	5.86	65.00	0.71
8/2/2006	965	SCWA 1	150	7.0	11.10	>20	7.69	>20	> 200	36	11	6.42	3.92	ND	5.71	35.10	0.73
Jan-03	11	SCWA 2	NA	NA	57.45	67.33	2.51	45.88	ND	ND	ND	0.30	ND	1001	5.04	20.93	0.05
SUMMER 03	106	SCWA 2	NA	NA	20.91	72.53	0.98	41.30	ND	ND	ND	0.05	ND	692	1.48	86.74	1.58
11/4/2005	754	SCWA 2	300	7.0	6.33	36.00	3.42	45.96	186	36	19	3.64	13.60	129	4.28	11.40	3.54
4/6/2006	864	SCWA 2	105	7.0	5.56	>20	3.07	>20	188	20	12	2.92	ND	168	5.18	4.87	3.90
7/6/2006	944	SCWA 2	150	7.5	8.95	>20	5.90	>20	> 200	34	9	4.91	7.20	296	4.31	74.50	0.23
8/2/2006	966	SCWA 2	150	7.0	9.95	>20	6.53	>20	> 200	46	19	5.16	4.20	ND	96.65	26.60	0.01
11/2/2006	1036	SCWA 2	120	7.1	8.44	>20	6.05	>20	> 200	51	11	20.40	2.71	ND	8.53	41.60	0.39
12/6/2006	1064	SCWA 2	140	7.1	9.17	>20	5.65	>20	> 200	44	8	49.60	1.48	ND	11.00	90.20	0.34
Jan-03	12	SCWA 3	NA	NA	26.99	78.97	3.10	27.29	ND	ND	ND	0.84	ND	1420	2.40	15.64	0.05
SPRING 03	35	SCWA 3	NA	NA	13.62	65.53	1.64	25.60	ND	ND	ND	0.60	ND	707	49.09	7.25	0.05
SUMMER 03	105	SCWA 3	NA	NA	8.72	77.92	3.50	57.34	ND	ND	ND	0.05	ND	754	1.04	81.23	0.05
11/4/2005	756	SCWA 3	250	7.5	5.88	>20	10.20	43.52	> 200	32	14	5.08	14.40	110	5.91	9.38	4.23
6/1/2006	911	SCWA 3	100	7.5	7.45	67.02	10.60	37.65	> 200	19	5	2.33	3.27	ND	3.37	12.10	0.29
7/6/2006	945	SCWA 3	170	7.5	9.02	>20	14.10	>20	> 200	27	6	11.52	3.15	263	8.05	65.50	0.09
8/2/2006	967	SCWA 3	200	7.0	7.89	>20	13.60	>20	> 200	33	11	8.87	2.89	319	7.45	23.80	0.12
9/7/2006	994	SCWA 3	120	7.0	7.74	>20	13.30	>20	> 200	48	13	11.10	3.69	ND	13.60	21.40	0.28
11/2/2006	1037	SCWA 3	180	7.1	7.56	>20	13.90	>20	> 200	35	8	16.95	1.92	207	10.00	45.70	0.26
12/6/2006	1065	SCWA 3	150	7.1	6.91	>20	12.60	>20	> 200	30	6	21.30	0.80	189	8.62	53.50	0.24
FALL 03	213	SCWA 4	NA	NA	149.10	49.21	1.82	108.10	ND	ND	ND	8.98	ND	357	13.53	513.96	0.05
12/2/2004	481	SCWA 4	400	7.0	>35	>20	0.31	>20	108	50	10	1.57	ND	177	10.02	26.20	ND
2/3/2005	532	SCWA 4	325	7.0	>35	>20	0.17	>20	88	50	28	0.98	ND	ND	12.95	22.20	ND
6/1/2006	910	SCWA 4	250	7.5	52.07	23.09	0.36	37.98	125	40	8	0.30	12.48	119	0.53	8.14	0.02
7/6/2006	946	SCWA 4	250	7.0	>35	>20	0.36	>20	129	47	11	1.58	11.15	128	3.71	21.60	0.02
10/4/2006	1012	SCWA 4	230	6.8	>35	>20	1.32	>20	160	59	10	45.90	6.90	117	17.10	26.10	0.08
11/2/2006	1038	SCWA 4	300	7.1	>35	>20	1.22	>20	153	60	7	28.98	4.33	78	12.10	22.40	0.06
11/2/2006	1038	SCWA 4	300	7.1	>35	>20	1.19	>20	151	58	7	29.29	4.22	ND	12.10	20.80	0.06
12/6/2006	1066	SCWA 4	300	6.8	>35	>20	0.90	>20	127	46	6	19.60	2.28	63	11.20	22.80	0.05
1/5/2007	1096	SCWA 4	100	6.8	33.70	17.90	0.81	>20	112	46	6	17.64	1.45	45	11.10	21.30	0.04
4/5/2006	854	SBn.100	100	6.5	6.64	7.20	4.75	>20	166	5	3	1.34	ND	ND	3.73	1.85	0.29
6/1/2006	927	SBn.100	300	7.0	4.35	6.79	3.36	33.73	170	6	< 1	0.24	0.10	35	1.47	2.58	0.03
8/2/2006	979	SBn.100	300	7.0	4.35	11.60	4.70	>20	> 200	9	3	0.12	0.66	59	3.62	4.65	0.05

Date	Lab	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
8/2/2006	979	SBn.100	300	7.0	4.14	11.40	4.59	>20	> 200	9	3	nd	0.60	ND	3.53	4.71	0.05
9/5/2006	984	SBn.100	300	7.0	5.55	16.00	5.63	>20	> 200	15	2	3.74	1.26	94	3.49	7.50	0.07
10/4/2006	1026	SBn.100	300	6.8	5.04	15.90	6.23	>20	> 200	15	2	2.36	ND	78	3.27	7.28	0.02
10/4/2006	1026	SBn.100	300	6.8	4.99	15.20	6.10	>20	> 200	15	2	2.31	1.29	37	3.31	7.65	0.02
11/3/2006	1052	SBn.100	300	6.8	3.30	10.20	4.32	>20	197	10	1	2.45	0.70	51	3.96	5.62	0.07
12/7/2006	1083	SBn.100	300	6.5	2.41	6.89	4.60	>20	154	7	1	1.80	0.25	27	4.39	4.32	0.07
1/5/2007	1109	SBn.100	250	7.4	1.96	4.26	3.93	>20	108	9	1	2.40	<0.1	15	5.09	5.36	0.07
FALL 03	222	SBn.100	NA	NA	4.20	46.49	6.58	65.61	ND	ND	ND	0.05	ND	272	0.10	69.07	0.05
SPRING 03	72	SBn.100	NA	NA	15.37	17.73	4.23	29.63	ND	ND	ND	0.71	ND	112	9.02	79.70	0.05
SUMMER 03	124	SBn.100	NA	NA	5.88	31.68	3.87	51.77	ND	ND	ND	8.15	ND	188	19.98	102.70	2.29
SPRING 03	102	SBn.40	NA	NA	79.95	38.13	4.89	21.43	ND	ND	ND	2.11	ND	768	14.82	217.18	0.05
SUMMER 03	126	SBn.40	NA	NA	60.43	46.81	3.23	16.28	ND	ND	ND	2.18	ND	702	3.66	153.24	0.05
11/3/2005	745	SBf.100	200	4.5	7.85	0.22	0.97	>20	4	12	7	0.07	<0.1	ND	3.59	2.48	<0.01
11/3/2006	1053	SBf.100	200	6.5	0.11	0.01	<30	<700	0	< 3	< 1	0.14	0.14	22	1.04	0.42	0.02
Feb-03	31	COo.100	NA	NA	38.51	10.34	3.19	106.90	ND	ND	ND	0.38	ND	83	25.75	185.09	0.05
SPRING 03	70	COo.100	NA	NA	23.19	19.25	2.99	101.70	ND	ND	ND	0.72	ND	157	18.23	4.78	0.05
SUMMER 03	120	COo.100	NA	NA	17.66	23.65	5.43	48.78	ND	ND	ND	0.40	ND	234	4.78	85.35	0.05
FALL 03	218	COo.100	NA	NA	17.87	50.89	1.85	30.42	ND	ND	ND	1.12	ND	317	4.03	86.36	0.05
12/1/2005	787	COo.100	20	\	0.94	0.11	0.18	>20	1	5	3	20.29	<0.1	ND	1.05	0.72	<0.01
7/6/2006	952	COo.100	30	\	6.23	>20	6.56	>20	> 200	10	3	2.67	ND	ND	7.20	9.47	0.34
Feb-03	16	EHo.100	NA	NA	24.78	45.49	6.90	118.20	ND	ND	ND	1.31	ND	387	6.04	162.35	0.05
SPRING 03	34	EHo.100	NA	NA	52.40	41.60	6.07	92.07	ND	ND	ND	0.23	ND	461	5.32	8.81	0.05
SUMMER 03	103	EHo.100	NA	NA	72.35	20.56	5.23	133.70	ND	ND	ND	0.05	ND	292	13.61	169.01	0.05
FALL 03	202	EHo.100	NA	NA	56.73	16.95	5.03	162.80	ND	ND	ND	4.04	ND	265	25.97	129.46	0.05
11/4/2005	762	EHo.100	260	6.0	61.01	11.20	2.65	57.01	132	545	514	0.77	<0.1	ND	46.33	8.30	0.03
4/6/2006	874	EHo.100	220	5.5	23.60	4.51	1.91	23.41	71	198	53	5.58	ND	51	28.60	18.23	0.35
6/1/2006	921	EHo.100	300	5.0	20.20	3.83	1.91	>20	69	111	73	0.26	ND	52	9.98	16.40	<0.01
7/6/2006	948	EHo.100	350	6.0	29.20	5.67	3.02	>20	92	259	298	nd	0.50	59	5.14	2.70	0.03
7/6/2006	948	EHo.100	350	6.0	29.50	5.88	3.10	>20	95	261	295	0.13	0.40	ND	15.40	14.90	0.02
8/2/2006	973	EHo.100	200	5.8	31.50	8.48	3.99	>20	122	380	427	nd	< 0.1	52	21.40	16.90	0.03
9/7/2006	1001	EHo.100	300	6.1	28.50	7.41	3.49	>20	126	423	408	0.49	< 0.1	41	31.50	23.00	0.04
10/4/2006	1021	EHo.100	300	6.5	27.90	6.58	3.25	>20	106	254	180	0.19	< 0.1	34	34.20	11.70	0.02
11/2/2006	1033	EHo.100	300	6.5	22.70	4.24	2.06	>20	72	204	56	0.93	< 0.1	ND	29.20	4.97	0.02

Date	Lab	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
12/6/2006	1061	EHo.100	310	6.5	17.60	3.82	2.05	18.20	66	152	30	0.96	< 0.1	52	21.80	10.70	0.02
1/5/2007	1101	EHo.100	300	6.5	16.00	3.82	1.74	18.50	66	76	11	3.73	< 0.1	40	18.70	16.00	0.02
1/5/2007	1101	EHo.100	300	6.5	16.00	3.81	1.70	18.50	67	75	11	3.72	< 0.1	ND	18.90	16.00	0.02
Jan-03	3	HAo.100	NA	NA	18.78	9.34	2.01	31.79	ND	ND	ND	5.23	ND	78	15.60	119.02	0.05
SPRING 03	45	HAo.100	NA	NA	16.72	10.52	6.91	32.56	ND	ND	ND	1.49	ND	98	4.97	19.25	0.05
SPRING 03	68	HAo.100	NA	NA	42.43	12.06	1.11	75.47	ND	ND	ND	1.59	ND	81	17.73	26.51	0.05
SUMMER 03	119	HAo.100	NA	NA	16.66	37.44	2.12	48.66	ND	ND	ND	2.59	ND	273	2.67	97.53	0.05
SUMMER 03	156	HAo.100	NA	NA	17.60	22.84	5.31	48.95	ND	ND	ND	3.19	ND	225	3.24	105.43	0.05
12/2/2004	490	HAo.100	300	6.5	26.60	13.20	7.73	>20	156	47	10	10.00	ND	64	12.74	18.14	ND
1/7/2005	512	HAo.100	340	6.5	19.60	9.13	7.03	>20	117	27	13	2.91	ND	40	8.50	20.66	ND
2/3/2005	536	HAo.100	300	7.0	15.40	7.57	6.09	>20	112	24	< 1	1.32	ND	ND	11.09	32.85	ND
3/4/2005	548	HAo.100	250	6.0	2.92	6.70	3.32	>20	52	11	< 1	0.98	ND	ND	4.89	19.03	ND
4/1/2005	571	HAo.100	200	6.5	12.50	6.44	5.35	>20	110	11	< 1	1.59	ND	ND	4.74	8.08	ND
5/6/2005	592	HAo.100	250	6.5	9.81	7.06	5.64	>20	125	11	< 1	1.79	ND	ND	2.38	6.73	ND
4/6/2006	858	HAo.100	350	6.1	20.20	4.78	7.26	24.45	116	24	13	12.35	ND	49	8.04	25.60	<0.01
6/1/2006	905	HAo.100	250	6.0	17.50	5.83	8.42	27.59	139	29	16	nd	113.00	94	3.46	31.00	<0.01
7/6/2006	934	HAo.100	300	6.0	20.60	7.81	11.10	>20	154	42	15	5.85	76.25	125	4.88	37.20	0.02
8/2/2006	960	HAo.100	250	6.5	20.00	7.70	10.70	>20	123	61	25	4.23	48.53	158	4.60	35.20	0.02
9/7/2006	986	HAo.100	250	6.1	21.40	8.30	13.80	>20	129	76	32	7.83	54.50	135	7.27	35.10	0.02
10/4/2006	1007	HAo.100	300	6.5	23.10	6.78	10.50	>20	113	67	28	8.95	45.35	115	6.33	39.30	0.02
11/2/2006	1047	HAo.100	300	6.5	27.30	7.69	12.50	>20	145	52	16	28.30	31.50	115	9.34	36.80	0.02
12/6/2006	1058	HAo.100	320	6.5	32.60	8.13	12.40	>20	173	46	13	26.10	30.70	99	11.60	61.40	0.02
1/5/2007	1088	HAo.100	270	6.5	24.20	5.56	9.42	>20	114	40	15	17.57	15.00	72	6.44	52.60	0.02
Jan-03	4	HAo.100c	NA	NA	37.51	21.10	5.22	37.42	ND	ND	ND	1.02	ND	225	9.21	50.19	0.05
Jan-03	0	HAo.120	NA	NA	12.35	11.78	2.24	35.45	ND	ND	ND	1.26	ND	159	5.23	50.65	0.05
Jan-03	5	HAo.120	NA	NA	10.97	11.65	1.84	34.37	ND	ND	ND	2.24	ND	153	50.89	102.75	0.05
SPRING 03	46	HAo.120	NA	NA	4.76	10.42	2.17	32.14	ND	ND	ND	1.91	ND	98	7.58	35.06	0.05
SUMMER 03	118	HAo.120	NA	NA	3.24	21.47	4.49	49.72	ND	ND	ND	2.30	ND	232	1.45	103.16	0.05
FALL 03	215	HAo.120	NA	NA	4.86	31.66	5.92	59.40	ND	ND	ND	6.68	ND	265	5.59	96.53	0.05
FALL 03	237	HAo.120	NA	NA	5.01	32.26	6.19	61.18	ND	ND	ND	6.40	ND	274	5.43	95.55	0.05
12/2/2004	491	HAo.120	300	\	4.00	>20	5.77	>20	105	22	8	4.11	ND	79	7.10	20.15	ND
1/7/2005	513	HAo.120	320	6.5	3.85	14.10	4.60	>20	57	17	5	1.86	ND	52	7.57	24.44	ND
2/3/2005	535	HAo.120	300	\	3.57	8.48	3.64	16.80	39	14	< 1	0.35	ND	ND	4.86	17.23	ND

Date	Lab	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
3/4/2005	549	HAo.120	300		11.70	4.54	4.50	17.40	41	13	< 1	1.22	ND	ND	13.12	9.08	ND
4/1/2005	568	HAo.120	250	6.5	2.69	6.32	3.25	>20	61	10	< 1	0.91	ND	ND	5.10	17.04	ND
11/4/2005	747	HAo.120	200	6.5	11.10	15.90	>20	>20	164	35	14	17.50	12.80	ND	15.50	22.20	10.70
6/1/2006	906	HAo.120	250	7.0	4.60	8.50	6.87	28.49	77	16	8	2.72	25.93	59	1.52	13.70	0.06
7/6/2006	932	HAo.120	250	7.0	5.81	16.60	10.50	>20	114	19	7	7.08	34.58	102	4.61	16.50	0.13
8/2/2006	961	HAo.120	250	6.5	6.14	17.50	11.30	>20	97	25	13	5.78	33.60	124	5.60	18.40	0.11
9/7/2006	988	HAo.120	240	6.1	4.66	18.00	19.00	>20	92	32	7	11.80	38.85	111	12.00	15.00	0.13
11/2/2006	1046	HAo.120	230	6.5	29.80	15.50	15.00	>20	> 200	131	12	nd	79.50	79	24.20	93.00	0.02
Jan-03	1	HAo.60	NA	NA	10.92	7.75	1.36	43.57	ND	ND	ND	0.90	ND	65	9.69	159.92	0.05
Feb-03	30	HAo.60	NA	NA	9.32	9.26	0.68	47.56	ND	ND	ND	0.81	ND	58	10.97	38.91	0.05
SPRING 03	47	HAo.60	NA	NA	6.80	10.64	1.42	49.51	ND	ND	ND	1.57	ND	102	12.01	100.11	0.05
SUMMER 03	116	HAo.60	NA	NA	7.91	28.46	2.41	61.49	ND	ND	ND	0.05	ND	261	6.26	106.53	0.05
FALL 03	217	HAo.60	NA	NA	11.88	41.08	2.40	51.09	ND	ND	ND	7.56	ND	272	8.51	105.52	0.05
12/2/2004	489	HAo.60	300	\	7.79	12.90	1.37	>20	83	83	< 1	2.18	ND	66	2.53	29.57	ND
1/7/2005	511	HAo.60	325	6.0	6.59	10.30	1.45	>20	85	73	7	0.64	ND	46	3.73	33.90	ND
2/3/2005	534	HAo.60	325	6.0	5.14	6.72	1.34	13.00	45	60	8	0.24	ND	ND	5.19	29.68	ND
3/4/2005	546	HAo.60	350	6.0	5.35	6.30	1.37	>20	75	67	21	0.57	ND	ND	4.54	20.54	ND
4/1/2005	570	HAo.60	350	3.0	4.98	5.26	1.38	>20	77	54	< 1	0.69	ND	ND	6.31	17.59	ND
5/6/2005	590	HAo.60	250	6.0	4.43	8.05	1.43	>20	88	33	< 1	0.34	ND	ND	1.64	11.09	ND
12/6/2006	1057	HAo.60	300	8.3	26.80	10.00	10.70	>20	> 200	113	11	37.40	38.05	68	16.80	105.00	0.02
1/5/2007	1087	HAo.60	200	6.5	21.90	7.30	7.89	>20	181	100	10	15.81	17.75	49	10.40	93.90	0.02
Jan-03	2	HAo.80	NA	NA	41.96	13.33	2.48	85.33	ND	ND	ND	3.05	ND	87	12.82	57.94	0.05
SPRING 03	48	HAo.80	NA	NA	41.43	11.78	1.31	72.30	ND	ND	ND	0.71	ND	80	6.88	24.05	0.05
SUMMER 03	115	HAo.80	NA	NA	41.24	28.68	1.45	83.67	ND	ND	ND	0.11	ND	248	4.46	132.38	0.05
FALL 03	216	HAo.80	NA	NA	42.31	36.28	1.84	73.55	ND	ND	ND	1.08	ND	232	4.34	110.79	0.05
SPRING 03	43	HUo.100	NA	NA	9.97	13.86	1.64	42.23	ND	ND	ND	4.35	ND	107	7.31	31.17	0.05
SUMMER 03	113	HUo.100	NA	NA	23.56	29.36	3.29	76.25	ND	ND	ND	15.25	ND	261	7.59	263.33	0.05
FALL 03	205	HUo.100	NA	NA	17.90	32.63	2.40	67.60	ND	ND	ND	9.98	ND	297	1.84	179.84	0.05
FALL 03	214	HUo.100	NA	NA	26.30	34.86	3.48	66.30	ND	ND	ND	10.42	ND	295	2.10	172.25	0.05
7/6/2006	936	HUo.100	250	6.5	>35	14.60	2.23	>20	137	43	5	5.98	68.50	82	3.48	24.90	0.01
9/7/2006	991	HUo.100	300	7.0	>35	11.80	2.94	>20	114	75	8	7.69	254.50	70	11.10	22.70	0.02
Jan-03	7	OAo.100	NA	NA	5.24	26.31	1.28	48.31	ND	ND	ND	2.98	ND	456	22.85	38.05	0.05
Jan-03	8	OAo.100c	NA	NA	12.81	40.43	4.33	37.03	ND	ND	ND	0.69	ND	781	16.62	20.78	0.05

Date	Lab	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
Feb-03	22	OAo.100	NA	NA	8.97	27.80	1.30	80.94	ND	ND	ND	3.55	ND	250	8.31	406.66	0.05
SPRING 03	42	OAo.100	NA	NA	36.81	19.37	1.21	69.87	ND	ND	ND	7.90	ND	132	11.50	40.45	0.05
SUMMER 03	109	OAo.100	NA	NA	24.57	36.10	1.17	57.41	ND	ND	ND	1.27	ND	417	3.53	88.36	0.05
FALL 03	207	OAo.100	NA	NA	29.06	55.11	1.84	85.73	ND	ND	ND	0.02	ND	603	0.62	84.46	0.05
12/2/2004	486	OAo.100	350	\	>35	>20	0.71	>20	> 200	130	49	6.43	ND	133	3.98	9.26	ND
1/7/2005	503	OAo.100	325	7.5	>35	>20	0.62	>20	> 200	103	41	8.24	ND	95	11.98	9.69	ND
3/4/2005	550	OAo.100	250	7.0	34.60	>20	0.61	>20	103	82	28	6.99	ND	ND	8.66	7.72	ND
4/1/2005	577	OAo.100	150	7.0	>35	>20	0.56	>20	> 200	65	5	5.01	ND	ND	9.05	8.41	ND
11/4/2005	760	OAo.100	300	7.0	24.40	15.70	0.60	49.98	175	118	37	0.00	<0.1	84	9.88	5.86	0.17
4/6/2006	868	OAo.100	300	6.5	15.40	9.31	0.38	40.85	152	34	19	0.25	ND	28	21.01	3.00	0.07
6/1/2006	919	OAo.100	300	7.0	17.30	11.70	0.56	56.81	> 200	38	12	0.03	0.77	43	14.67	3.03	<0.01
7/6/2006	941	OAo.100	300	6.5	17.70	13.20	0.64	>20	> 200	50	13	0.02	13.48	72	10.90	5.15	0.01
8/2/2006	972	OAo.100	100	7.0	20.80	17.30	0.74	>20	> 200	90	22	0.03	151.75	ND	8.64	3.61	0.02
9/7/2006	997	OAo.100	300	7.0	18.40	14.20	0.60	>20	> 200	118	25	0.00	109.75	142	10.10	4.26	0.02
9/7/2006	997	OAo.100	300	7.0	18.30	13.40	0.59	>20	> 200	119	23	0.02	157.25	ND	10.00	4.38	0.02
10/4/2006	1017	OAo.100	300	6.8	17.70	12.50	0.54	>20	> 200	109	26	0.06	53.00	84	12.50	5.59	0.02
12/6/2006	1073	OAo.100	300	6.5	18.60	14.00	0.48	>20	> 200	83	16	0.58	6.85	59	3.88	8.78	0.04
1/5/2007	1100	OAo.100	300	6.7	16.80	12.20	0.43	>20	> 200	85	14	7.52	16.00	41	16.60	8.66	0.02
Jan-03	9	OAo.120	NA	NA	11.20	6.19	2.12	16.42	ND	ND	ND	1.45	ND	258	9.63	42.48	0.05
Feb-03	25	OAo.120	NA	NA	9.38	2.85	1.10	10.53	ND	ND	ND	4.59	ND	106	9.78	17.31	0.05
SPRING 03	39	OAo.120	NA	NA	33.55	5.15	2.23	13.98	ND	ND	ND	2.37	ND	156	24.42	262.90	0.05
SUMMER 03	112	OAo.120	NA	NA	17.69	4.22	1.67	13.30	ND	ND	ND	0.05	ND	225	10.82	74.27	0.05
FALL 03	208	OAo.120	NA	NA	6.00	12.74	1.70	12.94	ND	ND	ND	0.98	ND	353	7.90	75.01	0.05
12/2/2004	488	OAo.120	300	\	8.38	>20	1.85	16.40	> 200	16	3	1.95	ND	108	4.43	3.11	ND
1/7/2005	504	OAo.120	330	8.0	17.30	10.90	1.59	12.40	143	17	< 1	0.75	ND	67	32.85	3.67	ND
3/4/2005	552	OAo.120	250	7.0	>35	8.61	1.68	11.70	120	14	< 1	0.71	ND	ND	56.85	3.54	ND
4/1/2005	580	OAo.120	180	7.0	>35	10.10	2.40	16.80	185	51	< 1	0.83	ND	ND	200.40	6.13	ND
11/4/2005	761	OAo.120	200	8.0	12.90	21.74	1.22	13.74	169	22	9	0.92	<0.1	ND	4.59	2.87	0.08
6/1/2006	920	OAo.120	280	8.0	44.78	4.47	1.60	7.00	81	13	4	0.43	1.33	66	16.13	2.54	<0.01
SPRING 03	41	OAo.60	NA	NA	52.42	27.94	1.98	80.82	ND	ND	ND	2.36	ND	211	7.92	136.90	0.05
SUMMER 03	149	OAo.60	NA	NA	111.10	29.06	2.89	64.84	ND	ND	ND	0.05	ND	381	0.10	135.72	0.05
FALL 03	206	OAo.60	NA	NA	97.38	36.27	2.74	88.71	ND	ND	ND	0.94	ND	396	0.75	97.15	0.05
1/7/2005	501	OAo.60	300	7.0	>35	>20	0.89	>20	> 200	83	< 1	18.46	ND	95	9.53	16.68	ND

Date	Lab	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
8/2/2006	970	OAo.60	100	7.0	>35	>20	0.84	>20	> 200	110	10	0.00	187.50	ND	2.11	56.50	0.02
11/2/2006	1041	OAo.60	280	6.8	>35	>20	0.45	>20	> 200	121	9	2.88	20.50	90	5.13	29.80	0.02
12/6/2006	1070	OAo.60	300	6.8	>35	>20	0.42	>20	> 200	85	5	34.90	30.75	72	23.00	59.30	0.02
Jan-03	6	OAo.80	NA	NA	11.88	34.29	1.22	24.35	ND	ND	ND	2.99	ND	340	9.33	51.60	0.05
SPRING 03	40	OAo.80	NA	NA	54.58	33.12	2.23	61.69	ND	ND	ND	0.39	ND	232	1.63	17.78	0.05
SUMMER 03	110	OAo.80	NA	NA	65.83	25.72	1.45	37.73	ND	ND	ND	0.05	ND	261	5.22	199.70	0.05
FALL 03	204	OAo.80	NA	NA	48.56	29.40	0.97	44.12	ND	ND	ND	1.62	ND	192	6.90	88.25	0.05
12/2/2004	485	OAo.80	400	7.0	>35	>20	1.37	<700	> 200	91	20	6.80	ND	100	3.93	9.14	ND
1/7/2005	502	OAo.80	350	7.5	>35	>20	1.09	>20	184	68	4	5.59	ND	65	4.23	10.84	ND
3/4/2005	551	OAo.80	250	7.0	>35	>20	0.92	>20	161	47	< 1	2.26	ND	ND	8.37	6.75	ND
4/1/2005	578	OAo.80	240	7.5	>35	16.00	0.83	>20	169	46	20	1.96	ND	ND	17.24	5.03	ND
5/6/2005	598	OAo.80	300	7.0	>35	>20	0.99	>20	> 200	38	15	1.56	ND	ND	19.36	4.76	ND
11/4/2005	759	OAo.80	300	7.5	34.20	35.31	0.75	46.22	189	181	28	0.07	11.40	111	6.69	3.39	0.12
4/6/2006	869	OAo.80	275	7.0	19.70	18.40	0.43	>20	153	33	8	0.21	ND	41	10.27	2.43	0.05
6/1/2006	918	OAo.80	300	7.5	16.40	23.13	0.55	52.41	> 200	38	5	0.91	67.50	76	6.25	2.90	<0.01
7/6/2006	940	OAo.80	300	7.6	18.30	>20	0.67	>20	> 200	69	5	4.99	610.00	98	13.60	19.40	0.02
8/2/2006	971	OAo.80	250	7.0	30.30	>20	0.90	>20	> 200	89	9	0.10	212.75	124	7.86	24.90	0.02
9/7/2006	998	OAo.80	290	7.0	27.90	>20	0.73	>20	> 200	140	15	0.00	81.50	108	7.12	20.30	0.02
10/4/2006	1018	OAo.80	300	7.7	28.90	>20	0.77	>20	> 200	100	14	0.00	34.70	ND	7.12	13.40	0.02
10/4/2006	1018	OAo.80	300	7.7	29.10	>20	0.76	>20	> 200	98	14	0.03	36.65	ND	6.86	13.80	0.02
11/2/2006	1042	OAo.80	250	6.8	33.20	>20	0.85	>20	> 200	81	9	0.31	11.15	80	6.17	11.10	0.02
12/6/2006	1071	OAo.80	300	7.4	>35	>20	0.93	>20	> 200	77	7	23.00	23.05	69	19.80	36.70	0.02
1/5/2007	1099	OAo.80	280	7.1	>35	>20	0.93	>20	> 200	84	6	39.10	34.30	52	29.60	157.00	0.02
11/4/2005	757	OAo2.100	300	7.0	29.50	36.77	3.31	55.67	> 200	38	25	24.36	5.20	143	6.64	47.00	0.08
4/6/2006	866	OAo2.100	320	7.0	29.30	>20	1.71	>20	125	23	31	5.56	ND	85	3.79	64.30	0.37
6/1/2006	914	OAo2.100	300	7.5	25.50	25.15	1.82	38.50	155	27	21	1.29	46.38	ND	1.21	53.80	0.03
6/1/2006	914	OAo2.100	300	7.5	22.80	>20	1.59	>20	142	24	18	3.36	45.98	128	1.25	56.20	0.03
7/6/2006	947	OAo2.100	300	7.0	>35	>20	1.56	>20	166	45	26	10.10	625.00	155	8.36	10.18	0.24
8/2/2006	968	OAo2.100	200	7.0	33.60	>20	0.97	>20	161	40	34	0.66	222.00	225	5.65	61.70	0.02
9/7/2006	995	OAo2.100	280	7.0	30.20	>20	0.91	>20	135	64	40	2.20	103.75	185	6.50	56.00	0.02
10/4/2006	1011	OAo2.100	230	6.8	26.40	>20	0.80	>20	124	51	33	0.81	52.50	139	9.62	49.70	0.02
11/2/2006	1040	OAo2.100	300	6.5	31.10	>20	1.37	>20	134	45	27	0.74	27.30	97	15.80	45.80	0.02
12/6/2006	1067	OAo2.100	300	6.5	>35	>20	4.28	>20	191	57	21	38.30	57.00	78	42.10	69.10	0.02

Date	Lab	Sampler	Vol. Collected	pH	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
12/6/2006	1068	OAo2.100	300	6.5	>35	>20	4.09	>20	187	55	21	43.90	55.50	25	42.00	67.30	0.02
1/5/2007	1097	OAo2.100	250	6.5	>35	>20	4.27	>20	155	53	26	12.20	29.75	64	24.00	121.00	0.02

Ion concentrations of road runoff

Date	**Sampler**	**Lab**	**Vol.**	**pH**	Na	Mg	K	Ca	Sr	Br	I	N-NO$_3$	ClO$_4$	B	Cl	SO$_4$	PO$_4$
Collected		**#**	mL		mg/L	mg/L	mg/L	mg/L	ug/L	ug/L	ug/L	mg/L	ug/L	ug/L	mg/L	mg/L	mg/L
4/2/2006	Route 112-1	R1	1000	6.1	278.30	5.05	17.90	53.37	> 200	175	32	6.23	6.60	372	486.34	167.00	0.01
4/4/2006	Route 112-1	R4	1000	6.1	>35	0.56	1.39	6.40	79.2	21	9	0.99	0.60	61	87.14	16.40	<
4/6/2006	Route 112-1	R11	1000	6.1	67.69	0.78	1.43	8.10	78.3	20	6	1.36	0.51	38	58.82	14.80	<
4/9/2006	Route 112-1	R18	1000	6.0	>35	2.14	>20	>20	> 200	56	16	2.06	3.51	96	192.54	47.10	<
4/15/2006	Route 112-1	R42	1000	6.0	142.82	3.28	7.96	50.65	> 200	80	16	4.67	12.80	1280	155.33	118.00	<
4/4/2006	Route 112-2	R5	400	6.1	42.52	0.49	1.13	6.20	24.4	24	7	1.11	0.28	53	34.38	24.90	<
4/15/2006	Route 112-2	R43	200	6.0	27.80	0.96	2.30	17.30	97.9	25	6	1.53	0.93	42	27.70	22.00	<
4/4/2006	Route 112-3	R6	100	5.8	160.02	2.30	15.80	13.10	60.9	55	13	nd	1.07	nd	236.98	52.30	1.64
4/6/2006	Route 112-3	R12	300	5.3	70.10	0.71	3.19	5.30	25.2	21	4	1.78	0.18	69	78.08	11.50	<
4/9/2006	Route 112-3	R19	900	5.3	33.90	0.36	1.55	3.50	15.7	11	3	0.39	0.22	31	40.09	7.98	<
4/15/2006	Route 112-3	R44	400	6.0	>35	0.82	2.25	10.60	47.4	30	7	nd	nd	657	nd	nd	nd
4/2/2006	Route 112-4	R3	400	6.1	>35	2.83	4.28	>20	161	96	24	2.84	2.66	195	439.57	78.70	<
4/6/2006	Route 112-4	R13	150	5.3	83.76	0.93	1.41	10.30	50.7	31	6	nd	0.55	49	85.38	21.30	<
4/9/2006	Route 112-4	R20	250	6.0	104.14	1.24	2.23	13.40	59.8	37	10	1.61	1.74	54	100.95	25.90	0.12
4/4/2006	Route 25-1	R7	1000	5.8	17.70	0.20	0.50	3.00	14.5	5	2	0.34	0.27	34	17.00	4.13	<
4/6/2006	Route 25-1	R14	580	5.3	15.70	0.32	0.61	4.70	20	10	3	0.32	0.12	50	14.48	4.41	<
4/9/2006	Route 25-1	R23	800	5.3	6.04	0.19	0.45	2.70	12.2	4	2	0.35	0.03	24	4.26	2.35	<
4/9/2006	Route 25-10	R30	600	5.5	54.58	0.34	1.00	2.80	26	11	4	0.48	0.40	44	47.64	7.67	<
4/15/2006	Route 25-10	R41	125	6.0	97.76	0.56	1.60	6.00	43.4	31	17	2.00	1.67	< 300	71.34	24.30	<
4/4/2006	Route 25-2	R8	1000	5.3	65.72	1.54	3.99	22.25	> 200	359	10	1.49	1.57	87	108.44	23.30	<
4/6/2006	Route 25-2	R15	1000	5.3	>35	1.64	2.51	>20	> 200	220	7	1.21	0.93	60	131.67	15.00	<
4/9/2006	Route 25-2	R24	1000	5.3	51.57	0.80	1.78	11.80	93.2	89	7	1.72	0.63	54	56.40	13.60	<
4/15/2006	Route 25-2	R35	1000	5.0	134.28	7.00	5.86	56.64	> 200	287	17	0.05	0.53	178	181.55	90.20	<

Date	**Sampler**	**Lab**	**Vol.**	**pH**	Na	Mg	K	Ca	Sr	Br	I	N-NO_3	ClO_4	B	Cl	SO_4	PO_4
4/9/2006	Route 25-3	R25	1000	6.0	>35	4.21	4.59	>20	> 200	95	22	2.76	2.50	179	384.70	69.40	<
4/15/2006	Route 25-3	R36	1000	5.5	282.15	11.40	8.40	150.43	> 200	155	24	0.07	1.75	186	620.23	126.00	0.01
4/9/2006	Route 25-4	R26	1000	5.3	54.23	0.53	1.11	4.40	37.6	19	7	1.30	0.97	39	48.66	13.30	<
4/15/2006	Route 25-4	R37	1000	5.5	188.84	3.35	5.13	28.71	> 200	81	16	0.05	0.28	174	247.47	51.40	<
4/9/2006	Route 25-6	R27	1000	6.0	>35	4.44	4.79	>20	> 200	99	21	2.89	18.50	134	353.68	81.20	<
4/15/2006	Route 25-6	R38	1000	5.5	227.77	5.51	5.29	61.99	> 200	110	20	0.08	0.11	185	326.85	93.40	<
4/9/2006	Route 25-7	R28	1000	5.3	128.88	1.27	3.14	9.30	120	51	13	2.86	3.15	137	132.47	32.30	<
4/15/2006	Route 25-7	R40	900	5.5	55.87	2.13	2.22	15.60	129	39	7	1.86	1.82	34	53.50	nd	<
4/9/2006	Route 25-8	R29	1000	5.3	120.62	1.17	2.33	8.20	57.3	38	10	2.74	1.39	58	121.55	27.70	<
4/15/2006	Route 25-8	R39	1000	5.5	107.43	1.73	2.54	13.10	107	38	9	0.03	0.55	102	108.44	29.90	<
4/4/2006	Route 25-A	R10	NA	6.1	185.00	1.55	1.41	9.40	118	46	6	0.34	7.20	40	415.57	7.54	<
4/6/2006	Route 25-A	R17	NA	5.8	272.78	1.96	1.44	11.70	128	55	5	0.09	8.72	58	505.40	6.33	<
4/9/2006	Route 25-A	R22	NA	6.0	152.57	0.89	1.00	6.00	87.9	22	4	0.32	2.01	< 30	193.56	4.65	<
4/14/2006	Route 25-A	R32	NA	7.6	228.30	1.40	1.52	8.50	102	34	5	0.15	2.61	53	383.19	18.30	<
4/15/2006	Route 25-A	R33	NA	7.6	221.69	1.41	1.29	8.50	109	35	4	0.26	1.94	94	353.68	5.89	<
4/4/2006	Route 25-C	R9	NA	6.1	208.53	1.38	1.34	9.20	92.7	52	5	0.45	3.10	46	321.35	9.64	<
4/6/2006	Route 25-C	R16	NA	5.8	179.39	1.57	1.38	11.20	101	52	5	0.43	1.94	43	352.24	9.29	<
4/9/2006	Route 25-C	R21	NA	5.5	100.41	0.68	0.84	5.30	42.4	18	4	0.37	0.83	53	107.05	5.29	<
4/14/2006	Route 25-C	R31	NA	7.1	159.16	1.33	1.93	8.20	66.4	31	4	0.21	0.62	< 30	218.99	7.26	<
4/15/2006	Route 25-C	R34	NA	7.7	160.69	1.31	1.25	7.90	66.6	30	4	0.29	0.82	43	213.54	7.61	<
12/13/2006	Route 25-C	R50	NA	5.5	2.59	0.78	0.90	3.70	43.9	9	1	0.00	0.125	nd	3.90	4.79	0.01
12/13/2006	SB basin #1	R51	NA	5.5	14.60	0.98	1.12	5.10	22.2	106	1	0.05	<0.1	nd	21.60	7.02	0.01
12/15/2006	SB basin #2	R52	NA	ND	9.51	2.30	0.90	7.90	36.6	79	2	0.84	0.344	nd	20.00	7.31	0.01