NITRATE LOADING IN THE SENECA LAKE WATERSHED:

Is Hog Farming Having An Effect?

Thesis submitted in partial fulfillment of the requirements
for Honors in Geoscience

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Acknowledgements

- First and most important, thank you John Halfman, for your help, time, and the answers to my constant questions.
- Mellon and the Tripp Foundation for their help with funding my summer stay and this project.
- Sandy Baldwin, Laura Calabrese, and Emily LaDuca for help with sample collection and lab workups.
- The National Science Foundation for the grants to make stream sampling and data collection possible (NSF EMD 99-50544 and NSF MRI 01-16078).
- My friends and family for all their love and support.
- Mr. Steinschnieder for funding to present this work at the Northeast Regional conference of the Geological Society of America.
- Julie for being great to share a lab with and a great friend.

Abstract

The Seneca Lake watershed provides an ideal natural hydrogeochemical laboratory to study the source and impact of non-point source pollutants. The 29 subwatersheds and drainages (adjacent first order streams) drain a variety of surface areas (from a few km^2 to over 100 km^2), land use areas (agricultural, forested and lesser amounts of urban land), bedrock types (Paleozoic carbonates, shales and coarser silicate-rich clastic rocks), soil types and other features. This project investigated the source of nitrates in the watershed.

Weekly water samples were collected from May through August of 2001 and analyzed for nitrate (ppm, N) and other common water quality parameters (pH, phosphate, alkalinity, hardness, conductivity, chloride, dissolved oxygen, temperature) from the terminus of seven subwatersheds that represent the array of available surface areas, land use areas and bedrock types in the basin. Samples were also collected at discrete sites along two streams, Kashong Creek and Big Stream, to locate point sources in these subwatersheds. This information was supplemented by the hydrogeochemical database from the watershed over the past 5 years.

The results indicate that streams that drain agricultural land have the largest nitrate concentrations (a few ppm up to 5 ppm), and a wastewater treatment facility provides a point source of nitrates to Big Stream. Hog farms at their present number are not the source of nitrates as feared by the local communities, however this study does not predict the long term effect of the farms nor the impact of additional farms in the future. Nitrates are removed by biological uptake both in the stream and in the lake (lake concentrations typically range from 0.1 to 0.5 ppm).

Introduction

Since the 1960's, when environmentalism became a popular cause, there has been interest in the concept of pollution. There are myriad questions on this subject that can be asked. First, what counts as pollution? Some substances, like heavy metals, are harmful in even the smallest amounts, where some substances are like medicines. In small doses they are useful, but in larger doses they can pollute the water, soil and air. "Pollution" is the introduction of foreign matter to the point where it becomes hazardous to the stability of the ecosystem humans depend on to survive (Barnhart, 1986).

Multiple sources of pollution to the water, soil, and air exist. The most obvious are point source pollutants. Point source pollutants have a single and definite source. They include drainpipes, chemical dumpsites, and sewage treatment facilities (ESA, 1998). However, since they are so easy to identify, they were the first pollutant sources that were identified by the EPA and are now either "cleaned up", in the case of dumpsites, or outflow is regulated, in the case of sewage and industrial drainage.

Non-point sources of pollution are more common now that most point sources have been dealt with, and much more insidious because they are more difficult to see and clean up. Pollutants from these sources are released to the environment over a large area and can change over both time and distance in their nature and intensity. This makes them both more difficult to monitor and more difficult to regulate (ESA, 1998). In the United States, agriculture is the most common non-point pollution (ESA, 1998). Others include atmospheric pollutants released from smokestacks and automobiles, and large scale pesticide applications.

Around the world, humans practice many different kinds of agriculture. In this country, there is mainly crop agriculture and animal husbandry. In upstate New York where this study was conducted, corn, wheat, wine grapes, and dairy products are the primary agricultural activities. However, in recent years there has been an increase in the amount of hog farming, a relatively new industry in the area.

Agricultural Concerns

A common pollutant from agriculture is fertilizer runoff to nearby watersheds. Fertilizers are the nutrients that plants need to grow and thrive. In nature, nutrients cycle between plants, animals, the soil and the water. Once plants assimilate nutrients from the soil and water, nutrients move through the food chain, moving from the plants to animals, then to bacteria. When the plants and animals die, bacteria decompose the organic matter and release the nutrients back into soil and water, at which point the cycle starts all over again (Figures 1,2). Nitrogen and phosphorus are the two primary nutrients of concern because both are critical to biological processes that require amino acids, proteins, and enzymes, and both are scarce. Phosphorus is scarce because the ultimate source is weathering of phosphorus-rich bedrock, which is very rare. Nitrogen ultimately comes from atmospheric N_2, but this source is difficult to tap because the breaking the triple bond in the N_2 molecule is an energy intensive process. Only a few species of blue-green algae and bacteria are able to fix atmospheric nitrogen into useful organic molecules.

Thus, organisms are constantly struggling to survive in a nutrient scarce world. Farmers combat this scarcity by applying fertilizers directly to the fields and by

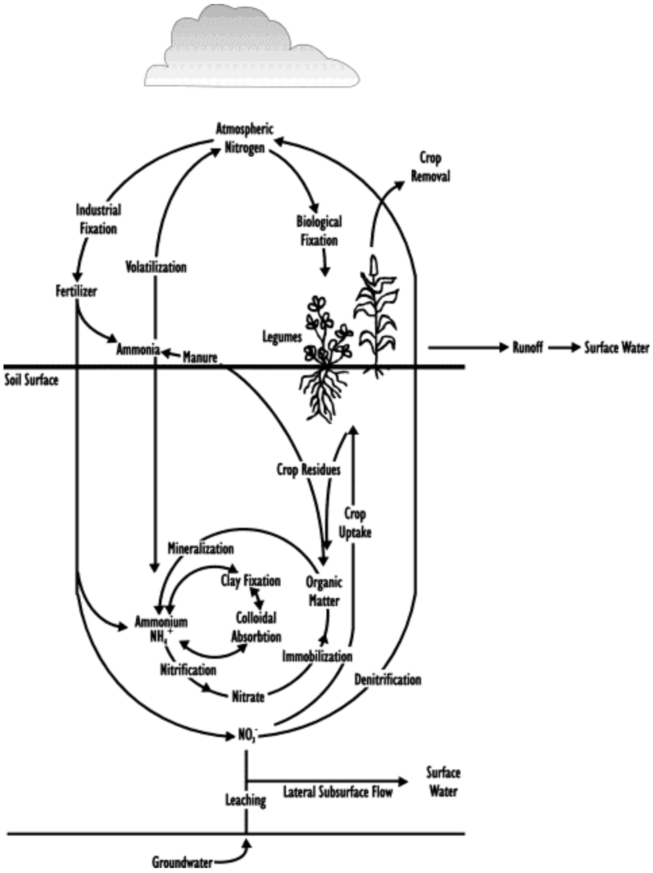


Figure 1- The Nitrogen Cycle (Cooke, 1999)

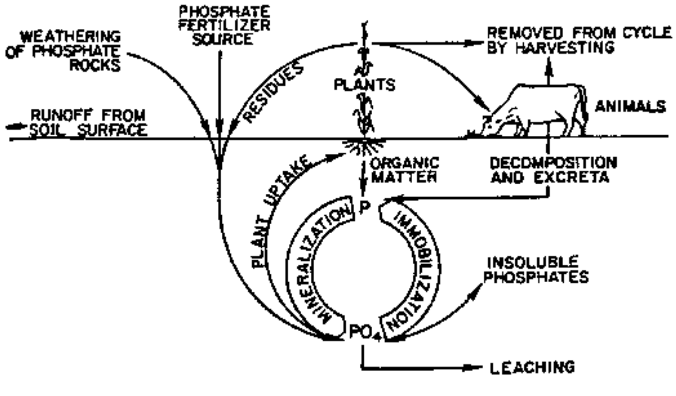


Figure 2- The Phosphate Cycle (Cooke, 1999)

alternating crops, as some crops, like peas, soybeans, and alfalfa, have symbiotic nitrogen fixing organisms. Maintaining an adequate supply of nitrogen (as useable nitrates, nitrites, and ammonium) is made more difficult for the farmer because these compounds are water soluble and easily runoff farm fields after a heavy rain. In contrast, phosphates are less likely to wash off because they bind to the surface of clay sized soil particles.

If too many nutrients find their way into a nutrient limited body of water, it can lead to a process called eutrophication. This is a process where the excess nutrients cause an algal bloom. Algal growth is limited by the availability of nutrients, and any extra nutrients entering a body of water will induce additional growth. Decomposition of the extra algae removes the oxygen from the lake. Decomposition of enough algae leads to a deoxygenated lake where nothing can live except a few bacteria, and provides undrinkable water (ESA 1998). Since nitrate levels are a good indicator of both agricultural impact and watershed health, this study focused on the sources of nitrogen to Seneca Lake.

Manmade Sources of Nitrogen

The manmade sources of nitrogen are numerous, but fertilizer runoff, animal husbandry, and sewer wastewater treatment are leading sources. Fertilizer use of nitrogen has increased 900% in the last 40 years in the US (Parkinson, 1993). Fertilizers are usually applied as ammonium (NH_4^+) salts. As of 1998, 80 million metric tons were produced worldwide per year (ESA 1998). This is of special concern because, on average, only 18% of nitrogen applied as fertilizer is incorporated into the crops in the US and Europe. The other 82% is surplus, about 174 kg per hectare, and is quickly converted to the more soluble nitrate form by bacteria in oxic environments (Heathwaite, 1993). These nitrates typically enter the aquatic system either by direct runoff or groundwater transport (ESA, 1998).

Animal husbandry, mostly pigs and cows, is also a significant source of nitrate to the environment. Animal waste is rich in nitrogen, and bacteria action breaks the waste down into the soluble inorganic forms of nitrogen. Farmers use this manure as a cheap and available source of fertilizer. However, in order for the nitrogen application to be within crop needs, the manure must be spread over an area 1,000 times the area of the animal complex where it was produced (ESA 1998). Since most farmers who raise animals do not have this much land, they spread it over what land they do have and spread the excess on neighboring farms. Occasionally, the manure is spread too thick and causes a surplus of nutrients that can runoff into nearby waterways or be absorbed into groundwater. In the US, two trillion pounds of animal waste are produced annually (Floegel, 2000). Recently, the EPA has initiated regulations for Concentrated Animal Feeding Operations (CAFOs) in an attempt to mitigate this problem.

Hog Farming

As a special case of animal agriculture, hog farming is a notorious polluter. Traditionally an issue in Virginia and North Carolina, in recent years hog farms have started to show up in New York. Hog farming as a whole in the state of New York was down 40% between 1992 and 1998. In the same period, however, Seneca, Yates, and Cayuga counties, which are adjacent to Seneca Lake, have increased hog production by 70%. The region now produces one third of New York’s 60,000 hogs annually, at over two dozen farms (Chen, 2001). These farms, on average, have over 1,000 hogs. This places them below the 1000 animal unit limit for a CAFO, which is about 2,500 hogs, but is still concentrated enough to generate a significant amount of manure. Most of these farms are northeast of Seneca Lake, between Seneca and Cayuga Lakes (Spitzer, 1999). Local efforts to mitigate this potential hazard include efforts by several New York politicians to change the law so that farmers with more than 200 hogs will be required to obtain a pollution permit (Chen, 2001). Until this law passes, however, New York has fairly lenient regulations on hog farming, a fact that is attracting hog farmers to the area.

The increase in the scale of hog farming in the area is a concern because with the hogs come hog waste, which is blamed for not only nutrient pollution but obnoxious smells and antibiotic pollution. On a per diem basis, animal manure contains 12 times as much nitrogen as human sewage (Heathwaite, 1993). This is in part because the average hog produces from 2 to 5 times more waste than the average human (Feuerbach and Hadish, 1997). The rest of the difference can be attributed to differences in diet. Hog waste is generally stored in lagoons; the resulting slurry is spread or injected onto fields as fertilizer (Spitzer, 1999). If this is done poorly, either by application beyond the capacity of the land to absorb nitrogen or by application at the wrong time (for instance when the fields are frozen), the excess nitrogen pollutes nearby waterways.

An additional potential hazard is the copper supplements fed to hogs. Studies have shown that around 250 mg/L of copper helps hogs grow faster. However, copper concentrations above 500 mg/L are toxic (Borak, 2001). In spite of this, about 1800 mg/L of copper is added to pig food (Kaydee, 2002). This excess doesn’t harm the hogs because the copper is in the form of copper sulfate, which is difficult for them to digest and metabolize (Borak, 2001). Due to this excess, there are between 590 and 760 mg/L of copper in hog waste (BioCycle, 2000). All of this excess copper has led to a 10% copper buildup per year in the soil in places where hog manure is spread. If this continues, it will soon reach toxic levels for plants, and metals like copper are difficult to remove from the environment (Warrick and Stith, 1995).

Wastewater Treatment

The last major source of nutrients is effluent from wastewater treatment plants. In the treatment procedure, impurities are removed from sewage and from so-called “gray water”, which is wastewater from sinks, showers, and storm drains. First, large solids are removed from the wastewater by screens. Next, in the “primary treatment” phase, sand filters and settling chambers continue physical separation. These solids are usually disposed of in a landfill. The water then undergoes “secondary treatment”, which is biological in nature, using bacteria to respire the dissolved organic matter and some of the particulate matter. Other particles settle to the floor of the treatment pool, where the sludge is collected and typically trucked to a local landfill. Many plants then allow this treated water to empty into a nearby stream or lake, even thought it is rich in dissolved nitrogen and phosphate. Some newer treatment plants incorporate tertiary treatment facilities that use primarily chemical methods to decrease the nutrient load in the effluent (Running Water, 2002). Many local treatment plants are not new enough and lack the funds to incorporate a tertiary treatment phase.

Health Impact

Elevated levels of both copper and nitrate are associated with health problems. High copper levels can cause liver failure (EPA 2002), and even at relatively low concentrations copper has been connected with outbreaks of the dinoflagellum *Pfiesteria* *piscida*, which has been linked to fish kills in North Carolina, and to rashes, sores, and neurological symptoms in humans (Shoemaker, 1998). As a result, the EPA has set a national limit for copper in water of 1.3 mg/L (EPA, 2002).

High nitrate levels have been linked to both gastrointestinal problems including stomach cancer, and methaemoglobinaemia or “blue-baby syndrome”. Both illnesses are caused by the buildup of nitrosamines (nitrate rich compounds) in the gut (Heathwaite, Burt, and Trudgill, 1993). Both of these problems are more prevelant in infants, who have not yet developed the capacity to metabolize excess nitrates. Due to these health risks, the EPA has set a limit on nitrates in drinking water at 10 mg/L (Shankar et al., 2000).

The motivation for focusing on nitrates and copper is somewhat different. Copper can serve as an indicator of hog farms, since the only other sources of this metal are identifiable sources such as old dumps, landfills, mine tailings, and construction sites. Another potential source of copper is fungicides applied to the grapes in wineries that surround Seneca Lake. Nitrate, on the other hand, can come from fertilizer, hog and other animal manure, construction sites, precipitation in the form of rain and snow, and even dry deposition from the atmosphere. Analysis of nitrate concentration can still, however, provide a good picture of the sources of nitrate in this watershed. The nitrate loading to the lake provides critical data on the health of the lake ecosystem as a whole.

Surface Hydrology

A basic understanding of hydrology, the movement of water at or near the earth’s surface, is required to understand the movement of water soluble pollutants. Water enters a watershed by precipitation, usually in the form of rain or snow. The water then can either return back to the atmosphere by evapotranspiration, enter the groundwater system by infiltration, or runoff the land surface to nearby creeks, streams, and standing bodies of water.

Water flows under the influence of gravity, and flows downhill. Topographic highs define watershed boundaries. Rain that falls inside a watershed flows to the stream or lake at the lowest point of the watershed, rain that falls outside the watershed will not, and instead flows in the neighboring watershed. The lowest place in any given area will become a permanent or semi-permanent stream, river, or lake. Watersheds can be further divided into subwatersheds. For instance, each stream that flows into Seneca Lake has its own, smaller subwatershed within the Seneca Lake watershed.

The downhill flow of water is critical for the movement of pollutants. Surface water can only move downhill from the source. Thus, sources of contamination in the watershed can be pinpointed. If a pollutant is not detected at one site in the stream but is detected at a downstream site, then the pollutant source is somewhere between the two sample sites.

Objectives

This project investigated the effects of agricultural runoff on the Seneca Lake watershed, and in particular the effects of agriculture and hog farming on the sources of nitrate to the lake. This watershed as a whole is about 40% agricultural land and about 42% forested land, with the remainder divided between developed and idle land (Figure 3). Developed land is usually urban, although there is also a military base and old testing ground on the northeast side of the lake. Idle land is primarily wetlands or

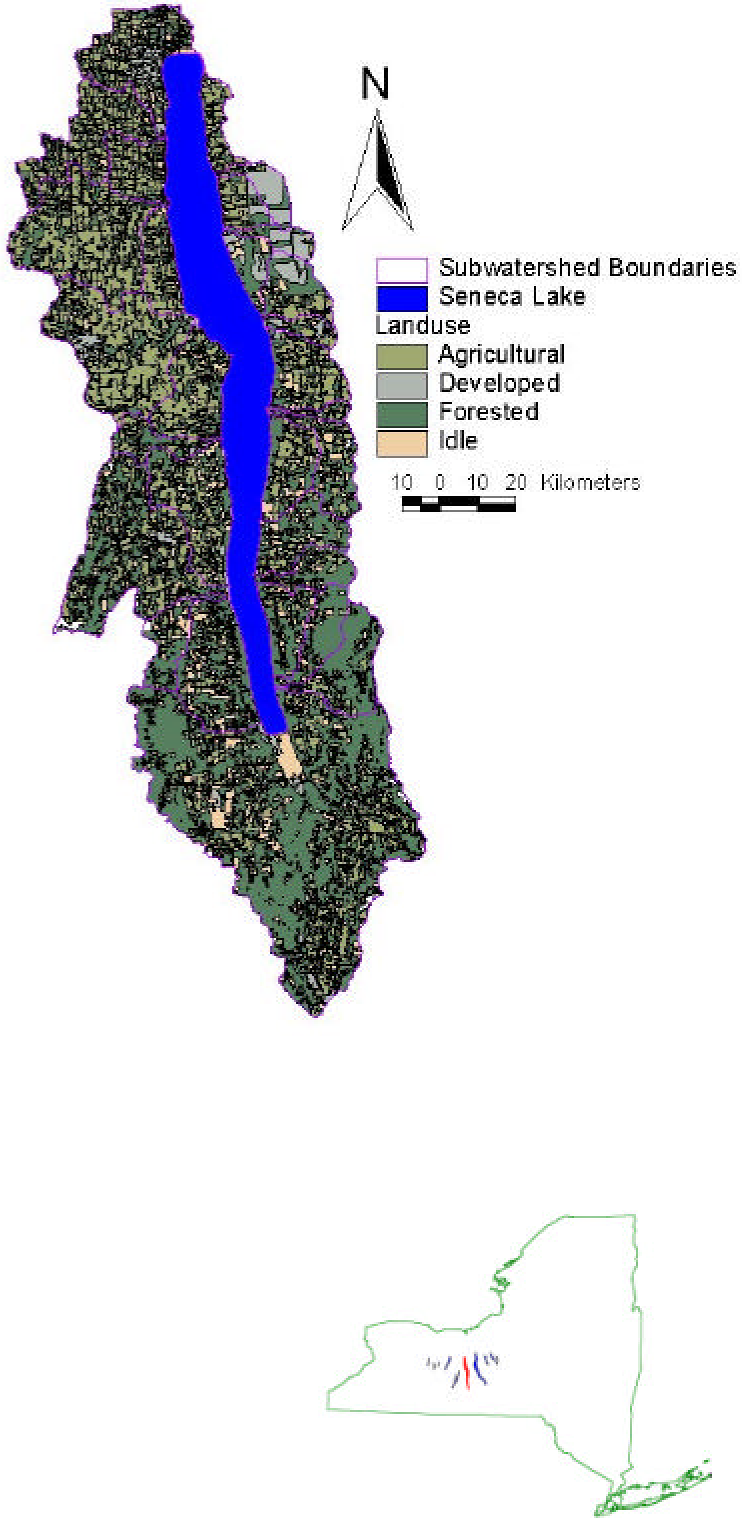


Figure 3- Land Use in the Seneca Lake Watershed
Insert shows the location of Seneca Lake in comparison to the other Finger Lakes in central New York

abandoned farmland. This study investigated seven watersheds of various land use areas Big Stream, Kashong Creek, Kendig Creek, Reeder Creek, Plum Point Creek, Wilson Creek, and Keuka Outlet to determine the impact on nitrate load to the lake. Particular attention was paid to Big Stream and Kashong Creek subwatersheds. Big Stream because a new hog farm started production approximately 6 months before the study began. Kashong Creek because it has more agricultural land than Big Stream, but without hog farms.

Methods

Seven streams in the Seneca Lake watershed were selected for sampling based on the representative array of agricultural land, placement in the watershed, underlying bedrock geology, and ease of sampling (Figure 4). The land use and surface areas for each of the subwatersheds and the lake's entire watershed are shown in Table One.

Table 1-Watershed Areas and Percent Land Use

Watershed	Area (km^2)	Agriculture (%)	Forested (%)	Developed (%)	Idle (%)
Seneca Lake	$1.29*10^6$	39 %	42 %	9 %	10 %
Big Stream	$9.43*10^4$	40 %	45 %	6 %	9 %
Kashong Creek	$8.63*10^4$	74 %	19 %	4 %	3 %
Reeder Creek	$2.74*10^4$	14 %	37 %	48 %	1 %
Kendig Creek	$5.04*10^4$	82 %	16 %	2 %	0 %
Keuka Outlet	$8.52*10^4$	66 %	18 %	10 %	6 %
Plum Point	$1.64*10^4$	45 %	42 %	9 %	4 %
Wilson Creek	$5.01*10^4$	71 %	19 %	5 %	5 %

Data: GIS (cugir.mannlib.cornell.edu)

Sites were selected near the terminus of each stream and sampled on a weekly basis from May to August of 2001. These samples should integrate the impact of the entire subwatershed.

Additional sites were selected along Big Stream and Kashong Creek. These sites were selected to bracket areas with potential nitrate sources like hog farms, towns, agricultural fields, and sewage treatment plants, as well as to provide a profile of these two streams from their headwaters to their mouth (Figures 5,6).

Temperature and conductivity were measured using an Oakton WD-35607-10 Conductivity meter, and pH measurements were taken with an Oakton pH2 meter. Stream discharge (the flow of water measured as volume/time) was measured using the ping pong ball method. Chloride (4503-DR), hardness (4824-DR-LT), dissolved oxygen (HI-9142), and alkalinity (4533-DR) were analyzed in the field using LaMotte titration test kits. Water samples were taken back to the lab and filtered to measure nitrates, phosphates, silica, total suspended sediment, and copper. The procedures were adapted from standard limnological procedures (Wetzel and Likens, 1991).

The data for nitrates and copper can be found in Appendices C, D, E, and F to this paper. The remaining data is not reported here, but is available from Hobart and William Smith Colleges.

The nitrate data was analyzed by a Hach low-level nitrate kit (24608-00), using a method based on a cadmium reduction. The nitrate was reduced to nitrite by shaking with particles of chromium metal, then decanted and reacted with a colored compound to form a shade of pink. The intensity is directly proportional to the nitrate concentration.

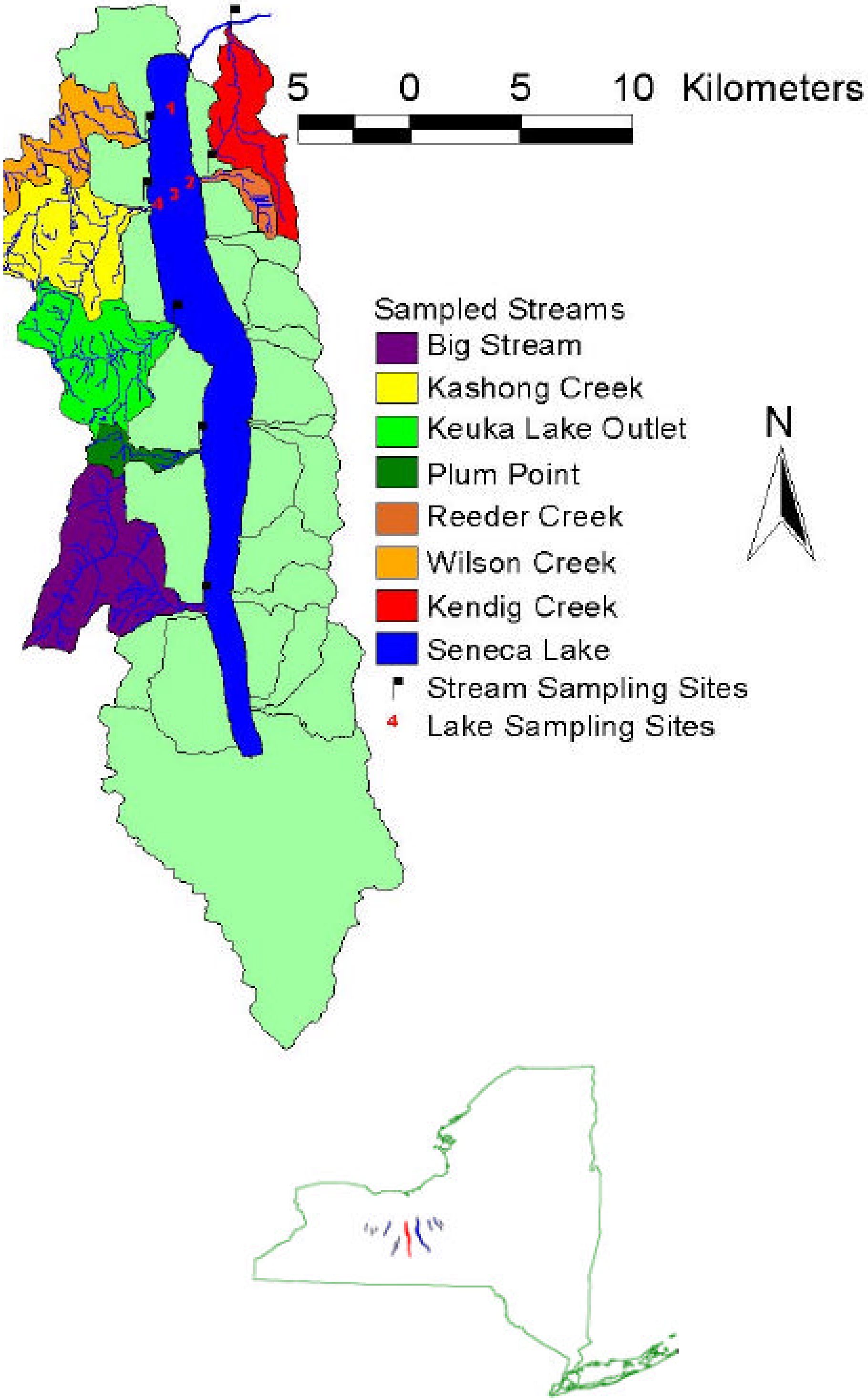


Figure 4- Seneca Lake Watershed and Sampled Streams
Insert shows the location of Seneca Lake in comparison to the other Finger Lakes in central New York

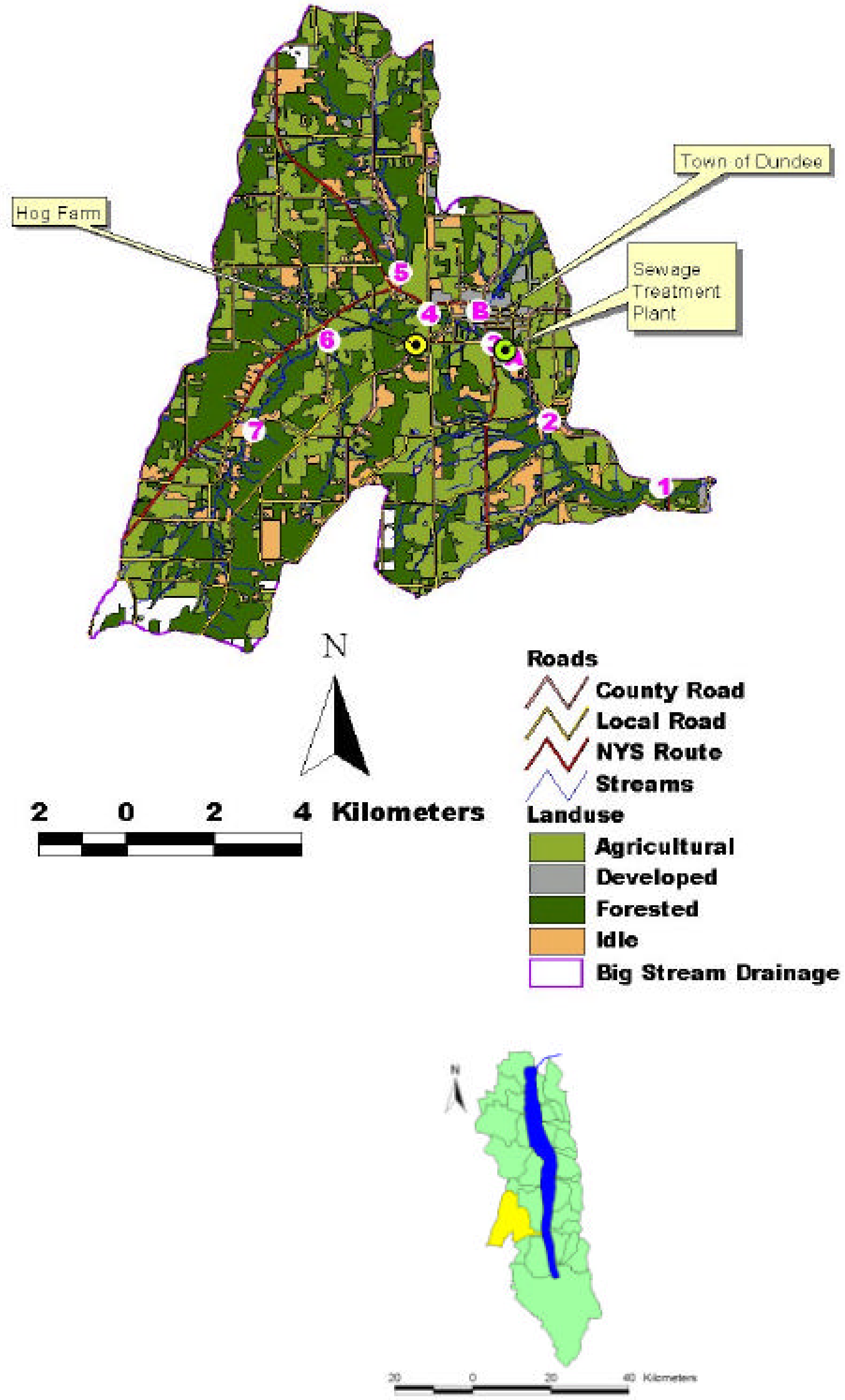


Figure 5- Big Stream Subwatershed and Sample Sites

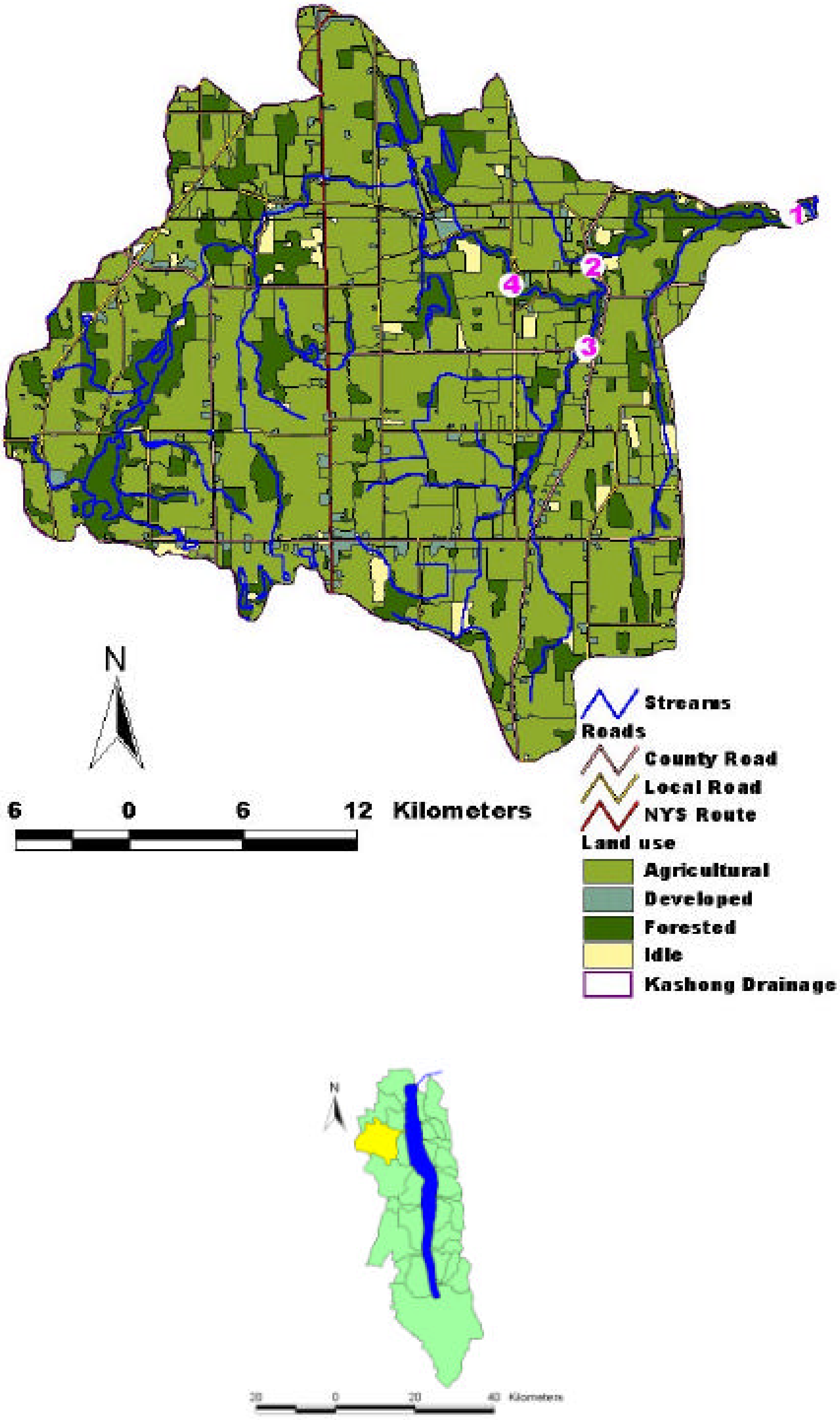


Figure 6- Kashong Creek Subwatershed and Sample Sites

The resulting solutions were analyzed for nitrite concentration with a spectrophotometer (Genesys 10 series) at 504 nm, relative to a potassium nitrate standard solution. A detailed procedure for this analysis can be found in Appendix A.

Copper concentrations were determined by complexing the aqueous copper with sodium diethyldithiocarbamate. This complex is not soluble in water and precipitates out, but can be dissolved in an organic solvent. The solvent fractions can then be separated on a separatory funnel. The complex is brownish orange in color and concentrations can be determined by spectrophotometer (Genesys 10 series) at 560 nanometers, relative to a standard solution of $CuSO_4$. This procedure was adapted from one developed by Walter Bowyer. A detailed procedure for this analysis can be found in Appendix B.

Results and Discussion

Data Analysis

The accuracy of the nitrate and copper analytical methods was determined by analyzing a series of standards of known concentrations (Figures 7+8). The nitrate results had an R-squared value of 0.993 over the range of concentrations under consideration, and the copper an R-squared value of 0.997. The closeness of the R-squared values to one, where one is a perfect fit, indicates the degree of accuracy of the procedure. Precision of the nitrate analysis was determined by triplicate replications of the standards. The average of the 1-sigma standard deviations of these triplicates was 0.014 mg/L. Precision of the copper results was tested by duplicate analysis of selected samples. The average of the 1-sigma standard deviations was 0.017 mg/L.

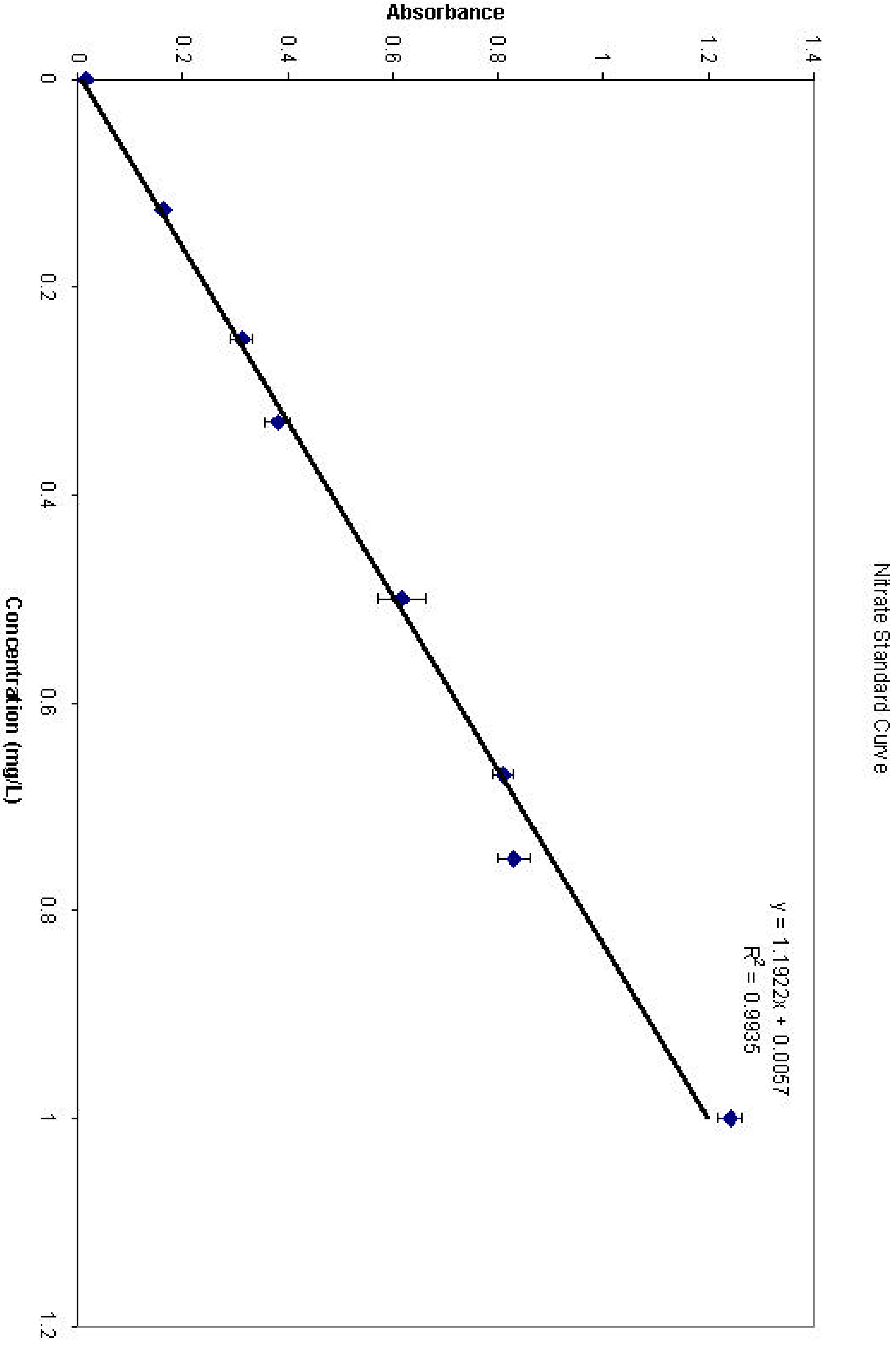


Figure 7-Nitrate Standard Curve

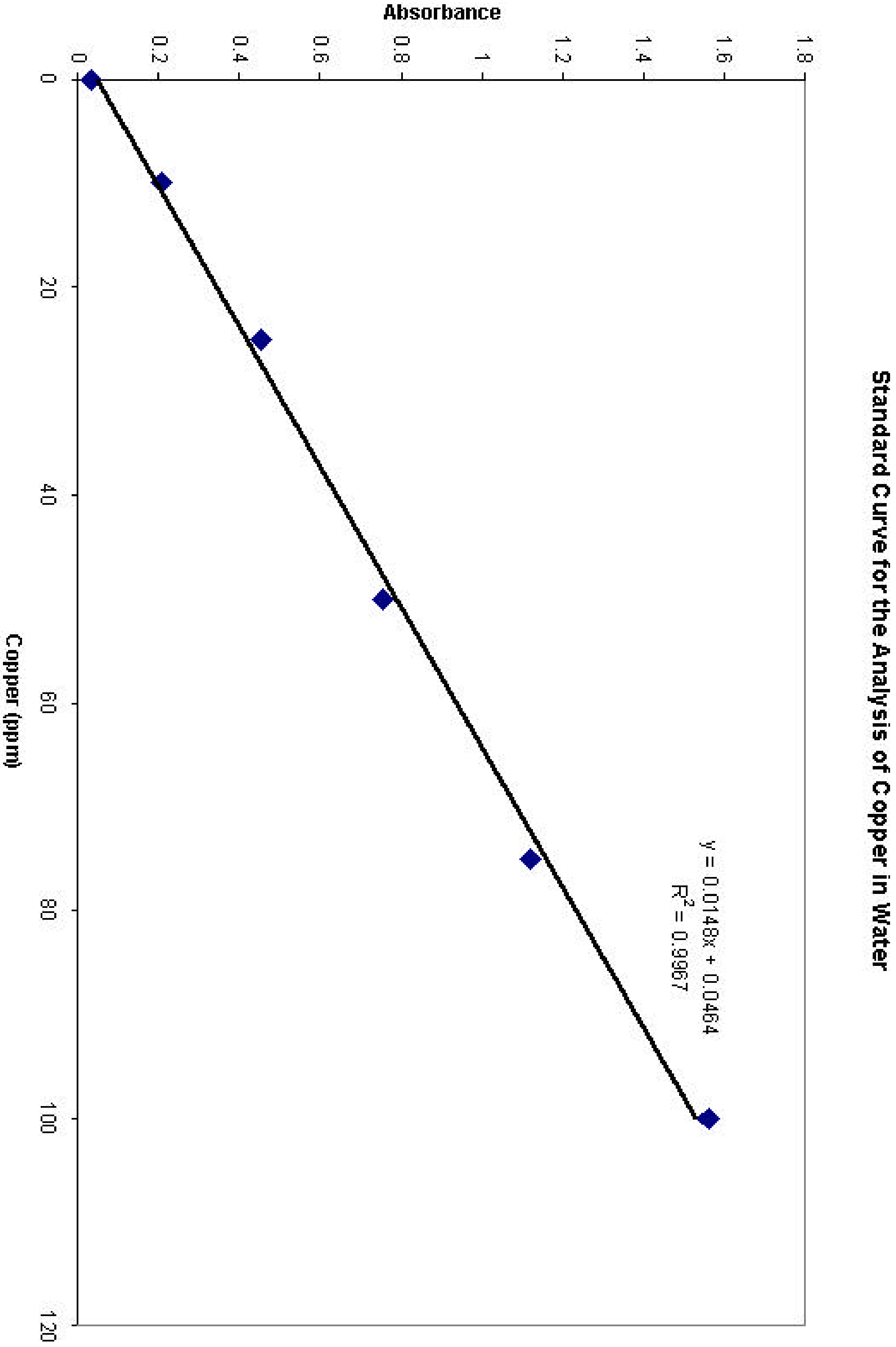


Figure 8- Copper Standard Curve

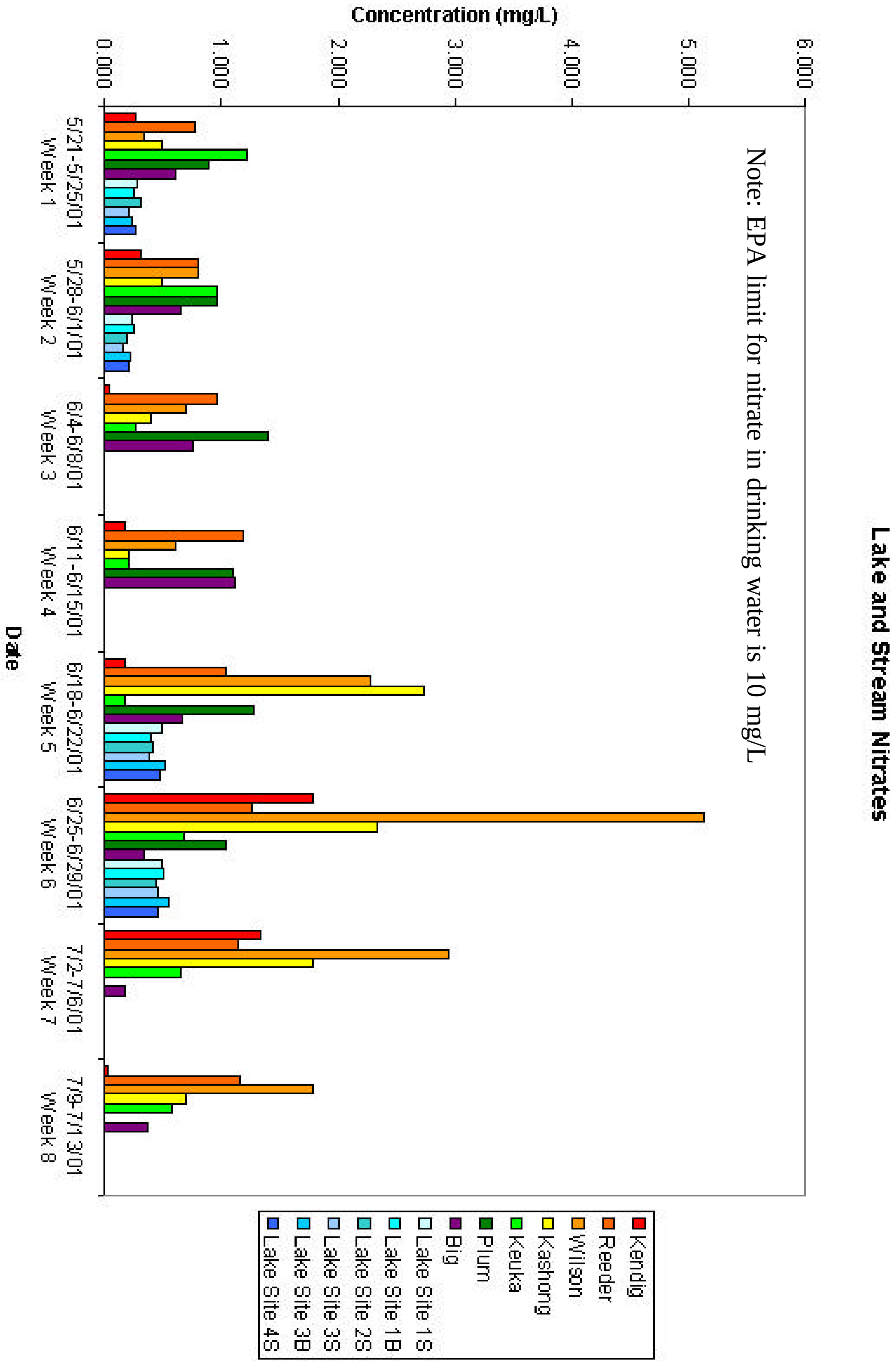
The stream and lake nitrate concentrations ranged from a high value of 5.5 to a low value of 0 mg/L (Figure 9). The stream and the lake nitrate data displayed the same temporal pattern over the course of the study. Nitrate concentrations were small until mid June, increased in mid June, and decreased again to smaller values in August, although the maximum concentration in mid June varied between subwatersheds, with more nitrate in the agricultural subwatersheds. Spatially, the northern streams with more agricultural land, most notably Reeder and Wilson Creeks, have larger nitrate levels.

In Big Stream, nitrate concentrations ranged between 2.0 and 0 mg/L (Figure 10). Nitrate concentrations reveal spatial and temporal patterns. The concentrations are larger at sites three and downstream, and smaller at sites four and upstream. The temporal pattern is the same as the other subwatersheds. Phosphate concentrations reveal the same spatial and temporal trends as nitrates (Figure 11).

Kashong Creek nitrate concentrations ranged from 3.0 to 0.1 mg/L. Nitrate concentrations were elevated at sites two and four. These sites are downstream from the largest area of agricultural land (Figure 6). The data reveal the same low-high-low temporal pattern as the other streams (Figure 12). Phosphate concentrations reveal the same spatial and temporal trend, although the phosphate concentrations were five time smaller than those in Big Stream (Figure 13).

Nitrate concentrations in Seneca Lake ranged from 0.4 to 0.7 mg/L (Figure 9). The same temporal pattern is observed. No spatial pattern is observed within the lake.

Copper levels were analyzed at each site on two different days, the first a day with generally low nitrate concentrations, and the second a day with generally high nitrate



Note: EPA limit for nitrate in drinking water is 10 mg/L

Figure 9- Nitrate Concentrations in Seneca Lake and Sampled Streams

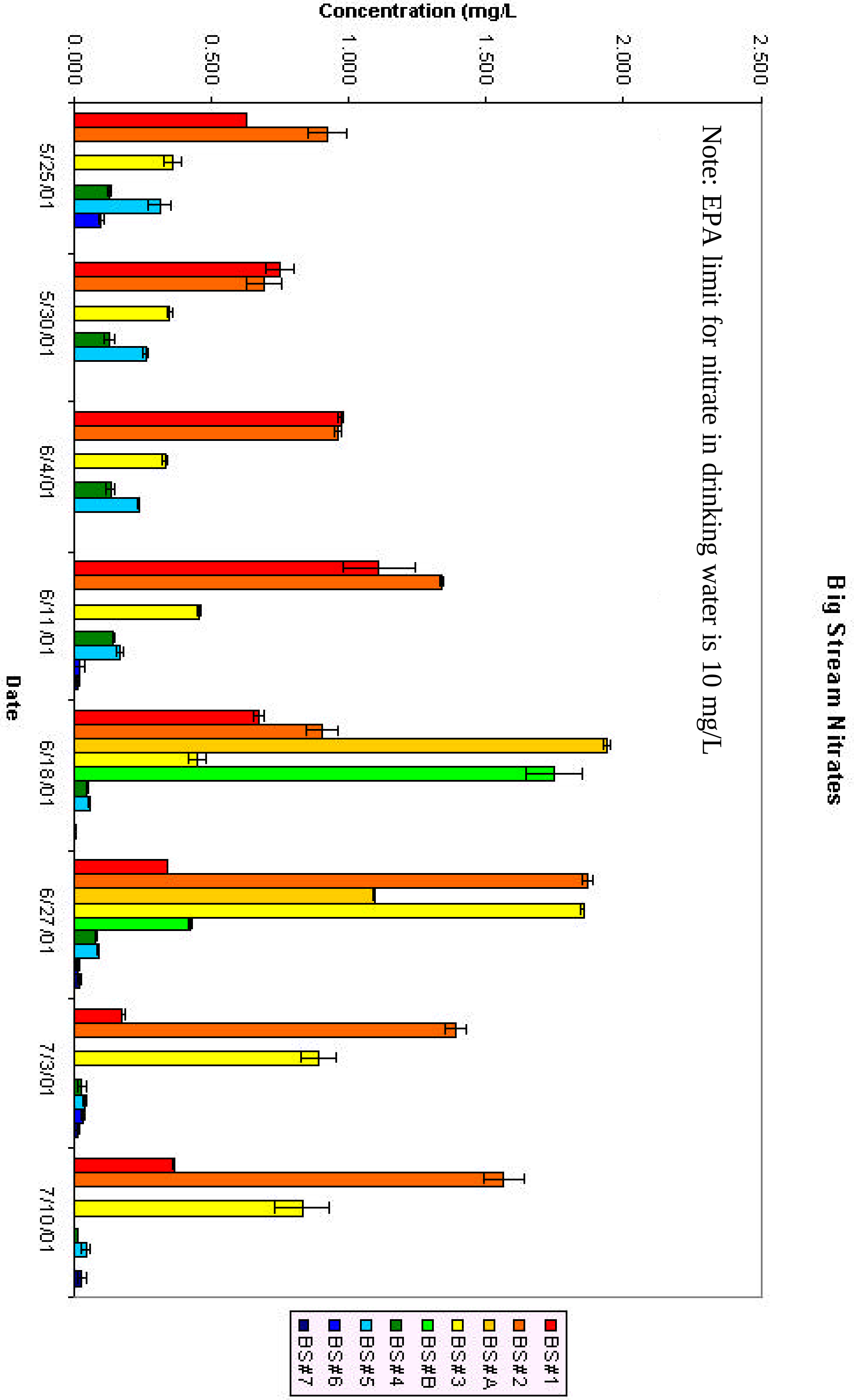


Figure 10- Nitrate Concentrations in Big Stream (See Figure 5 for site map)

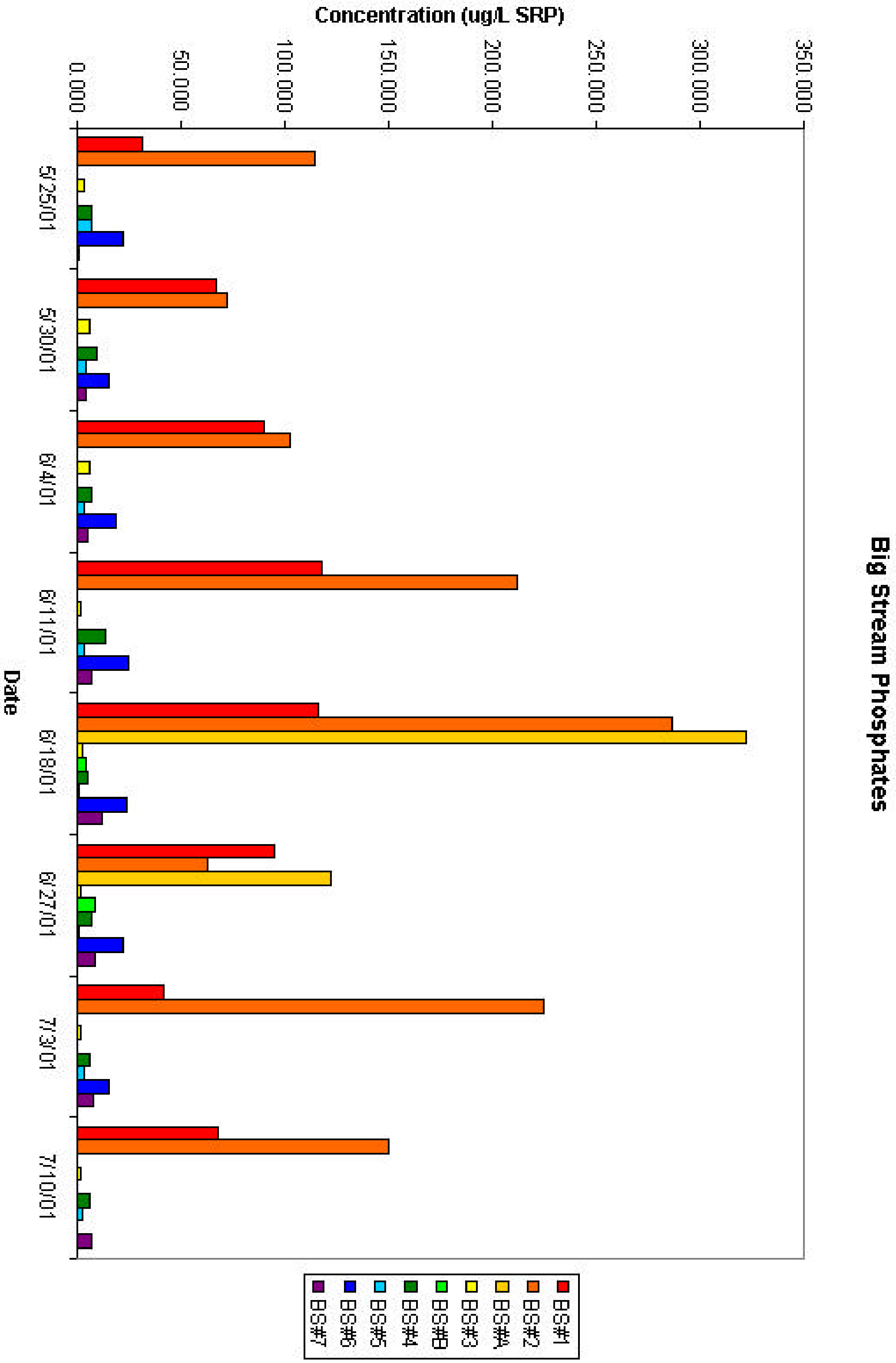
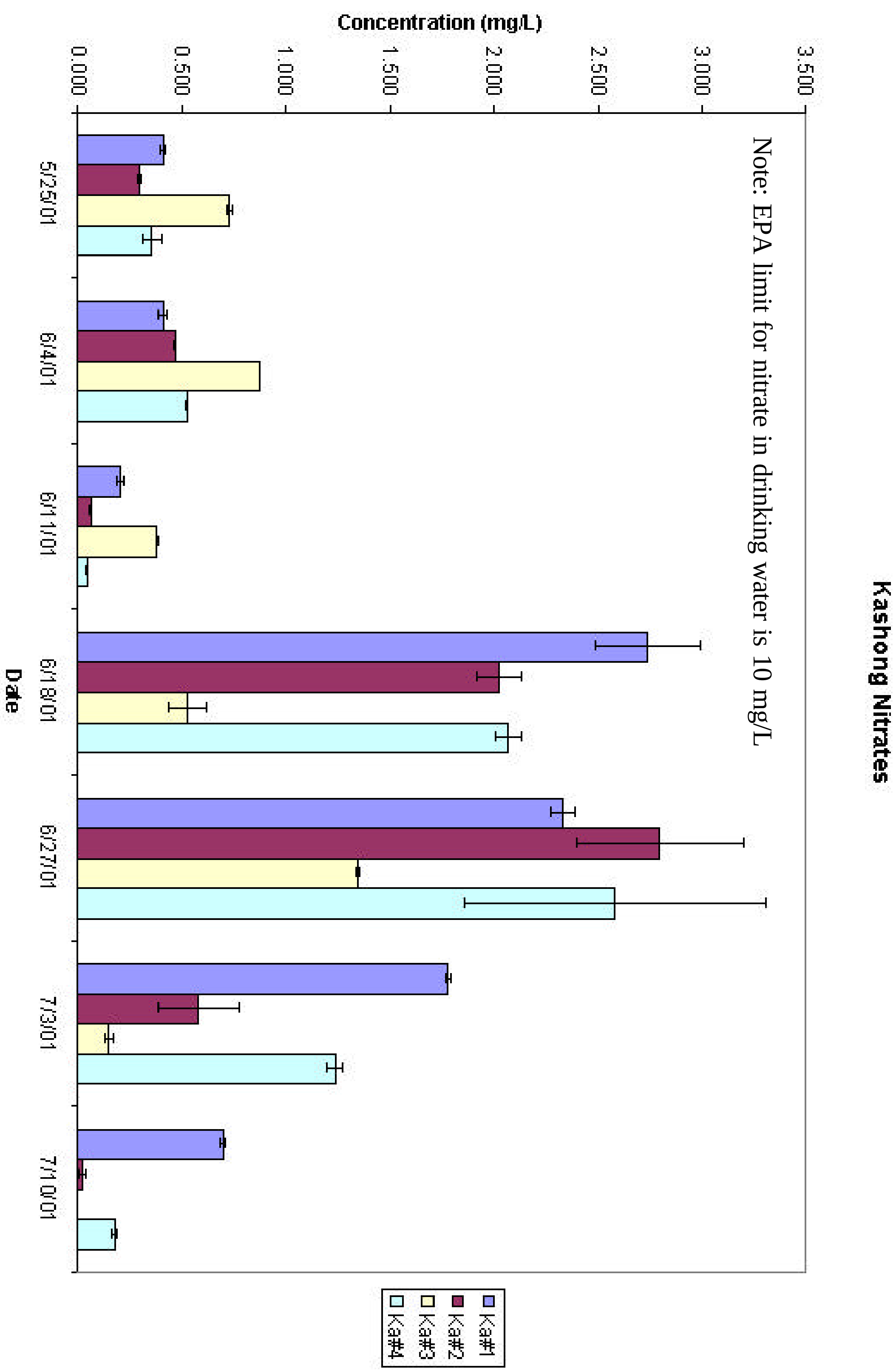


Figure 11- Phosphate Concentrations in Big Stream


Kashong Nitrates

Note: EPA limit for nitrate in drinking water is 10 mg/L

Figure 12- Nitrate Concentrations in Kashong Creek (see Figure 6 for site map)

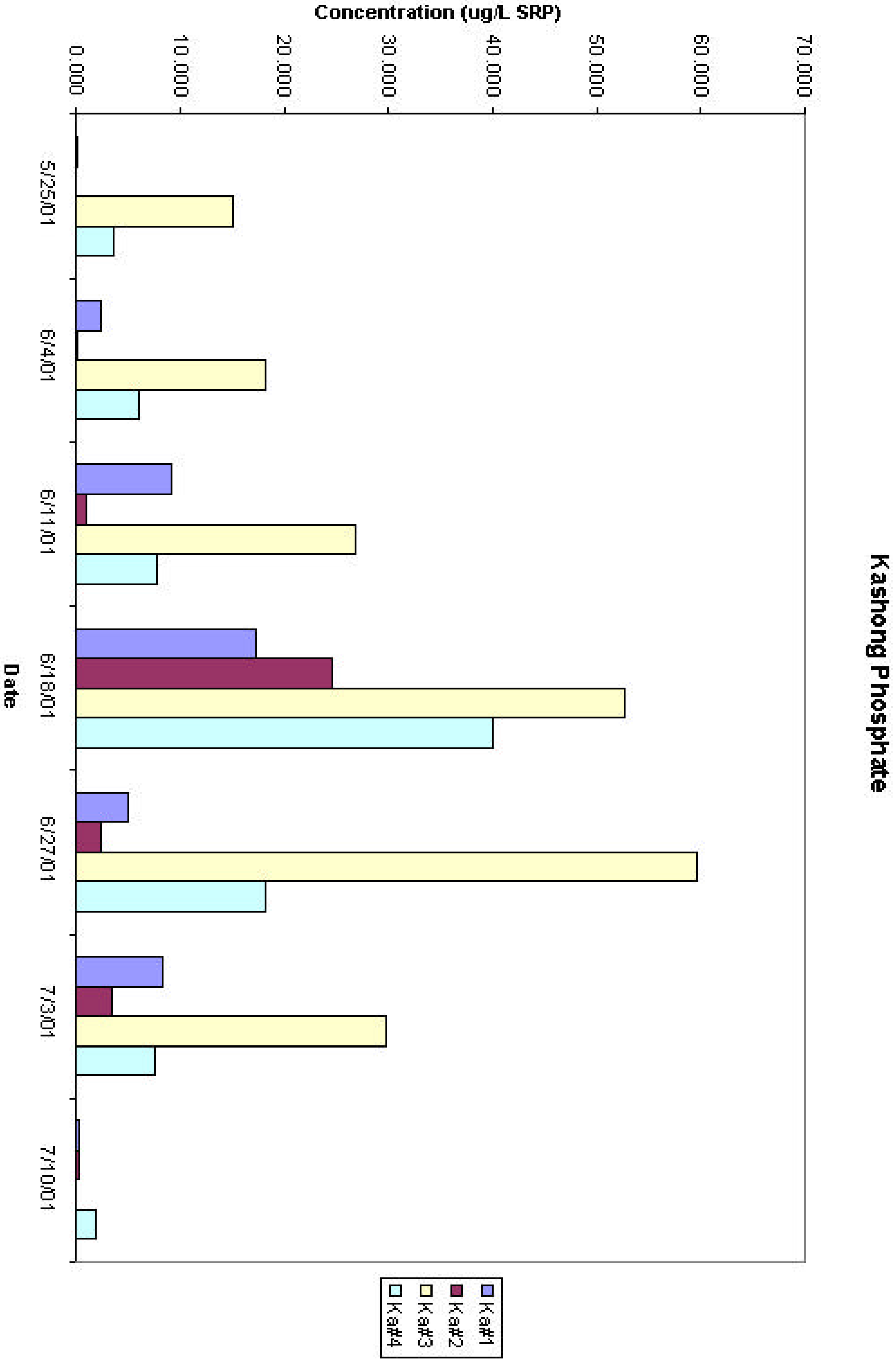


Figure 13- Phosphate Concentrations in Kashong Creek

concentrations. One set of copper data was discarded and repeated due to a poor-quality drying compound that interfered with spectroscopic detection. Copper concentrations ranged from 0 to 5.5 mg/L. No spatial or temporal patterns were evident (Figure 14). These results however are very close to the lower detection limit of the analytical method and are suspect.

Watershed Health

The Maximum Contaminant Limit (MCL) set by the EPA for nitrate in drinking water is 10 ppm (Shankar et al, 2000). All of the data in this study are lower than this limit. Thus, the watershed water is not a health risk for nitrate. However, the nitrate data do reveal human impact, because these concentrations are generally greater than pristine concentrations of 0.1 ppm (Heathwaite, Burt, and Trudgill, 1993).

The MCL set by the EPA for copper is 1.3 ppm (EPA, 2002). The levels of copper in all of the sites tested are near or above this limit. This would be a concern if the data were not suspect.

Agricultural Effects

The temporal pattern in the nitrate data is consistent with a fertilizer origin for the nitrates. Farmers in this area typically fertilize their fields twice per growing season, once in April or early May, and again around 6 weeks later in mid June (Spitzer, 1999). Thus, the observed mid-June rise in nitrate concentrations probably reflects fertilizer runoff. The reason that the elevated portions of the pattern extend beyond their initial appearance and are not restricted to the week of fertilizer application is that nitrates are extremely soluble, and nitrates reach nearby streams from both groundwater flow and

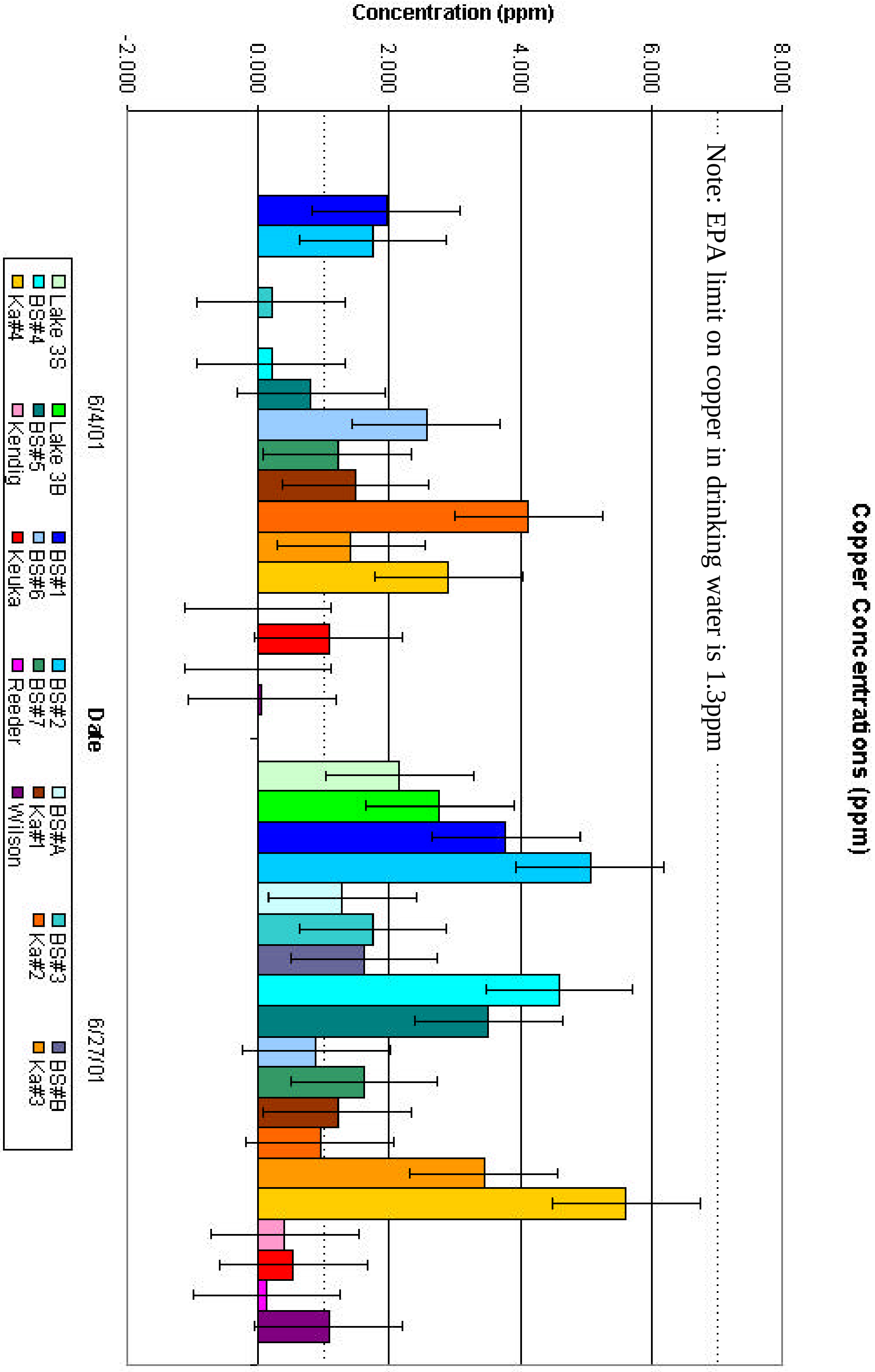


Figure 14- Copper Concentrations

surface runoff (Schilling and Wolter, 2001). Since groundwater flow is significantly slower than surface runoff (weeks to months vs. hours to days), and surface runoff is dependent on significant precipitation events, the pulse of high nitrate concentrations should last for a few weeks to a month after fertilizer application. The temporal pattern is inconsistent with hog farm runoff because the waste from hog farms is spread later in the summer, significantly after the rise in nitrates observed in mid June.

The spatial distribution of nitrates during mid June in the watershed reveal a positive correlation to agricultural land use, with some scatter (Figure 15). The variations that make the correlation less than perfect are due to the unique features of each watershed. Some are more forested, and others more urban. There are other potential sources in a few places; for instance, several construction sites and in one case an army base. Keuka Outlet nitrates are diluted by outflow from Keuka Lake, a nutrient poor source.

The occurrence of a runoff event in mid June (6/17) contributed to the high concentrations of nitrates that washed off of fields at this time (Figure 16).

Hog Farming

Nitrate concentrations in Big Stream do not correlate with nitrate loading from the hog farm. Topography dictates that runoff from the farm would impact Site 4, assuming that the farmer spreads manure on his own or adjacent properties. However, elevated nitrate concentrations were not discovered at Site 4. Instead, elevated nitrates appeared at Sites B and 3, suggesting that the main sources of nitrate to this stream are point sources within the town of Dundee and the sewage treatment plant. Nitrate levels decrease further downstream. The decrease may result from dilution by nitrate free water from

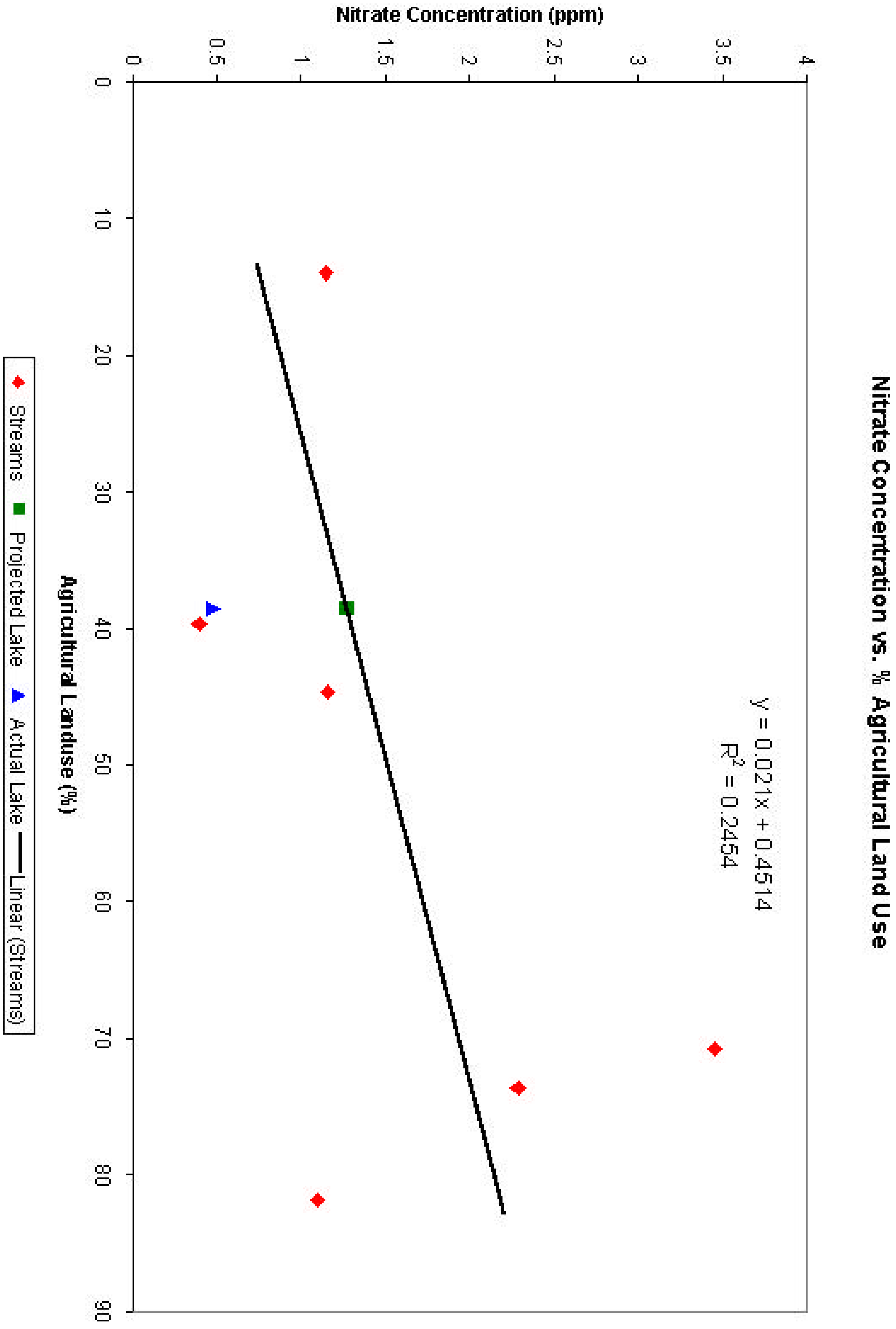


Figure 15- Agricultural Land Use vs. Mid June Nitrate Concentration

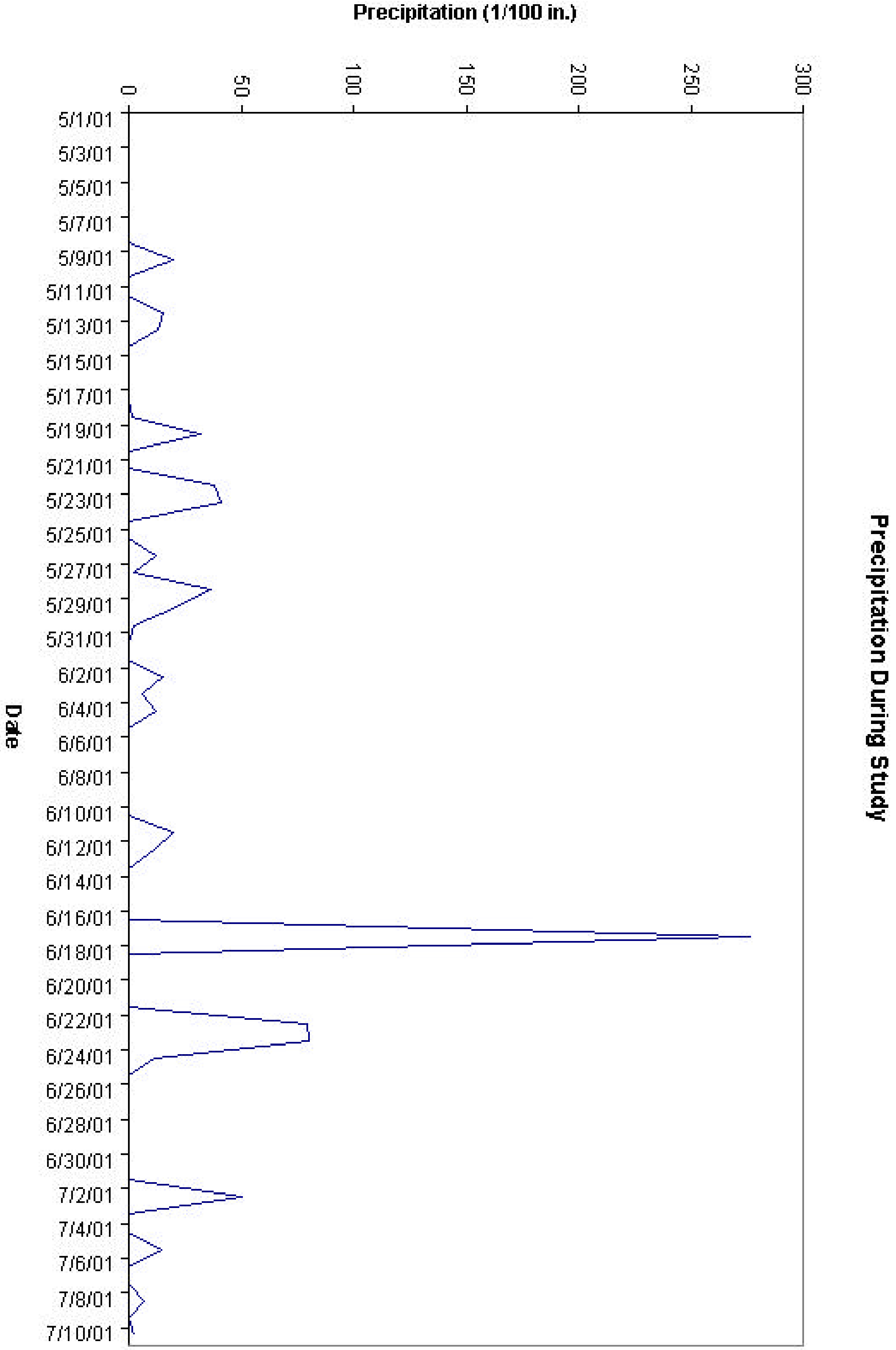


Figure 16- Precipitation During Study Period in Geneva
(http://www.nysaes.cornell.edu/weather/history/g2001)

downstream tributaries and/or the uptake of the nitrate by the lush growth of plants and algae in the stream. Dilution by ground or surface water is probably negligible because stream discharge is fairly constant between the sites. In addition, the water temperature stays constant at around 18 C, implying minimal addition of colder groundwater to the stream.

Additional support for the idea that hog farms, at present levels, are not significant contributors of nitrate to the watershed is that of the streams tested, Kendig Creek has the most hog farms, but one of the lowest nitrate concentrations (Spitzer, 1999). The low nitrates, however, may be due to dilution by nitrate free water or more likely nitrate uptake by aquatic vegetation in the streambed.

The copper data, while of limited usefulness, does not reveal significant trends along Big Stream and perhaps reflects minimal impact from hog farm waste.

However, it is dangerous to assume too much based on these results. The Big Stream hog farm is only in its first year of operation and the density of other hog farms surrounding Seneca Lake is still relatively low. The results of this study do not allow for the prediction of future trends as the hog farms continue operation, or in the event that more hog farms move to the area. According to Spitzer (1999), a density of 50 hog farms in the area would negatively impact water quality in the watershed.

Wastewater Source

The spatial pattern, where elevated concentrations appear around Sites B and 3 in the nitrate data suggests that the nitrates are being released from the town of Dundee and, more notably, the sewage treatment plant for the town of Dundee. Wastewater that has not been chemically treated contains from 15 to 20 mg/L nitrogen and from 4 to 16 mg/L phosphorus (Metcalf and Eddy, Inc., 2003). The high phosphate concentrations in Big Stream (several orders of magnitude above the lake) probably reflect this source.

Nitrate Uptake by the Streams and Lake

A theoretical mean stream nitrate concentration of 1.3 ppm is delivered to Seneca Lake after extrapolating the entire watershed's percentage of agricultural land use using the land use vs. nitrate concentration correlation developed above (Figure 15). The actual concentration of nitrate in the lake is 0.7 mg/L, and much lower. Seneca Lake is lower than the streams because precipitation and the outflow of Keuka Lake, and the observed biological uptake of nitreates in the streams and exected algal uptake in a large body of water probably dilute the fluxional input. The mean concentration suggests a nitrate flux of 830,000 kg/yr assuming a discharge of $8.63*10^9$ m^3/yr to the lake. However, more detailed nitrate numbers and estimates for fluxes from other sources are required before a complete assessment of the relative contributions of each source can be determined.

Conclusions

- Nonpoint pollution in the form of nitrates and other nutrients impact the Seneca Lake watershed.
- Stream concentrations are higher than pristine concentrations. However, nitrate concentrations are not above drinking water limits set by the EPA in the Seneca Lake watershed.
- Temporal and spatial patterns in nitrate concentrations indicate that the main source of nitrate in this watershed is runoff after the application of fertilizers.

- Spatial patterns in the Big Stream watershed reveal minimal impact by the current hog farm. However, this study cannot predict the impact of continued farming or additional farms in the area.
- The largest nitrate concentrations in Big Stream were detected downstream of the wastewater treatment plant and suggest the plant is a major source of nitrates to the stream.
- Biological uptake appears to reduce nitrate concentrations within the streams and in the lake.

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Appendices

Appendix A-Nitrate Lab Procedure

Highlights: A water sample is treated with cadmium filings to reduce nitrate to nitrite. The sample is then treated with another set of reagents, which cause the sample to turn pink. The intensity of the pink color is proportional to the nitrate concentration in a linear fashion. The intensity is measured with a spectrophotometer at 504 nm, relative to a standard solution.

Supplies

Spectrophotometer. 1 cm spectrophotometer cells. 5mL pipetter with tips. 20x150 test tubes and stoppers. Hach Low Range Nitrates Test Kit, including NitraVer3 and NitraVer6 reagent powder pillows. Nitrate Standard. Water Samples. Separate waste bottle labeled “Nitrate Waste”.

Nitrate Standard Solution

Dilute 0.3609g of KNO_3 to 1 liter with clean deionized water in a 1 liter volumetric flask. Use a funnel, Pasteur pipette, and 100 mL volumetric flask to transfer 100mL to another 1 liter volumetric flask. Dilute to 1 liter. Use a funnel, Pasteur pipette, and 100 mL volumetric flask to transfer 100mL to another 1 liter volumetric flask. Dilute to 250mL in a 250mL volumetric flask. This yeilds 250mL of 2.0mg/L nitrate standard solution.

Note: Turn on the spectrophotometer to warm up before you begin analysis.

Sample and Standard Preparation:

Samples

Use pipetter to measure exactly 5mL sample into numbered test tube. Repeat for each sample. Rinse pipetter by dispensing distilled water between each sample.

Standard

Use pipetter to measure exactly 5mL of standard solution into three marked test tubes.

Blanks

Use pipetter to measure exactly 5mL of deionized water into three marked test tubes.

Samples, Blanks, and Standards:

Add one NitraVer 6 Nitrate reagent powder pillow to each tube, and stopper. Shake for 3 minutes, either in a shaker or manually. Let sit for 30 seconds.

Decant solution into extra test tube, leaving cadmium behind, and carefully wash cadmium into marked waste bottle. Rinse test tube, and replace solution. Repeat for each sample, blank, and standard.

Add one NitraVer Nitrite reagent powder pillow to each tube, stopper, and shake for 30 seconds.

Let sit out of sunlight (in the test tube rack is fine) for not less than 10 minutes, and not more than 30 minutes, and analyze with spectrophotometer.

Spectrophotometer Analysis:

Pick up cuvette using Kimwipe, and wipe down outside. Make sure inside is clean. Touch only the top half of the cuvette, and only with Kimwipes. Fill cuvette with distilled water, and insert into spectrophotometer. Close top. Push the "Measure Blank" key, and wait for the machine to zero. You will want to repeat this every six samples. If the distilled water gives an absorbance of more than .002 or less then -.002, hit the "Measure Blank" key again. For each sample, standard, and blank, fill the cuvette at least 1.5 cm from the bottom full of solution. (Most cuvettes have a line) Insert cuvette into machine, close top, and wait 5 seconds or until numbers stop changing. Record absorbance, and dump sample into labeled waste bottle. Rinse cuvette with distilled water, and repeat for each sample.

Standard Check:

The mean standard absorbance – the mean blank absorbance should be about 2.6.

Calculations:

Concentration (mg/L) = (Al-Ab)/(As-Ab)*Sc

Al= Absorbance of Sample
Ab= Mean Absorbance of Blanks
As= Mean Absorbance of Standards
Sc= Standard Concentration

WASTE: Waste should be dumped into large bottle labeled "Nitrate Waste". Cadmium is quite toxic and needs to be disposed of professionally.

Appendix B-Copper Lab Procedure

Highlights: A water sample is treated with diethyl dithiocarbamate to complex copper and make it insoluble in water. The complex is then dissolved in an organic solvent, butyl acetate, and the solvents are separated. The presence of this compound causes a brown color. The intensity is measured with a spectrophotometer at 560 nm, relative to a standard solution.

Supplies:

Spectrophotometer. 1 cm spectrophotometer cells. 5mL pipetter with tips. Separatory Funnels. 250 mL Erlenmeyer Flasks. $CuSO_4*5H_20$. Citric Acid. Sodium Diethyldithiocarbamate (NaDEDTC). Anhydrous Sodium Sulfate. Concentrated HCl. 5M Ammonium Hydroxide. Butyl Acetate. Absolute Methanol. 95% Ethanol. Water Samples. Separate waste bottle labeled “Copper Waste”.

Reagent Preparation:

Copper Standard Solution:

Dilute 0.393g of $CuSO_4*5H_2O$ to 1 liter with clean deionized water in a 1 liter volumetric flask. This will give a 100ppm solution.

Citric Acid Reagent:

Dissolve 15g of citric acid in around 50mL distilled water in a 100mL volumetric flask, then slowly add 10mL concentrated HCl and fill to line with distilled water.

NaDEDTC:

Add one gram NaDEDTC to a 100 mL volumetric flask. Dissolve in 5mL ethanol, then fill to line with distilled water.

Sample and Standard/Blank Preparation:

Pipet 10.0mL of each sample/standard into a clean, dry 100 mL Erlenmeyer flask. Pipet into each flask 1.0 ML citric acid reagent, 2.0mL 5M ammonium hydroxide, and 1.0mL NaDEDTC solution. Mix after each addition. Wait one minute, then add 10.0mL butyl acetate and 5.0mL absolute methanol. Shake for 30 seconds and separate organic layer. Dry organic layer with anhydrous sodium sulfate.

Spectrophotometer Analysis:

Pick up cuvette using Kimwipe, and wipe down outside. Make sure inside is clean. Touch only the top half of the cuvette, and only with Kimwipes. Fill cuvette with distilled water, and insert into spectrophotometer. Close top. Push the “Measure Blank” key, and wait for the machine to zero. You will want to repeat this every six samples. If the distilled water gives an absorbance of more than .002 or less then -.002, hit the “Measure Blank” key again. For each sample, blank, and standard, fill the cuvette at least 1.5 cm from the bottom full of solution. (Most cuvettes have a line) Insert cuvette into machine, close top, and wait 5 seconds or until numbers stop changing. Record absorbance, and dump sample into labeled waste bottle. Rinse cuvette with distilled water, and repeat for each sample.

Calculations:

$$\text{Concentration (mg/L)} = (Al-Ab)/(As-Ab)*Sc$$

Al= Absorbance of Sample
Ab= Mean Absorbance of Blanks
As= Mean Absorbance of Standards
Sc= Standard Concentration

WASTE: Waste should be dumped into large bottle labeled “Copper Waste”. The complex and the organic solvents are toxic and needs to be disposed of professionally.

Appendix C- Lake and Stream Nitrate Data

Date eg., 1-Apr-97	Site # e.g., BS#1	Nitrate S1 mg/L (ppm)	Nitrate S2 mg/L (ppm)	Avg Nit.	Discharge m^3/s	Flux kg/yr
5/23/01	Kendig	0.257		0.257	0.11	892.1089
5/23/01	Reeder	0.769		0.769	0.10	2426.713
5/23/01	Wilson	0.336		0.336	0.18	1908.551
5/23/01	Kashong	0.493		0.493	0.32	4978.391
5/23/01	Keuka	1.218		1.218	1.00	38436.1
5/23/01	Plum	0.895		0.895	0.09	2541.895
5/23/01	Big	0.606		0.606	0.330	6310.716
5/29/01	Kendig	0.311		0.311	0.07	710.5593
5/29/01	Reeder	0.791		0.791	0.08	1912.059
5/29/01	Wilson	0.803		0.803	0.24	6171.307
5/29/01	Kashong	0.482		0.482	0.40	6030.827
5/29/01	Keuka	0.969		0.969	0.90	27374.6
5/29/01	Plum	0.966		0.966	0.05	1613.353
5/29/01	Big	0.65		0.650	0.33	6793.103
6/4/01	Kendig	0.284		0.284	0.04	371.4017
6/4/01	Reeder	1.002		1.002	0.02	673.4187
6/4/01	Wilson	0.899		0.899	0.09	2544.937
6/4/01	Keuka	1.773		1.773	0.32	17917.89
6/4/01	Plum	1.184		1.184	0.05	1702.756
6/7/01	Kendig	0.047		0.047		
6/7/01	Reeder	0.966		0.966		
6/7/01	Wilson	0.696		0.696		
6/7/01	Kashong	0.394		0.394		
6/7/01	Keuka	0.257		0.257		
6/7/01	Plum	1.395		1.395		
6/7/01	Big	0.756		0.756		
6/11/01	Wilson	0.598		0.598		
6/11/01	Keuka	0.202		0.202		
6/11/01	Plum	1.1		1.100		
6/11/01	Kendig	0.168		0.168		
6/11/01	Reeder	1.189		1.189		
6/18/01	Kendig	0.168		0.168		
6/18/01	Reeder	1.041		1.041		
6/18/01	Wilson	2.269		2.269		
6/18/01	Keuka	0.168		0.168		
6/18/01	Plum	1.269		1.269		

6/27/01	Kendig	1.782		1.782
6/27/01	Reeder	1.256		1.256
6/27/01	Wilson	5.138		5.138
6/27/01	Keuka	0.673		0.673
6/27/01	Plum	1.042		1.042
6/22/01	Rain	0.233		0.233
7/3/01	Kendig	1.343		1.343
7/3/01	Reeder	1.140		1.140
7/3/01	Wilson	2.948		2.948
7/3/01	Keuka	0.649		0.649
7/10/01	Kendig	0.031		0.031
7/10/01	Reeder	1.158		1.158
7/10/01	Wilson	1.787		1.787
7/10/01	Keuka	0.583		0.583
7/10/01	Rain	0.623		0.623
6/14/01	1surf	0.493		0.493
6/14/01	1bott	0.406		0.406
6/14/01	2surf	0.413		0.413
6/14/01	3surf	0.387		0.387
6/14/01	3bott	0.524		0.524
6/14/01	4surf	0.468		0.468
6/21/01	1surf	0.48		0.480
6/21/01	1bott	0.505		0.505
6/21/01	2surf	0.444		0.444
6/21/01	3surf	0.454		0.454
6/21/01	3bott	0.553		0.553
6/21/01	4surf	0.458		0.458
COLOR WHEEL				
5/24/01	1surf	0.28		0.280
5/24/01	1bott	0.25		0.250
5/24/01	2surf	0.31		0.310
5/24/01	3surf	0.2		0.200
5/24/01	3bott	0.24		0.240
5/24/01	4surf	0.26		0.260
5/31/01	1surf	0.24		0.240
5/31/01	1bott	0.25		0.250
5/31/01	2surf	0.19		0.190
5/31/01	3surf	0.16		0.160
5/31/01	3bott	0.22		0.220

5/31/01	4surf	0.21		0.210

Appendix D- Big Stream Nitrate Data

Date eg., 1-Apr-97	Site # e.g., BS#1	Nitrate S1 mg/L (ppm)	Nitrate S2 mg/L (ppm)	Avg Nit. mg/L (ppm)	Discharge m^3/s	Flux kg/yr
5/25/01	BS#1	0.633	0.623	0.628		
5/25/01	BS#2	0.994	0.851	0.923		
5/25/01	BS#3	0.391	0.325	0.358		
5/25/01	BS#4	0.136	0.122	0.129		
5/25/01	BS#5	0.274	0.354	0.314		
5/25/01	BS#6	0.106	0.089	0.098		
5/25/01	BS#7	0.000	0.000	0.000		
5/30/01	BS#1	0.698	0.800	0.749		
5/30/01	BS#2	0.631	0.751	0.691		
5/30/01	BS#3	0.338	0.359	0.349		
5/30/01	BS#4	0.111	0.147	0.129		
5/30/01	BS#5	0.252	0.273	0.263		
5/30/01	BS#6	0.000	0.000	0.000		
5/30/01	BS#7	0.000	0.000	0.000		
6/4/01	BS#1	0.976	0.964	0.970	0.25	7652.508
6/4/01	BS#2	0.972	0.946	0.959	0.16	4842.066
6/4/01	BS#3	0.336	0.322	0.329	0.2	2076.433
6/4/01	BS#4	0.117	0.148	0.133	0.29	1212.568
6/4/01	BS#5	0.243	0.229	0.236	0.03	223.4217
6/4/01	BS#6	0.000	0.000	0.000	0.1	0
6/4/01	BS#7	0.000	0.000	0.000	0	0
6/11/01	BS#1	1.238	0.978	1.108		
6/11/01	BS#2	1.346	1.332	1.339		
6/11/01	BS#3	0.458	0.449	0.454		
6/11/01	BS#4	0.145	0.147	0.146		
6/11/01	BS#5	0.179	0.155	0.167		
6/11/01	BS#6	0.002	0.036	0.019		
6/11/01	BS#7	0.024	0.004	0.014		
6/18/01	BS#1	0.7	0.689	0.671		
6/18/01	BS#2	0.846	0.964	0.905		
6/18/01	BS A	1.930	1.950	1.940		
6/18/01	BS#3	0.414	0.482	0.448		
6/18/01	BS B	1.643	1.848	1.746		
6/18/01	BS#4	0.044	0.051	0.048		
6/18/01	BS#5	0.054	0.059	0.057		
6/18/01	BS#6	0.000	0.000	0.000		
6/18/01	BS#7	0.003	0.003	0.003		

6/27/01	BS#1	0.335	0.339	0.337
6/27/01	BS#2	1.892	1.850	1.871
6/27/01	BS A	1.092	1.096	1.094
6/27/01	BS#3	1.844	1.858	1.851
6/27/01	BS B	0.425	0.418	0.421
6/27/01	BS#4	0.075	0.083	0.079
6/27/01	BS#5	0.088	0.090	0.089
6/27/01	BS#6	0.007	0.021	0.014
6/27/01	BS#7	0.015	0.026	0.020
7/3/01	BS#1	0.185	0.168	0.177
7/3/01	BS#2	1.353	1.428	1.390
7/3/01	BS#3	0.957	0.825	0.891
7/3/01	BS#4	0.016	0.040	0.028
7/3/01	BS#5	0.030	0.040	0.035
7/3/01	BS#6	0.029	0.036	0.032
7/3/01	BS#7	0.001	0.024	0.012
7/10/01	BS#1	0.360	0.365	0.363
7/10/01	BS#2	1.638	1.488	1.563
7/10/01	BS#3	0.930	0.733	0.831
7/10/01	BS#4	0.017	0.010	0.014
7/10/01	BS#5	0.025	0.061	0.043
7/10/01	BS#6			
7/10/01	BS#7	0.011	0.045	0.028

Appendix E- Kashong Nitrate Data

Date eg., 1-Apr-97	**Site #** e.g., BS#1	**Nitrate S1** mg/L (ppm)	**Nitrate S2** mg/L (ppm)	**Avg Nit.**
5/25/01	Ka#1	0.397	0.422	0.410
5/25/01	Ka#2	0.284	0.306	0.295
5/25/01	Ka#3	0.716	0.738	0.727
5/25/01	Ka#4	0.398	0.309	0.354
6/4/01	Ka#1	0.388	0.430	0.409
6/4/01	Ka#2	0.471	0.459	0.465
6/4/01	Ka#3	0.872	0.878	0.875
6/4/01	Ka#4	0.522	0.526	0.524
6/11/01	Ka#1	0.220	0.189	0.205
6/11/01	Ka#2	0.059	0.058	0.059
6/11/01	Ka#3	0.381	0.380	0.381
6/11/01	Ka#4	0.048	0.037	0.043
6/18/01	Ka#1	2.991	2.5	2.739
6/18/01	Ka#2	1.915	2.132	2.024
6/18/01	Ka#3	0.440	0.620	0.530
6/18/01	Ka#4	2.006	2.128	2.067
6/27/01	Ka#1	2.273	2.391	2.332
6/27/01	Ka#2	2.395	3.201	2.798
6/27/01	Ka#3	1.353	1.338	1.346
6/27/01	Ka#4	1.855	3.308	2.582
7/3/01	Ka#1	1.766	1.793	1.780
7/3/01	Ka#2	0.385	0.771	0.578
7/3/01	Ka#3	0.125	0.169	0.147
7/3/01	Ka#4	1.275	1.202	1.238
7/10/01	Ka#1	0.712	0.685	0.699
7/10/01	Ka#2	0.003	0.035	0.019
7/10/01	Ka#3			
7/10/01	Ka#4	0.187	0.167	0.177

Appendix F-Copper Concentration Data

Date	**Site**	**Absorbance** 560 nm	**Concentration** mg/L (ppm)
6/4/01	Kendig	0	0.000
6/4/01	Reeder	0	0.000
6/4/01	Wilson	0.001	0.068
6/4/01	Keuka	0.016	1.081
6/4/01	Plum	0.029	1.959
6/4/01	BS#1	0.029	1.959
6/4/01	BS#2	0.026	1.757
6/4/01	BS#3	0.003	0.203
6/4/01	BS#4	0.003	0.203
6/4/01	BS#5	0.012	0.811
6/4/01	BS#6	0.038	2.568
6/4/01	BS#7	0.018	1.216
6/4/01	Ka#1	0.022	1.486
6/4/01	Ka#2	0.061	4.122
6/4/01	Ka#3	0.021	1.419
6/4/01	Ka#4	0.043	2.905
6/21/01	Lake 3S	0.032	2.162
6/21/01	Lake 3B	0.041	2.770
6/27/01	Kendig	0.006	0.405
6/27/01	Reeder	0.002	0.135
6/27/01	Wilson	0.016	1.081
6/27/01	Keuka	0.008	0.541
6/27/01	Plum	0.001	0.068
6/27/01	BS#1	0.056	3.784
6/27/01	BS#2	0.075	5.068
6/27/01	BS#A	0.019	1.284
6/27/01	BS#3	0.026	1.757
6/27/01	BS#B	0.024	1.622
6/27/01	BS#4	0.068	4.595
6/27/01	BS#5	0.052	3.514
6/27/01	BS#6	0.013	0.878
6/27/01	BS#7	0.024	1.622
6/27/01	Ka#1	0.018	1.216
6/27/01	Ka#2	0.014	0.946
6/27/01	Ka#3	0.051	3.446
6/27/01	Ka#4	0.083	5.608