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Variation of nitrogen concentrations in stormpipe discharge in a residential watershed

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Abstract

Use of lawn chemicals in residential areas may contribute non-point source (NPS) pollutants such as nutrients, pesticides, and herbicides to streams. We conducted a 2-year screening study of discharge in stormwater pipes in the Wissahickon Valley Wastershed (suburban Philadelphia) using nitrogen as an indicator of lawn chemical use. Storm water samples representing first flush and composite runoff were collected approximately twice a month using automatic samplers triggered by rise in water level during storms. The runoff collected by the storm pipes was from neighborhoods with 15 to 100 residences, and from 2 to 18 Ha (5 to 45 acres). Several factors were examined to evaluate effects on nitrate concentration. These factors included time of sampling (season), number of homes, total area, size of the storm, and time since last storm. Nitrate levels were generally less than 5 mg/L, but still above background in typical undeveloped areas. Concentrations were slightly higher in the first summer than during a drought the second year, but the difference was not statistically significant. There was a positive correlation between size of the neighborhood (capture area) and peak concentration of nitrate. Storm characteristics (size of storm and time since last storm) did not correlate with nitrate concentrations. The variation in both space and time suggests that a more local control may be a factor. Although individual lawn chemical applications were not monitored, they may influence the timing of increased loading. Furthermore, the variability indicates that quarterly monitoring will not capture discharge characteristics of storm basins.

KEYWORDS: nitrogen, urban hydrology, nonpoint source pollution, monitoring, storm sewer discharge

Introduction

Background

In the 1990's environmental groups concerned with continued poor stream quality and habitat degradation in many streams began suing the U.S. Environmental Protection Agency (EPA) to enforce the parts of the Clean Water Act that concerned monitoring water quality, not just discharge. EPA in turn began requiring local municipalities to develop plans for managing stormwater, which was identified as a major source of unregulated loading. This attention has increased interest in stormwater quality (U.S. EPA, 1997).

Nutrients, such as nitrogen and phosphorous, are among the water quality factors that frequently lead to stream degradation. Inorganic nitrogen (N) is typically in the form of nitrate (NO_3-N), but can also occur as ammonium (NH_4-N). Phosphorous occurs as phosphate (PO_4-P). When nutrients enter streams from agricultural and urban land application, they can increase growth of algae. The algal growth can lead to excessive algal biomass and oxygen depletion (eutrophication), both of which degrade the habitat for macro-invertebrates and other stream biota (U.S. EPA, 2000a). Nutrients are second only after siltation in causing degradation in stream quality (U.S. EPA, 1998). There is not uniform agreement on the criteria for nutrient levels causing degradation in streams (U.S. EPA, 1998). In general, two factors are considered: formation of algal biomass that can limit light and monitoring of “natural” stream conditions (U.S. EPA, 2000a). Specifics of whether total dissolved N be used or total nutrients should be used are still debated. Furthermore, the degree of light blocking can vary based on local conditions. In one basin, nuisance growth occurred as low as 0.3 mg/L Total N, and eutrophication at 1.5 mg/L (U.S. EPA, 2000b).

Several studies have sampled extensive basins to try to establish natural and effected conditions. The U.S. Geological Survey (USGS) conducted an assessment of nutrients and pesticides in 50 major river basins and aquifers in the US (USGS, 1999). The report included a comparison of nutrient concentrations in urban areas, agricultural areas, and undeveloped areas. In undeveloped areas, background concentrations averaged 0.6 mg/L NO_3-N. In urban streams, the median concentration was 1.5 mg/L with a range of 0.5 to 4.5 mg/L total N. Herbicides and pesticides were found at low levels in 92 to 100% of samples (greater in agricultural areas). Their study helped establish levels of background versus excess loading. Most samples fall in a narrow range, so the authors suggest that concentrations above the average can be considered "affected". The EPA has suggested using ecoregions that assume different background concentrations for different regions of the country, based on sampling reported in Rohm et al., 2002. Pennsylvania is in region IX, with background concentrations of total N between 0.07 to 1 mg/L (U.S. EPA, 2000b).

Although non-point sources are believed to be a major source of these nutrients, the intermittent nature of loading has made detailed studies difficult (Carpenter et al., 1998). Non-point sources include overland flow from agricultural land use, overland flow in urban areas, septic systems, and atmospheric deposition. Urban sources are believed to be secondary to agricultural sources in terms of non-point loading of nutrients (Mueller and Helsel, 1996). However, urban runoff is reported to be similar in nutrient loading to pasture that does not include animal waste (U.S. EPA, 1999). Thus, there is potential for nutrient contamination in both urban and agricultural regions. One of the reasons for high loading in urban areas is the tendency to over-fertilize lawns (Nielson and Smith, 2005).

Some of the lessons learned about runoff in agricultural and turf research provide insight into urban runoff. Studies of irrigation practices in agricultural areas (Baker and Richards, 2002) have indicated that nutrient loadings to streams can be reduced by improving infiltration (e.g., reducing impervious surfaces and allowing for more gradual irrigation). Planting tall grass reduced golf course nutrient runoff (Moss et al., 2006). Shuman (2002) reported that runoff volume depends on intensity and antecedent soil moisture. They measured nutrient concentrations in runoff from controlled plots, and found NO_3-N increased from around 1 to 1.5 mg/L in a second infiltration event following initial wetting. They attribute the increase in concentration to more soil moisture and more time for ammonium to oxidize to nitrate. The amount of loading was proportional to amount of fertilizer used.

Urban runoff has not been studied as much, but there are several research reports which have quantified release of nutrients. Fong and Zedler (2000) found that both an urban stream water and sediment contributed to release of nutrients to an estuary plagued by algal blooms. Density of housing was correlated with nutrient concentration (P and organic N) from six urban streams (Carle et al., 2005). Age of homes and contiguous impervious surface were secondary factors in predicting loading. Even highways contribute significantly to nutrient loading because of accumulation near the roadside on berms and landscape areas (Reginato and Piechota, 2004). A nation-wide study of 99 urban basins was conducted by the USGS (Driver and Tasker, 1990) to develop regression models to predict contaminant loadings. Key factors were drainage area and amount of rain; land use and impervious surface were also factors in some cases. The regression coefficients (R^2) in the models were between 0.2 and 0.65. The USGS in Wisconsin measured phosphorous in stormwater from very specific sources of urban runoff: streets, driveways, lawns, parking lots, and roofs (Waschbusch et al., 1999). Streets and lawns were found to be the biggest source of phosphorous that leads to eutrophication in local lakes.

Rates and fluxes of nitrogen have been measured in a Long Term Ecological Research (LTER) project in an urban watershed in Baltimore. Nitrogen input to the urban system came from nearly equal amounts of lawn chemicals (estimated by usage surveys) and atmospheric deposition (Groffman et al., 2004). In agriculture systems, significant portions of nitrogen are flushed through the streams, but in the urban/suburban system studied, 75% of the nitrogen was retained rather than moving out through the streams. This urban system produced more nitrate than a paired forested watershed because the water table was lower (enhancing nitrification, slowing denitrification) and because there were more sources of nitrogen in the urban system (Groffman et al., 2002). The rapid movement of water through stormflow and stormpipes reduced the influence of the riparian zone in nitrogen cycling.

Typically, urban stormflow is captured by storm sewer systems and discharged to streams or to drainages that become part of the local surface water basin. Relatively few studies have been conducted on storm pipe discharge. One such study was conducted by LeBoutillier et al. (2000) who monitored storms for 5 years (28 precipitation events) in an urban storm drain in Saskatchewan. They tested the hypothesis that nutrients build up between storms, then are flushed out. They created a model that incorporated antecedent conditions, amount and duration of rain by using stepwise regression on the observed NO_3-N and PO_4-P concentrations. However, when using partial data sets to predict concentrations, the models were not particularly accurate (up to 88% error). The relative importance of factors such as rainfall intensity and time since last rain could be predicted, but not the concentrations. These data confirm that there are multiple factors involved in mobilizing nutrients, and the factors probably change over time.

Purpose

We initiated a study of stormpipe discharge at the request of a local watershed association and citizen's group, concerned about the impact of urbanization on stream water quality. As such, we designed a low-cost screening study to assess whether lawn care products were a significant source of water quality degradation. Thus, the scope of the project was to find simple screening tools for assessing stormwater, conduct sampling that had not been done before, and identify future needs.

In addition to answering a basic question about the stream water quality, another purpose of this project was to develop a "point source" understanding of what is generally believed to be a "non-point source" of contamination to streams. Specifically, we conducted an assessment of urban runoff in the Wissahickon Creek watershed of southeastern Pennsylvania by monitoring stormwater at the point of pipe discharge.

The questions we addressed were as follows. What are the concentrations of nutrients and organic lawn chemicals found in the storm discharge? Do the concentrations vary with different storms or different times of year? Are the concentrations affected by neighborhood characteristics? And are antecedent conditions influencing concentrations?

Methods

Study area

The Wissahickon Creek watershed is located in the northwestern suburbs of Philadelphia, PA and encompasses 13 townships or municipalities. The creek originates in the suburban area then travels southward to discharge in the Schuykill River in Philadelphia and on to the Delaware River (Fig 1). The Philadelphia Water Department withdraws water for the city water supply 0.4 km below the confluence with the Schuykill. Five of the municipalities discharge treated wastewater to the Wissahickon creek daily. The 165 km^2 area is predominantly wooded (40%) and residential (39%) but also includes open land (17%) and commercial property (4%). The area has seen a rapid growth rate in recent decades.

The Philadelphia Water Department conducted a bioassessment of the basin in 2001 (Butler et al., 2003). They examined benthic populations, fish, and water quality at 15 locations. Based on lack of diversity and decline of sensitive species, all locations were listed as impaired, with 9 of them severely impaired.

Six storm pipes were selected for sampling in neighborhoods near Ambler, PA representing typical suburban development (Fig 1). The storm pipes captured the runoff from streets and lawns and carried it underground to the discharge point. We obtained maps of storm grates on the streets and pipe networks from two local townships, and the capture areas were delineated by a combination of engineering maps and field reconnaissance of the local topography since the piping typically followed topography. None of these areas had combined sewage and storm water drains.

The sites were selected from the township maps to provide a variety of lot sizes and drainage areas (Table 1). The name of each site came from either the neighborhood or from the location of the pipe discharge. Three of the neighborhoods (Ridings, Greystone, and Wissahickon-North) had more than 50 homes, with large lot sizes (approximately 2000 m^2). Two of the neighborhoods were smaller, one with large lot size (Beecham) and one with small lot size (Meadowbrook, approximately 1000 m^2). Meadowbrook had the highest density of residences, and the other neighborhoods were similar (see lot size). Only the Wissahickon-N neighborhood had a storm pipe that discharged directly to the Wissahickon. Two neighborhoods discharged to a large tributary, Prophecy Creek: Greystone directly to the Prophecy Creek and Ridings through a drainage 150 m from the creek. The other two neighborhoods (Beecham and Meadowbrook) had pipes that discharged to stormwater drainages rather than the creek.

The sixth pipe was selected as a control because it drained a small undeveloped field on township property called Robbins Park. This grass field received no lawn chemicals. A 15 cm plastic pipe drained water from a field to prevent flooding of the parking lot. However, the drainage area for this pipe was not clearly delineated, and it was suspected that some runoff from neighboring lawns may have been captured. Furthermore, the small size of the drainage area made it more susceptible to additional sources of runoff.

Sampling

Samples were collected inside the storm pipes. We instrumented the sites with automatic samplers from Global Water®. The samplers were secured by chaining them to a cinderblock and locking. These samplers turn on when the water level in the pipe rises enough to trigger a sensor. The sensors were set approximately 1 cm above the dry pipe and the intake was placed inside the pipe. The samplers had two 4 L plastic collection bottles. One bottle filled as soon as the stormwater turned on the sampler. This is called the first flush sample. The second bottle filled gradually over the course of the stormwater discharge. This is called a composite sample. Composite sampling potentially blurs peaks. The sampler was programmed to fill 500 mL every 30 minutes, thus collecting 4 hours of stormwater. The average length of a rainfall event in the area was 4 hours, based on rain gage data. The storm length was estimated be similar to discharge time because of the fast response, but there was variation from storm to storm. Thus, the collection interval of the composite sample was not a true average over the course of every storm. As a check on compositing, a 24-bottle ISCO® sampler was used at the Beecham site for a storm in August 2003. This 24-bottle sampler was set to collect samples hourly, and compared to the 2-bottle sampler used simultaneously.

Samples were collected from March through October or November over the course of two years. The samplers were removed during the winter months. During the other three seasons, typically two storms per month were collected. The number of samples collected depended on the weather and on equipment stability. If there was water in the pipe in between storms, a grab sample was collected during site visits. These samples are referred to as "pipe" samples, taken between storms. In addition, at two of the sites located on creeks, a creek sample was taken during site visits. The two creeks were Wissahickon Creek and Prophecy Creek.

Samples were collected within 48 hours of the storm events. A small aliquot of the 4 L bottle was poured off and the remaining sample discarded. All samples were refrigerated until analyzed.

Three times per year samples for herbicide analysis were collected. A 4 L glass bottle was placed in the sampler to collect a composite sample. The sampler would only accommodate one glass bottle, so the resulting sample represented a composite for the entire storm. The bottles were washed in dilute hydrochloric acid before use. The samples were stored on ice and taken to the Philadelphia Water Department for analysis shortly after collection.

Rain data were available from a rain gage at the Ambler Wastewater Treatment plant, situated roughly in the middle of the study area (Fig 1). The rain gage recorded continuously, and data were transcribed to obtain daily rainfall rates for the entire study period.

Concentrations of nitrogen and herbicides were measured, but not loading (i.e., not flux or mass). Concentrations provide a screening tool to determine whether the storm pipe lawn chemical concentrations are beyond levels that cause degradation; if the concentrations are not high in either the first flush or the composite samples, then there are probably not a significant periods of loading during storms to provide concentration spikes in the stream.

Chemical Analysis

The primary indicators for lawn care chemicals selected were nitrate, ammonium, and phosphate, all components in fertilizers and weed and feed products. A complete suite of major dissolved cations (including potassium, K^+) and anions (including chloride, Cl^-) were measured using a Dionex DX-500 ion chromatograph. Nitrate and ammonium concentrations are reported as nitrogen (NO_3-N and NH_4-N). The form of reduced nitrogen in the stormwater samples was mostly likely NH_4-N (ammonium) based on typical rainwater pH (below 6). The detection limit was 0.5 mg/L for NO_3-N and NH_4-N. The detection limit to screen for PO_4-P was 0.5 mg/L, but only 10 samples had detectable concentrations so further data were not reported.

In addition to the indicator elements, specific herbicides were analyzed periodically. The herbicides were analyzed at the Philadelphia Water Department (PWD) using a gas chromatograph with mass spectrometer detector (GC-MS). PWD used EPA method 515.3 which includes 19 herbicides.

Statistical methods

We used a variety of statistical methods to look for causal relationships between concentrations observed and environmental factors. Spearman and Pearson correlations were used to assess whether concentrations of different ions pairs were correlated (at the 95% confidence level). Pearson assumes normal distributions whereas Spearman is non-parametric. All possible regression and step-wise multiple regression were used to try to find a model of environmental factors that could predict the NO_3-N concentrations. Concentrations from first flush samples were used. We examined all samples, and also examined a subset of samples with NO_3-N greater than 1.5 mg/L to assess the impact on high concentrations only. This concentration was selected based on the nationwide study of urban stream quality by the USGS (USGS, 1999) and typical concentrations leading to eutrophication (U.S. EPA, 2000b). Regression statistics were also used with just two components: peak NO_3-N and one environmental factor. To compare neighborhood characteristics, rank regression was used since the characteristics did not vary continuously. Rank regression substitutes the rank for the actual value, i.e. number of homes and basin size. Lot size did not vary enough to be considered. The peak NO_3-N was used to represent discharge concentration when lawn chemicals were in use. Two locations were omitted from the rankings. The small (0.5 Ha or 1 acre) untreated field was omitted because the sampling was more limited and it did not have neighborhood characteristics. The Greystone site was eliminated because the concentrations were similar to the creek during storms and the sampler may have collected backwash instead of stormflow from the pipe. To compare populations from the first year to the second, a T-test and an Aspin-Welch test (non-parametric) were used. In calculating averages, samples below the detection limit are treated as zero concentration.

Results

Approximately 500 samples and 30 storms were analyzed in the two years of the project. Of the rain events sampled, 10 were greater than 2.5 cm, including a tropical storm of 16 cm (6/16/01). Time between sampled rain events varied from 2 to 35 days, with a mean of 10 days. Summary plots of the nitrogen data and tables of the herbicide data are available on the web at www.temple.edu/geology/gg.

NO_3-N

The NO_3-N concentrations in stormwater (Fig 2, Table 2) varied between the limit of detection and 6.5 mg/L. The highest concentrations were seen at Ridings and Wissahickon-N (two large neighborhoods), where summertime peak concentrations around 4 mg/L were observed. The mean concentration of NO_3-N in the sampled stormpipes (0.7 to 1.7 mg/L, Table 2) is only slightly higher than the USGS background (0.6 mg/L). The range in Total N concentrations in urban streams from the USGS study was 1 to 5 mg/L (with one outlier at 15 mg/L).

A limited number of samples were collected at the small field that did not receive lawn chemicals. Equipment down time and failure of the pipe to fill sufficiently with water inhibited sample collection, and reduced the number of samples by 1/3. The concentrations observed were 0 to 3 mg/L except for one sample (7/10/02) which reached 5.2 mg/L. These concentrations are not significantly different from those observed at the neighborhoods. The recharge area for the pipe could extend beyond the field to nearby yards. Thus, it may be difficult to obtain a true background concentration within this urbanized area with only limited zones restricted from lawn chemical use.

The variation in concentration through time was not uniform from site to site. There was no specific storm that mobilized NO_3-N more than another, although the highest observed concentration in the neighborhood stormpipes (4.5 mg/L at Wiss-N) was observed in the summer. Because the timing of the peak concentration was not uniform, these increases might be attributed to a local application of lawn chemicals, but there is no information to determine the exact source.

In the second year of study, the NO_3-N did not rise above 3 mg/L in the summer (Fig. 2) except for one apparently anomalous sample from the small field on 7/10/02. The summer of 2002 was a drought year, and there were restrictions on lawn watering. It may be that homeowners avoided fertilizing their lawns when there was no rain and they could not water the lawns. Nonetheless, the average concentrations from one year to the next were similar. A two-sample T-test indicated that mean NO_3-N values were not significantly different.

There was a correlation between the first flush and the composite samples but the R^2 was only 0.4. Furthermore, the highest concentrations of NO_3-N alternated between the first flush, composite, and pipe samples (Fig. 3). If the first flush sample was higher than the composite, it would indicate the NO_3-N mobilizes quickly. Instead, the means differed by less than 0.5 mg/L (Table 2). The similarity between samples suggested that variability through the storm was not high.

Concentrations of NO_3-N in pipe samples (between storms) varied from non-detect to 5.8 mg/L, but most samples were less than 3 mg/L (Fig 3). Thus, the overall water quality did not change significantly during storms. In other words, NO_3-N was mobilized by stormwater, but the concentrations were nearly constant. For a storm in August 2003 where samples were collected hourly in addition to the composite sample, the range in NO_3-N concentrations was from 0.2 to 1 mg/L. The average concentration was 0.5 mg/L and the composite concentration was 0.7 mg/L. The difference between the average and composite was small, basically within analytical error.

Concentrations of NO_3-N in Prophecy Creek were similar to those observed in the Greystone stormwater, which directly discharges to the creek. Occasionally higher concentrations (4 mg/L) were observed in the creek; this suggests additional sources of NO_3-N upstream. During high water level, creek water was observed to flow back into the pipe. This backflow perhaps dilutes the stormwater samples collected from the pipe at Greystone. The Greystone site had the lowest concentrations overall. The Ridings stormpipe also drains to Prophecy Creek, but travels through a buffer zone (approximately 150 m). In the summer and winter of 2001, the concentrations at Ridings were 2 to 3 mg/L higher than the creek. The Wissahickon-N stormpipe discharges directly to Wissahickon Creek. The creek reaches higher concentrations (Fig 3) in the fall of 2001 and summer of 2002 (up to 8 mg/L with the stormwater peak only 6 mg/L). Again, this suggests additional sources of NO_3-N upstream (such as wastewater discharge) are adding more nitrogen than runoff from lawns and streets. There is a municipal sewage treatment plant 6 km upstream.

NH_4-N

Ammonium (NH_4-N) was only analyzed at a few sites the first year because it was originally believed that the NH_4-N would oxidize to NO_3-N in the soil or storm pipes. This transformation, called nitrification, is common in soils where both microorganisms and oxygen that facilitate the two-step reaction are readily available (Focht and Verstraete 1977; Buss et al., 2004). Because detectable levels were found, NH_4-N was added to the analysis for all samples the second year of the study.

The NH_4-N ranged from non-detect to 7.5 mg/L (Table 2), and there were a considerable number of non-detectable concentrations at every site, giving the NH_4-N concentrations a more variable pattern (Fig 4). Concentrations above 3 mg/L were observed in different seasons, most commonly from the Ridings and Wiss-N sites. NH_4-

N was not detected in creek samples or pipe samples collected after the storm, again suggesting that it was oxidized through microbial mediation except where transported rapidly. The NH_4-N was a significant portion of total N in solution when present, typically more than 60%.

Potassium

Potassium (K) can occur as a nutrient in lawn care products, but it is also present in road salt and natural organic matter. With multiple sources, the K concentrations varied throughout the year and higher concentrations were not correlated with nitrogen. Concentrations of K over 10 mg/L were found in first flush, composite, pipe, and creek samples at all times of the year. Concentrations varied from non-detect to 29 mg/L.

A comparison between the K:N ratios in the Wissahickon Creek and the storm discharge provides insights into sources of nitrogen. There is a significant correlation ($R^2 = 0.89$) between K and total-N in the Creek (Fig 5). The molar K:N ratio in Wissahickon Creek is 0.7 $\pm$ 0.1 (2.1 $\pm$ 0.2 weight ratio). This is within the range observed in stream-water output from temperate deciduous forests (e.g., Likens and Bohrmann, 1995). The relation between N and K suggests that weathering of plant material dominates the concentration of these nutrients in the creek. This is consistent with the upstream sewage treatment plant as a source of these nutrients in the creek.

In contrast, there is no correlation between K and total N in storm water (Fig 5). The data form a scatter plot, with K:N ratios ranging from 0.5 to 13. If the source of the nutrients was lawn chemicals, rather than biological, one would expect variation in the ratios because lawn product ratios vary, and also uptake of the nutrients can change the ratios. The distinctly different plots for the creek and the stormwater are evidence that the nitrogen concentration of storm discharge has a different source, and the high K suggests the source of N is lawn chemicals, not just atmospheric deposition of nitrate.

Herbicides

Herbicides were analyzed in samples from April and June the first year of the study, and from April, July, and August of the second year of the study. Two samples were collected in the summer of the second year, since this was the time of year when the nitrogen was observed to be highest the first year, and it was thought that the runoff from other lawn chemicals might also be higher at this time.

Most of the herbicides were below detection. There were no detections in April 2001 and July 2002. There were mostly non-detects and only a few low levels (1 to 7 μg/L) of herbicides in June 2001, April 2002, and August 2002. The following herbicides were detected at one to three sites: 2,4-D (2,4-Dichlorophenoxyacetic acid), Dicamba (3,6-dichloro-2-methoxybenzoic acid), Bentazon (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide), and Triclopyr (3,5,6-trichloro-2-pyridinyl oxyacetic acid). All of the herbicides detected are used on broadleaf weeds. Dicamba and Bentazon are soluble, but considered to be only slightly toxic (to both humans and aquatic life). There are no known reports of long-term health effects due to exposure. A drinking water standard for Bentazon has been established at 20 μg/L. The analyses reported here are well below that (a maximum of 5 μg/L). The herbicide 2,4D is a skin and eye irritant, and toxic only at very high doses. The levels found in this study were less than 7 μg/L.

In summary, most of the herbicide analyses showed non-detect. A few relatively mobile but low-toxicity herbicides were detected sporadically. The concentrations were below drinking water standards.

Examination of environmental factors using statistical analysis

Pairwise correlations between each of the ions analyzed were examined by calculating matrices of Pearson (parametric) and Spearman (rank, nonparametric) correlation coefficients (r_p and r_s, respectively). A positive correlation between ions would be an indication that dilution by low ionic strength rainwater is occurring. Lack of significant positive correlation is an indication that other reactions or sources influence the concentrations. In the Wissahickon Creek, significant correlations were found among the ions. As previously discussed, NO_3-N and K were positively correlated, with $r_p=r_s=0.9$; similarly Cl (a conservative ion) and NO_3-N were also significantly correlated, with $r_p=r_s=0.6$. The confidence level, indicated by the probability of incorrect prediction (p) was <0.01 in these tests. The K:N ratio was discussed in a previous section; positive correlation between other ions suggested that dilution is a factor in the variation in concentrations of Wissahickon Creek water.

In the storm water samples, correlation coefficients were calculated for all the cations and anions, and no correlations were found between NO_3-N and other ions. Two examples shown (Fig 6) were typical: NO_3-N vs. NH_4-N and NO_3-N vs. Cl were not significant with both r_p and $r_s<0.2$ and with $p=0.3$ and 0.2, respectively. These examples were typical for both first flush and composite samples, and for individual sites. The changes in concentration observed from stormwater were apparently not due to dilution alone.

To look at the influence of neighborhood characteristics, a rank regression was used. The characteristics considered were area and number of residences. A correlation was observed between the number of homes and peak NO_3-N as well as between the total area and peak NO_3-N. As the total area and number of homes increased, the peak NO_3-N increased with r_s and r_p of 0.8 and 0.85, respectively ($p < 0.0001$). The correlation observed would not be due to greater surface area alone, because the increase in surface area would also increase the discharge, thus resulting in similar concentrations. Instead, the correlation may be related to usage of lawn chemicals at individual homes. As the number of homes and area increase, it may be more likely that homes using lawn chemicals are part of the area, which results in nutrients being transported in the stormwater discharge. When there are a smaller number of homes, the likelihood that treatment has been applied decreases. Thus, the observed concentrations seem to be linked to localized occurrences of lawn chemical application. Although correlation was observed, it is important to note that the data set was limited (small ranges in concentration and small number of ranks). Thus, the interpretation may not help predict concentrations.

Storm characteristics were also examined. For each of the dates sampled, the total rainfall and the time since the last storm were recorded. There was no correlation observed between time since last storm and NO_3-N or NH_4-N (Fig. 7a, shown for Ridings site). There was no significant correlation between amount of rain and NO_3-N in the first flush or the composition samples (Fig. 7b) or for NH_4-N concentrations at any of the sites.

While it is likely that storm characteristics play some role in transport of nutrients, it would seem that the nutrient concentrations are influenced by other factors. If several homeowners apply lawn chemicals at similar times, even a small event might trigger a release. It is even possible that topography and location of certain plots make them more influential in nutrient loading. There was not enough information to consider these factors in the analysis.

The multiple regression techniques were used to address the possibility that several environmental factors, not just one, simultaneously influence NO_3-N concentrations. The results showed no significant correlation with NO_3-N concentrations (Table 3). Six factors were considered: season (Julian day), total precipitation (ppt), time since last rain, number of residences, plot size, and total basin area. All of the nearly 60 different combinations involving six independent variables were tested, and the best R^2 are shown for each combination of factors (all 6 factors, then decreasing by 1 progressively). None of these R^2 were significant, however. Multiple regression did not provide a good prediction of NO_3-N concentrations.

Lessons learned and future work

Although conducted as a screening study, some important lessons from this project are that (1) it is difficult to predict concentrations of lawn chemicals in storm pipes based on environmental factors (e.g., lot size, rainfall amounts), and (2) there are cases where more detailed sampling such as conducted here is beneficial and cases where it would not be.

A model to predict concentrations based on environmental factors could not be obtained for the stormwater dataset from the Wissahickon basin. The reasons for variation in concentration are likely related to a combination of factors, but also missing information. Specifically, lack of information on timing of homeowners' applications of lawn chemicals could play an important roll because source term variations are ultimately responsible for discharge concentrations. In our data, the periodic concentration spikes at one discharge point, but not others for the same storm suggest that local source terms vary and influence the discharge concentration. Furthermore, the correlation between basin area and peak NO_3-N may relate to timing of homeowners' applications since area alone would not increase NO_3-N.

Even though this work was conducted as a screening study, the variation observed points out difficulties in interpreting monitoring data. Our data showing variation within seasons and among similar storms points out the difficulties in detecting source terms with more limited sampling. Seasonal sampling may miss the peak, as there isn't a "typical" concentration for each season. Sampling only a certain storm type (dry antecedent conditions or a certain intensity) may miss the peak because lawn chemical application timing varies.

This variation also makes non-point source discharge difficult to control. But the question arises, is the cost of detailed monitoring going to lead to benefits? The answer depends on three issues: stream quality, the type of contaminant, and the need for background information. First, stream quality should be determined to decide where storm discharge needs to be monitored. From this, one can decide if an occasional spike has any significant impact on overall stream quality. In Prophecy Creek, the stormwater discharge was higher than the creek concentrations, and detailed monitoring may show whether the stormwater is an important source term. In Wissahickon Creek, an upstream source (i.e., the sewage treatment plant) led to higher concentrations in the creek, so the occasional spike in concentration did not lead to a spike in the observed creek nitrogen concentrations. Second, some contaminants will not be diluted during storms. For example, organic contaminants can sorb to sediment or bioaccumulate. Detailed monitoring to measure the spikes is important because they may be the main source of loading. A third issue to consider is whether there is benefit from collecting background information. Sometimes non-point sources are suspected of larger loadings than occur, and relatively inexpensive but detailed storm monitoring such as conducted here can establish possible ranges in concentration, perhaps eliminating a source term.

A strategy that could be effective is to identify a monitoring point in the stream that integrates water quality factors. After determining the overall health of the stream, target points for more detailed monitoring can be added to the plan. The detailed monitoring should be continuous if possible to find both seasonal and within season variation such as observed in this study.

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made two years of rainfall records available, and township engineers (Upper Dublin and Lower Whitpain) provided maps of storm pipe networks.

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Table 1: Site characteristics

NAME	TOWNSHIP	CREEK/ DRAINAGE	APPROX AREA, Ha	APPROX # RESIDENCES	AVE LOT SIZE, M^2
Ridings	Whitpain	Prophecy	18	60	2040
Greystone	Whitpain	Prophecy	18	100	1860
Wiss N	Whitpain	Wissahickon	12	60	1860
Beecham	Upper Dublin	Rose Valley (N)	4	20	2040
Meadowbrook	Upper Dublin	Tannery Run	2	15	1115
Robbins Park	Upper Dublin	Rose Valley (N)	0.4	0	NA

Table 2: Summary of nitrogen concentrations (NO_3-N and NH_4-N) for each site.

	RPP	Beecham	Ridings	Greystone	Meadowb	Wiss N	Prophecy Creek	Wissahickon Creek
PIPE NO3 AVE	**0.9**	**2.1**	**1.1**	**1.3**	**1.3**	**1.4**	**1.1**	**3.2**
PIPE NO3 PEAK	1.4	2.6	3.1	3.0	2.2	5.8	2.3	7.5
PIPE NO3 n	10	15	25	33	24	13	20	25
FIRST FLUSH NO3 AVE	N/A	**1.2**	**1.3**	**0.7**	**1.1**	**1.1**		
FIRST FLUSH NO3 PEAK		3.0	3.6	2.4	2.2	3.9		
FIRST FLUSH NO3 n		16	31	25	21	27		
COMPOSITE NO3 AVE	**1.7**	**1.6**	**1.3**	**0.6**	**1.1**	**1.1**		
COMPOSITE NO3 PEAK	5.2	3.3	3.6	2.5	1.9	3.1		
COMPOSITE NO3 n	12	16	30	24	29	25		
PIPE NH4 AVE	N/A	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
PIPE NH4 PEAK		0.0	3.1	0.0	3.8 (1 value)	0.0	0.0	0.0
PIPE NH4 n		9	19	13	15	5	10	11
FIRST FLUSH NH4 AVE	**0.7**	**1.1**	**2.1**	**0.3**	**0.0**	**1.0**		
FIRST FLUSH NH4 PEAK	2.3	3.4	7.4	1.0	3.5 (1 value)	6.3		
FIRST FLUSH NH4 n	12	11	18	12	15	11		
COMPOSITE NH4 AVE	N/A	**1.5**	**1.2**	**0.6**	**0.1**	**0.3**		
COMPOSITE NH4 PEAK		3.7	4.5	4.6	1.8	1.1		
COMPOSITE NH4 n		11	23	12	16	11		

PIPE samples were collected from pipe or creek after storm
N/A means insufficient samples for statistics
n is number of samples, lower for NH4 because only a few samples were analyzed the first year of the study

Table 3: Examples of sets of environmental factors used in multiple regression to predict NO_3-N concentrations. Factors: A=ppt,B=days since last rain, C=Julian day, D=catchment area, E=number of residences, F=lot size.

VARIABLES	**NO_3**	**R^2**
ABCDEF	all NO_3	0.12
ABCDEF	$NO_3 > 1.5$	0.07
BCDEF	$NO_3 > 1.5$	0.06
CDEF	$NO_3 > 1.5$	0.06
DEF	$NO_3 > 1.5$	0.06
DE	$NO_3 > 1.5$	0.04

FIGURE CAPTIONS

Fig 1: Wissahickon Creek watershed with study area outlined, estimated basin areas of storm pipes sampled, and location of rain gage.

Fig 2: NO_3-N concentrations in first flush samples by site. Note that data are missing from Beecham Rd for the second year because the sampler was stolen.

Fig 3: Comparison of NO_3-N concentrations by samples type (first flush, composite, pipe sample collected between storms, and creek) for Wissahickon-N sampling site.

Fig 4: Concentrations of NH_4-N in first flush samples by site. Note that only limited samples were analyzed for NH_4-N the first year, and that data are missing from Beecham Rd for the second year because the sampler was stolen.

Fig 5: Correlation between total N (NO_3-N plus NH_4-N) versus concentration of K in the Wissahickon-N stormpipe (squares) and in the Wissahickon Creek (x's). Stormpipe showed variable K:N ratio while Wissahickon Creek showed nearly constant K:N ratio (R^2=0.9).

Fig 6: Comparison of selected ions in storm samples, showing dilution is not the primary factor in ion variation. Both NO_3-N v Cl and NO_3-N v NH_4-N had correlation coefficient of 0.1, p not significant. Data from all sites.

Fig 7: Nitrogen concentration versus rainfall effects at Ridings. No correlations are observed at this or other sites. (a) NO_3-N and NH_4-N concentrations in first flush samples versus time since last rain and (b) NO_3-N concentration in first flush and composite versus amount of rain.

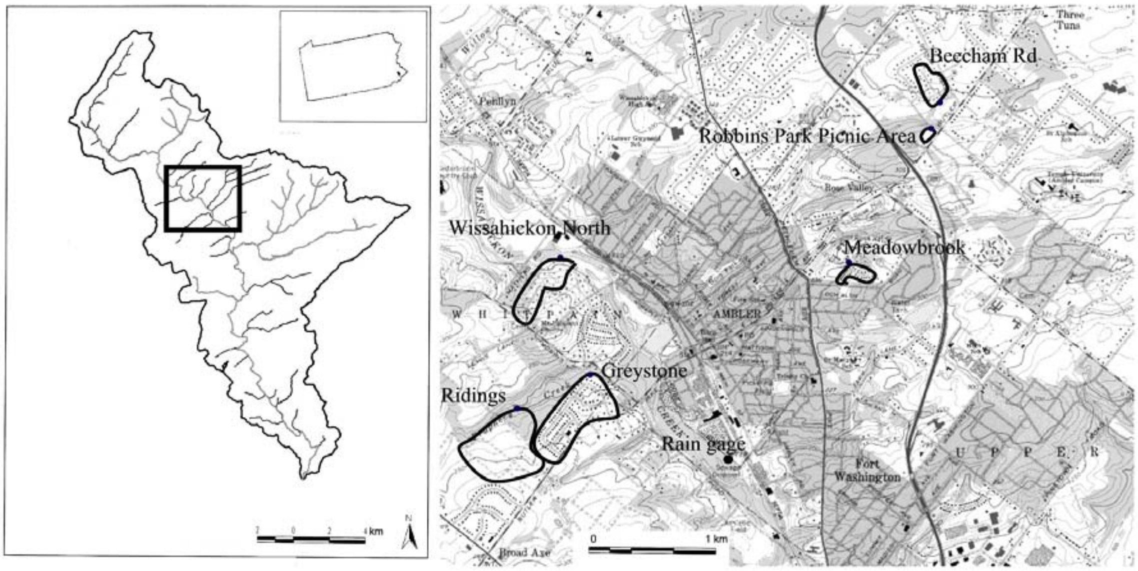

km
N
Three Tuns
Beecham Rd
Penllyn
Robbins Park Picnic Area
Rose Valley
Wissahickon North
Meadowbrook
W H I T P A I N
AMBLER
Greystone
Ridings
Rain gage
Fort Washington
U P P E R
0
1 km
Broad Axe

Figure 1

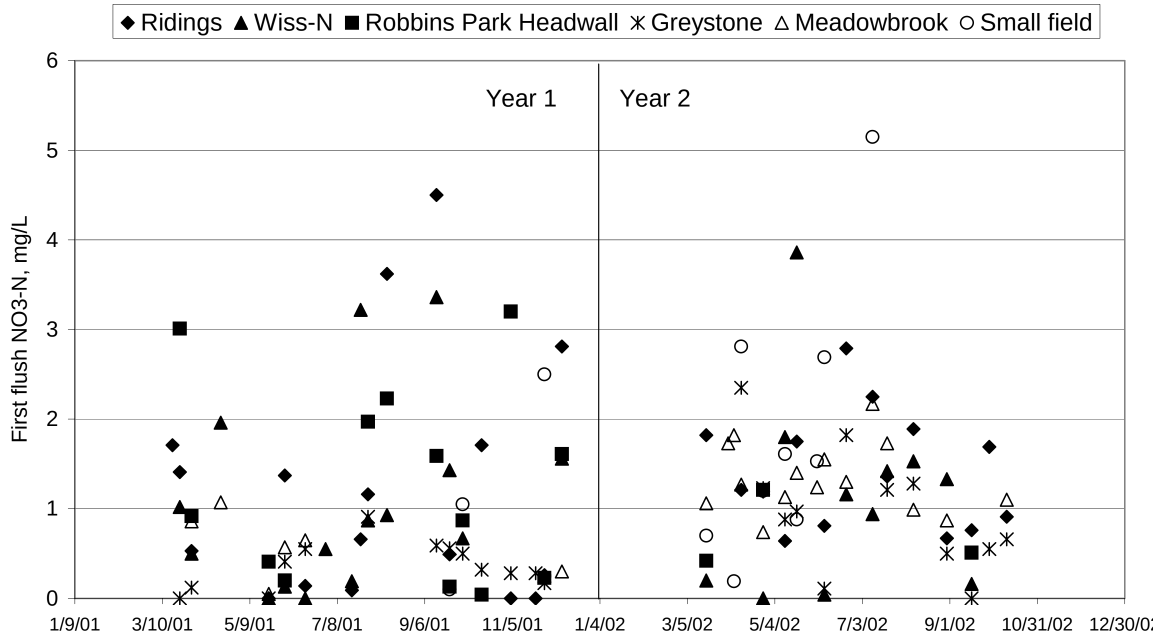
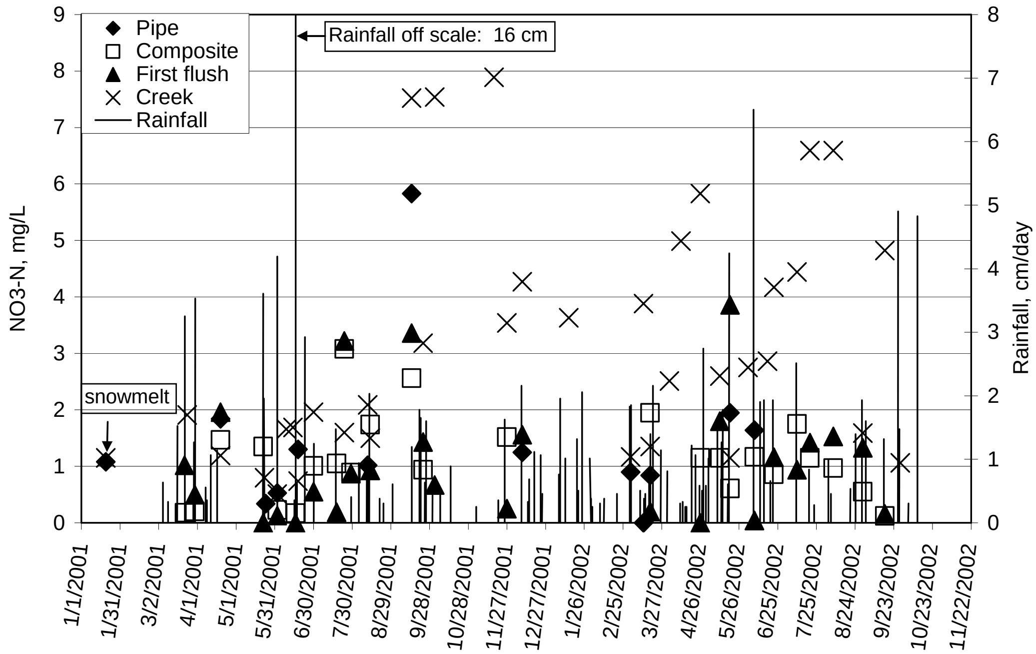

◆ Ridings ▲ Wiss-N ■ Robbins Park Headwall ✳ Greystone △ Meadowbrook ○ Small field
Year 1
Year 2
First flush NO3-N, mg/L
0
1
2
3
4
5
6
1/9/01
3/10/01
5/9/01
7/8/01
9/6/01
11/5/01
1/4/02
3/5/02
5/4/02
7/3/02
9/1/02
10/31/02
12/30/02

Figure 2



Pipe
Composite
First flush
Creek
Rainfall
Rainfall off scale: 16 cm
snowmelt
NO3-N, mg/L
Rainfall, cm/day
0
1
2
3
4
5
6
7
8
9
1/1/2001
1/31/2001
3/2/2001
4/1/2001
5/1/2001
5/31/2001
6/30/2001
7/30/2001
8/29/2001
9/28/2001
10/28/2001
11/27/2001
12/27/2001
1/26/2002
2/25/2002
3/27/2002
4/26/2002
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6/25/2002
7/25/2002
8/24/2002
9/23/2002
10/23/2002
11/22/2002

Figure 3

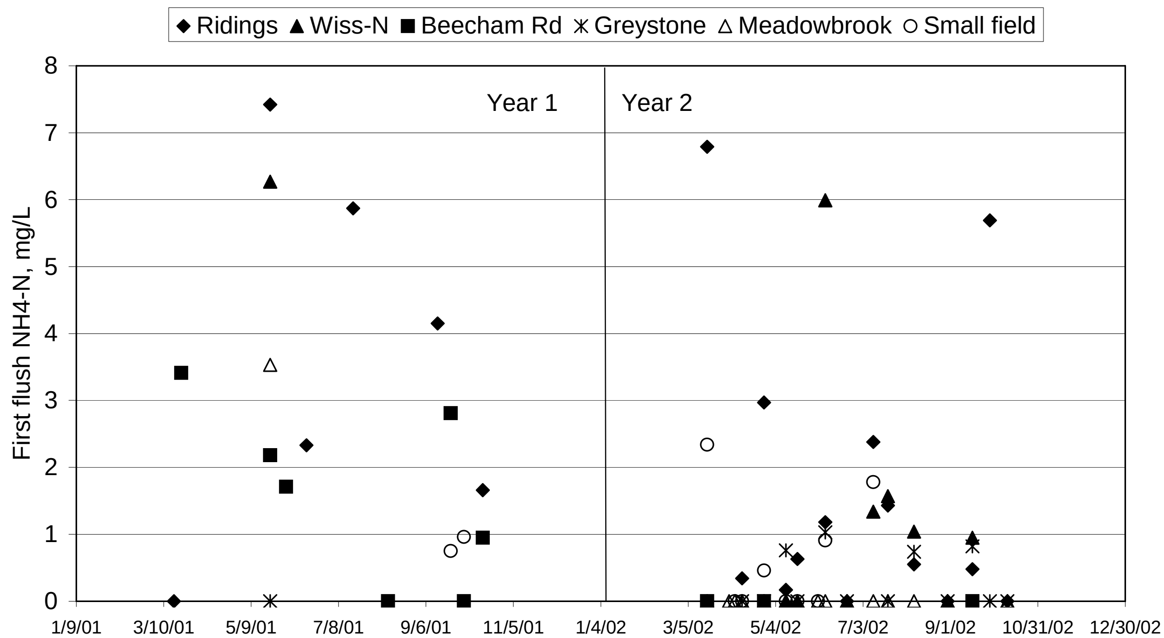
◆ Ridings ▲ Wiss-N ■ Beecham Rd ✳ Greystone △ Meadowbrook ○ Small field
First flush NH4-N, mg/L
Year 1
Year 2
0
1
2
3
4
5
6
7
8
1/9/01
3/10/01
5/9/01
7/8/01
9/6/01
11/5/01
1/4/02
3/5/02
5/4/02
7/3/02
9/1/02
10/31/02
12/30/02

Figure 4

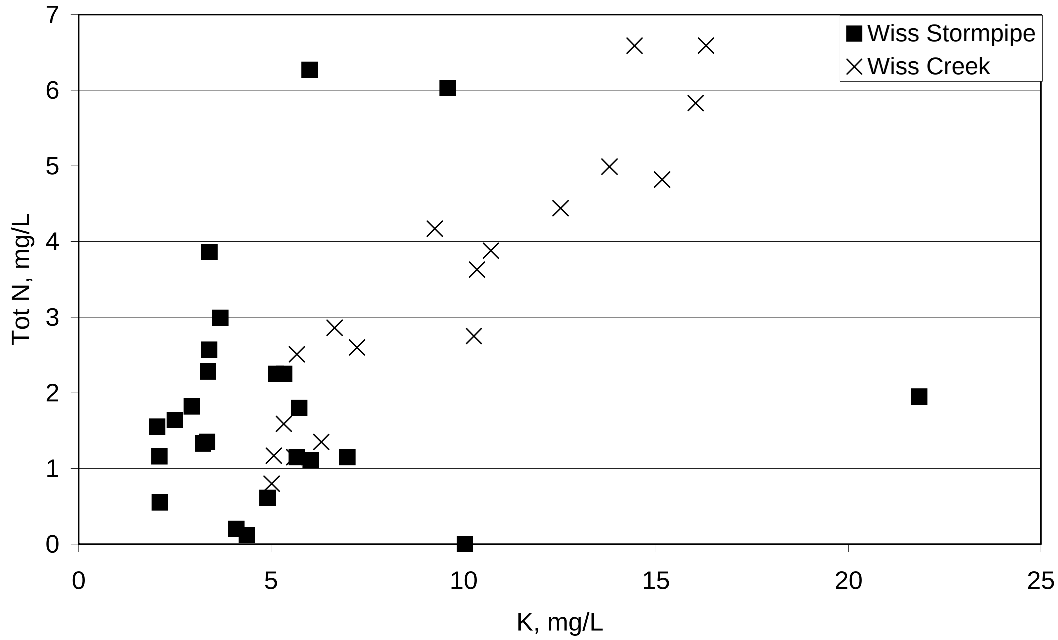
7
6
5
4
3
2
1
0
0
5
10
15
20
25
Tot N, mg/L
K, mg/L
Wiss Stormpipe
Wiss Creek

Fig 5

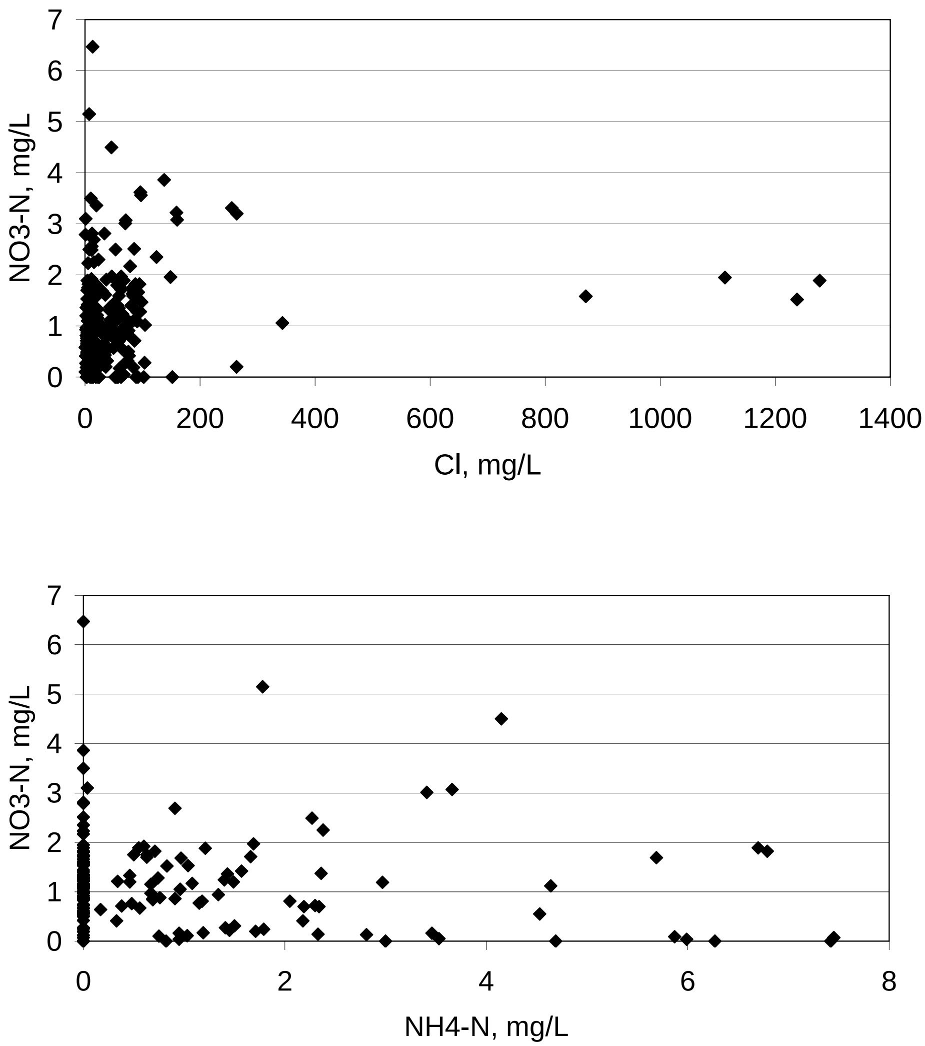
NO3-N, mg/L
Cl, mg/L
0
1
2
3
4
5
6
7
0
200
400
600
800
1000
1200
1400
NO3-N, mg/L
NH4-N, mg/L
0
2
4
6
8

Figure 6

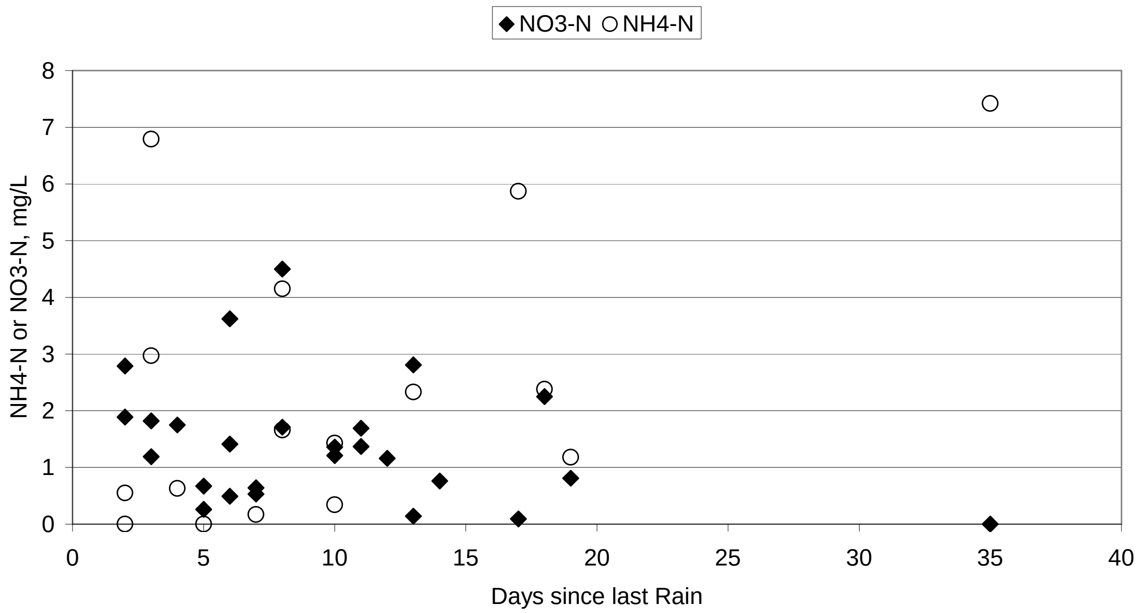

Figure 7a

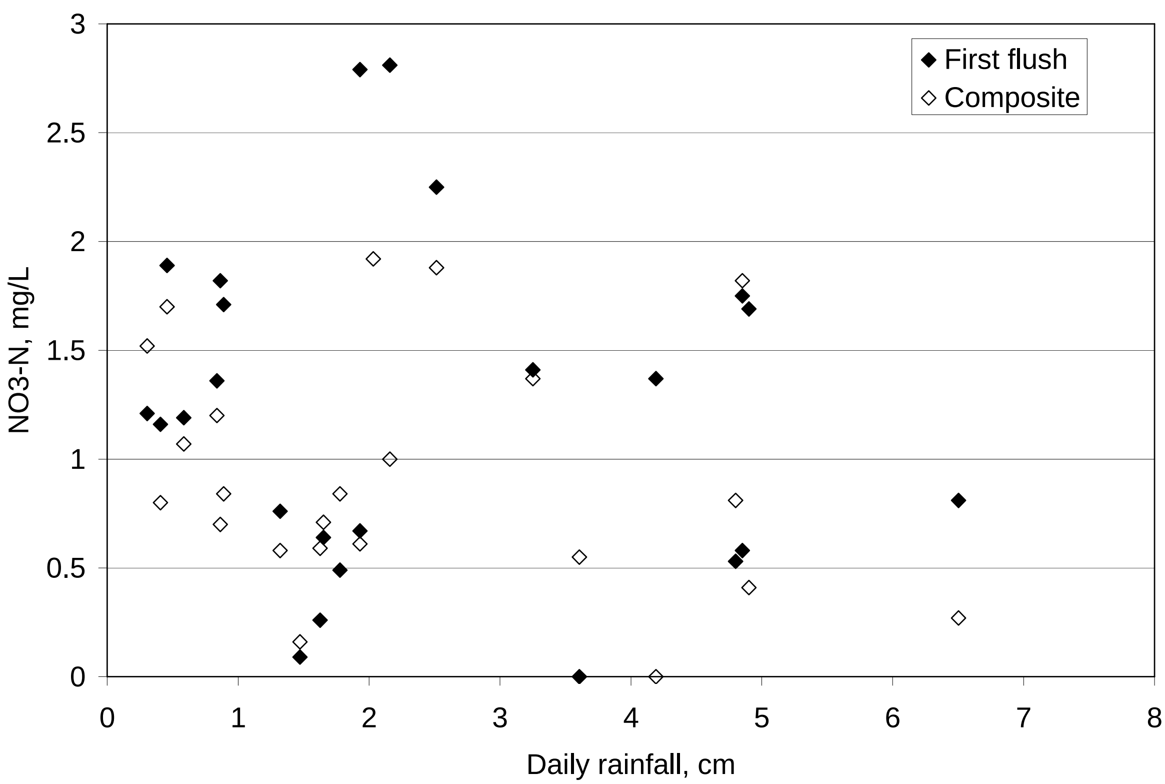

Figure 7b