SOURCES AND DYNAMICS OF REACTIVE NITROGEN TO AN URBAN WATERSHED

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Excess nitrate contributes to the overall degraded quality of streams in densely populated, human-engineered regions, compounding existing problems of pollution in urban landscapes. Urban watersheds receive and export reactive nitrogen (Nr) from a myriad of sources, including sewage, vehicular emissions, stationary source emissions, and lawn fertilizers, whereas forested systems receive Nr from atmospheric deposition and in-situ soil microbial communities. These sources are likely concentrated in urban areas, with the result that urban watersheds can contribute significant amounts of Nr to downstream waterways. Excess nitrogen contributes to downstream eutrophication of water bodies, as seen in large bays and estuaries such as the Chesapeake Bay and Gulf of Mexico. The excess Nr loadings from urban areas will likely increase in the future, as fossil fuel emissions are expected to rise and infrastructure such as sewer networks are expected to degrade over time. Identifying, quantifying, and understanding Nr in urban ecosystems is essential to success in efforts to manage and mitigate as future urban growth is realized.

Stable isotope analysis of nitrogen and oxygen in nitrate is an effective method of providing information about Nr sources and reactions in many ecosystems. Nitrate-nitrogen is persistent in the environment, easily transported via hydrological pathways, and has detrimental ecological effects. This work presents a comprehensive analysis of the sources and fluxes of nitrate to Nine Mile Run, an urban stream in Pittsburgh PA. Inverse modeling methods are used to estimate the extent of sewage leaking from the impaired pipe system and indicate DIN contributions from sewage range from 6 to 14 kg ha^{-1}yr^{-1}. Further, this work reveals that rates of DIN retention in NMR are 84%, on the high end of rates observed in other suburban/urban watersheds. Dual-isotope analysis of nitrate in water samples demonstrates during stormflows that proportionally, atmospheric deposition contributes 22% of nitrate to streamwater, and sewage contributes the remainder. Triple oxygen isotope analysis is used to unequivocally quantify the contributions of atmospheric deposition on streamwater nitrate in urban streams, with flux calculations using this technique indicating higher ADN export than observed through dual-nitrate isotope analysis.

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PREFACE

This successful dissertation is the result of a community effort on all fronts: research, educational, and personal. This community allowed me to thrive and complete the dissertation process, and I'm immensely grateful to all in my life who gave me so much.

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My husband, Kevin, has always been there every step of the way. Words cannot express how much he has given me, and sustained me.

1.0 INTRODUCTION

1.1.1 Nitrogen in urban systems

Nitrogen is the most abundant gas in the atmosphere, existing as the nitrogen gas dimer, N_2. However, most living things cannot access the large atmospheric reservoir of N_2 because substantial energy is required to break the triple bond between N atoms. Instead, gaseous N_2 must be "fixed" or transformed into biologically available forms, referred to as reactive nitrogen, or Nr. Before the industrial revolution, Nr was fixed by processes such as lightning, bacteria, and biomass burning. As a consequence of scant Nr availability, ecosystem productivity is generally limited by the availability of fixed nitrogen. Therefore, large sources of concentrated nitrogen, such as bird guano or accumulations of nitrate salts, were historically a source of wealth for overseas colonial empires (Smil 2001).

As human populations grew, nitrogen became essential to feeding growing populations. Population growth worldwide was limited by Nr availability; before chemical fertilizers were used, agricultural land could support only 5 people on 1 hectare of land (Smil 1997). The need for fertilizer to feed growing populations, as well as ammonia-nitrogen to create munitions, led Haber and Bosch to develop processes catalytically fixing gaseous N_2 into ammonia (Smil 2001). As fossil fuel use, chemical fertilizers, and populations all grew at exponential rates, Nr became abundant, and in some ecosystems, limits in productivity became controlled by other nutrients

(Galloway, Dentener et al. 2004), with some regions exporting Nr at rates 2-20 times as much as in pre-industrial periods.

Table 1.1 Forms of nitrogen discussed in text

Abbreviation	***Definition***	***Description***
Nr	Reactive nitrogen	Any form of nitrogen available to biota wherein strong triple bond has been broken
N_2	Diatomic nitrogen	0 oxidation number
TKN	Total Kjeldahl Nitrogen	Sum of ammonia-nitrogen & organically bound nitrogen but does not include nitrate-nitrogen or nitrite-nitrogen
DON	Dissolved organic nitrogen	
DIN	Dissolved inorganic nitrogen	Nitrate, ammonium, and nitrite
NO_3^-, NO_3^--N	Nitrate ion, and nitrate measured as amount of “N”	+5 oxidation number for nitrogen
HNO_3	Nitric Acid	+5 oxidation number for nitrogen
NO_2	Nitrogen dioxide	+4 oxidation number for nitrogen
NO_2^-, NO_2^--N	Nitrite ion, and nitrite measured as amount of “N”	+3 oxidation number for nitrogen
N_20	Nitrous oxide	+1 oxidation number for nitrogen
NH_3	Ammonia	-3 oxidation number for nitrogen
NH_4^+, NH_4^+-N	Ammonium ion, and ammonium measured as amount of “N”	-3 oxidation number for nitrogen

Excess reactive nitrogen, particularly in the form of nitrate (NO_3^-) is easily dissolved and transported in water, resulting in measureable concentrations that increase the effect of Nr on ecosystem health, biodiversity, and human health (Howarth, Billen et al. 1996). The contribution of Nr to downstream waters is positively correlated to human activity in watersheds, including population centers and agricultural lands (Caraco and Cole 1999) . Urban streams and surrounding watersheds contribute nitrate from multiple human sources including sewage, fossil fuel nitrogen emissions from cars and industrial sources, and lawn fertilizer to receiving waters. As a result of urban run-off and drainage infrastructures, urban watersheds and downstream receiving waters are commonly ecologically impaired (Walsh, Roy et al. 2005). Fluxes of Nr from cities are expected to increase in the future, as urban centers continue to grow (Walsh, Fletcher et al. 2005).

Recent studies focus on understanding the biogeochemical processes unique to urban ecosystems (e.g.(Hook and Yeakley 2005; Kaye, Groffman et al. 2006)) . Yet key questions remain about the mechanisms controlling delivery, transport, transformations, and export of Nr from urban watersheds to streams. The work presented here aims to identify and understand the dynamics of Nr sources and delivery to an urban stream via modeling and isotopic analysis.

1.1.2 Reactive nitrogen sources to urban streams

Urban systems generally receive Nr from multiple sources: atmospheric deposition, lawn fertilizer, human-sourced sewage, and legacy nitrogen from lands previously in agriculture (EPA 2012). Atmospheric deposition includes both wet and dry atmospheric deposition and in urban systems, is generally considered to result from fossil fuel combustion from stationary and mobile sources (Redling, Elliott et al. 2013). Dry atmospheric deposition includes particulate nitrate, as well as gaseous nitric acid (HNO_3^-) (CASTNET 2009). Although nitrogen dioxide (NO_2), ammonia (NH_3), and dissolved organic nitrogen (DON) contribute to total N deposition, these are not routinely measured at monitoring locations (Golden, Boyer et al. 2008). Wet atmospheric deposition species include dissolved nitrate (NO_3^-) and ammonium (NH_4^+) (NTN 2012).

Another possible nitrate input to urban systems is lawn fertilizer, which is commonly applied as ammonium nitrate. A study of fertilizer usage in Baltimore, MD found rates of fertilizer application were strongly dependent on factors such as house and neighborhood age, and income levels (Law, Band et al. 2004).

Leaky sewers and combined sewer overflows contribute Nr to urban ecosystems, although the extent of these contributions and the associated speciation is poorly understood. Urine comprises >80% of the total nitrogen in sewage, and the rest is in solids (Kirchmann and Pettersson 1995; Viessman, Hammer et al. 2009). Wastewater streams in anaerobic conditions are dominated by DON, with a smaller contribution of ammonium (Sedlak 1991; Pescod 1992). Environmental engineers generally measure DON and ammonium together in a single term, Total Kjeldahl Nitrogen (TKN) (ASA 2013). Leaking pipes would most likely introduce DON or ammonium to underground environments. These compounds are then subject to further oxidation (i.e., nitrification) in aerobic microsites in soils or near pipe fill, in degraded sewers, or in-stream. Nitrification of these inputs to nitrate, and to a lesser extent, to nitrite, constitute a poorly characterized but potential source of nutrients to urban streams (Eiswirth and Hotzl 1997).

While environmental engineers are reluctant to consider the fact that nitrification, a natural component of soil and in-stream nitrogen processes, can occur within or near leaking sewers (Parker 2013), through this work, we find evidence to the contrary (Divers, Elliott et al. 2013). Samples collected as part of this study were taken from shallow surface waters, moreover from a restored urban stream system engineered to oxygenate water via artificial hydraulic jumps. Sewers in this watershed drain a region with high relief (over 150 meters from head to mouth) and are known to leak (Edgewood Borough Sewer Operations and Maintenance Plan 2001). Given temperate climate and locally severe problems with stormwater runoff (which precludes a portion of rainwater infiltration), groundwater levels are likely dynamic and therefore assumptions of saturated soil conditions creating complete oxygen limitation would only apply to limited portions of the year if at all. These conditions create ample opportunity for substantial gravity head to develop and for aerobic soil conditions in near pipe areas around the aging pipe network. Aerobic biodegradation in unsaturated zones surrounding sewer leaks is well documented (Eiswirth, Hotzl et al. 1995; Eiswirth and Hotzl 1997). These conditions, conducive to converting ammonium to nitrate, would account for the low ammonium concentrations observed in the study stream. Lastly, headspace within sewers allows aeration and thereby provides aerobic conditions necessary for mineralization and then nitrification of organic N in sewage, even within the closed sewer environment (Neethling, Mah et al. 1989; Sydney, Esfandi et al. 1996). In summary, organic nitrogen originating from sewage can be transformed to nitrate in a number of well-documented environmental situations (Divers, Elliott et al. 2013).

The nutrient budget approach used in this work carefully characterizes potential sources of Nr, and concludes that without including sewage derived Nr inputs, the nitrogen budget cannot be closed. While this work and documented infrastructure impairments (Edgewood Borough Sewer Operations and Maintenance Plan 2001) indicate sewer-derived Nr is an important source of Nr to Nine Mile Run, it is clear that diverse disciplinary perspectives will likely be required to more fully unravel the complex interactions of Nr cycling and sources in urban systems that are a hybrid of built infrastructure and natural ecosystems.

1.1.3 Fate of nitrogen species in the urban ecosystem

The impact of Nr on downstream systems is strongly dependent on the hydrologic connectivity between nitrogen source and surface waters (Elliott and Brush 2006). Fertilizer is generally applied to upslope residential lawns (i.e., not in riparian areas), distant from surface waters.

Isotopic analysis of Baltimore streamwater lacks a fertilizer signature (Kaushal, Groffman et al. 2011), suggesting that fertilizer applied to lawn surfaces is retained via utilization by plants. Further, data suggests that lawns have a high capacity for N retention (Raciti, Groffman et al. 2011).

Similarly, atmospherically deposited nitrogen species are deposited relatively uniformly across the landscape. Atmospherically deposited nitrogen species deposited on permeable land surfaces (such as lawns or urban parkland) is likely to act as fertilizer, and be utilized by plants, and is therefore likely retained via utilization (Raciti, Groffman et al. 2008). In contrast, dry atmospheric nitrogen deposited on impervious surfaces such as roads, sidewalks, and roofs is washed from these surfaces into storm sewers and ultimately to receiving waters.

Sewer systems are often closely located to surface water systems, both groundwater and storm sewers, and therefore are particularly poised to introduce Nr to streamwater. Additionally, there is potential for retention of nitrogen from sewage sources. Leaking sewer pipes likely could create their own “denitrification hotspots,” moist, carbon-rich sediments (Burks and Minnis 1994) which promote denitrification of sewage-sourced nitrogen (Parkin 1986; Groffman and Crawford 2003; Groffman, Dorsey et al. 2005). Further, retention of sewage-sourced nitrogen is possible via processes such as anammox (anaerobic, bacterial conversion of ammonia and nitrite to nitrogen gas) (Shivaraman and Shivaraman 2003; Groffman, Dorsey et al. 2005). A network of leaking pipes may thus form a network of denitrification zones in near-pipe environments throughout the watershed (Eiswirth, Hotzl et al. 1995).

1.1.4 Hydrologic and geologic setting of study location

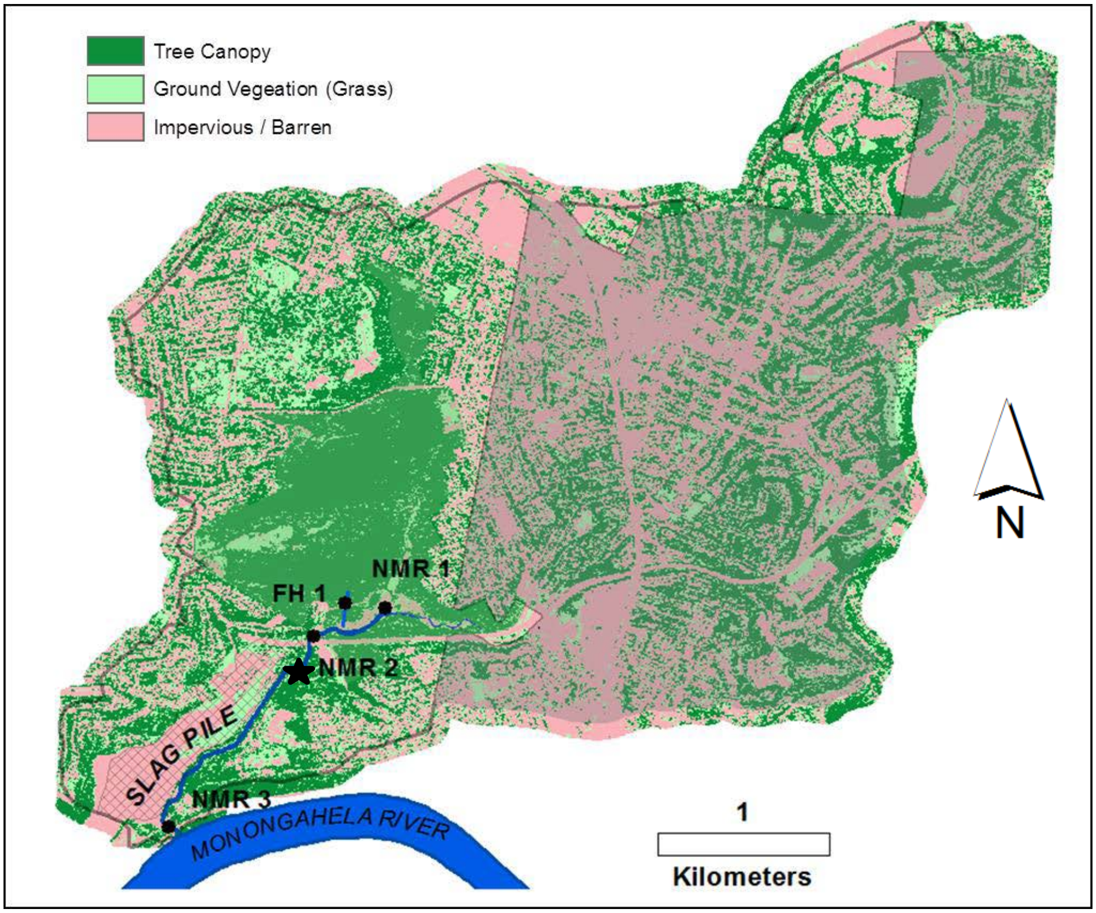


Figure 1.1 Map of the NMR watershed and sampling sites

The star downstream of NMR2 indicates the location of the USGS gauge #03085049. The shaded portion of the map (right hand side) indicates regions serviced by sanitary sewer systems, the unshaded portion of the map (left hand side) indicates regions serviced by combined sewer systems.

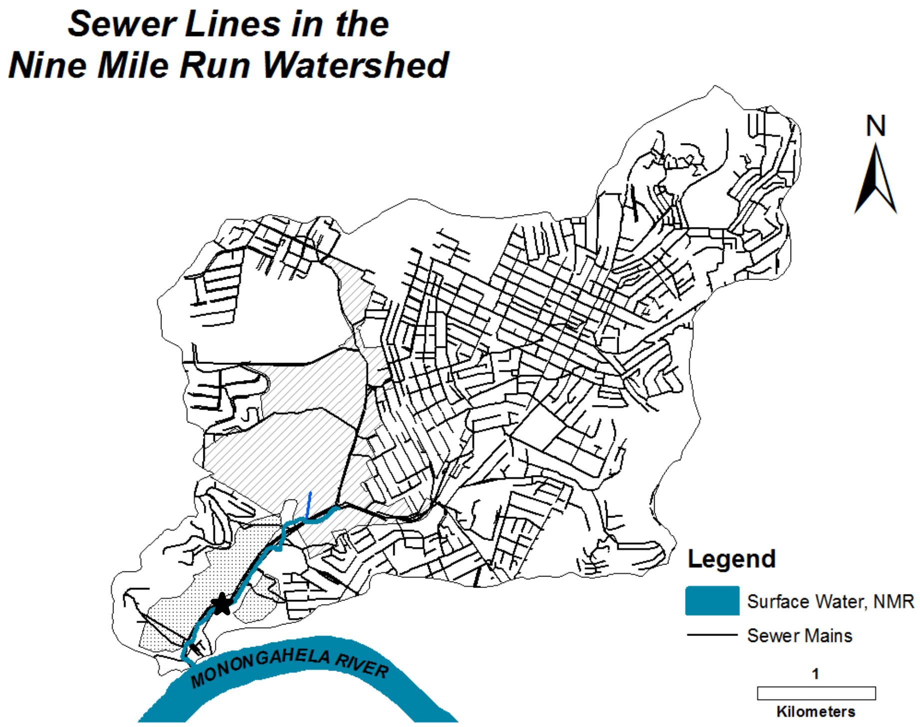


Figure 1.2 Sewer lines and surface water in NMR watershed

Map of the NMR watershed showing sewer lines and surface water. The star marks approximate location of monitoring well.

NMR is one of the few remaining above-ground streams in Pittsburgh, draining a 1,570 ha urban watershed with 38% impervious cover (Homer, Huang et al. 2004). Bedrock in the area is composed of shale, limestone, siltstone, and sandstone (Leighton 1927). The upper portions of NMR now flow through culverts or storm sewers (Figure 1.1, Figure 1.2), with the stream re-emerging aboveground 3.5 kilometers upstream of the Monongahela River. This places the stream course and sewer pipes in close proximity, and potentially allowing interaction between the culverted stream and sewer pipes (Figure 1.2) (3RWW 2011). Human populations in the NMR watershed are served by both sanitary (52% of the total watershed area) and combined sewer systems (36%), with remaining areas (12%) in parkland. Each sewer system is designed to direct waste from households and businesses directly to the sewage treatment plant in dry weather, while in wet weather, combined sewers can direct mixed sewage and stormwater fluxes to rivers and streams. Between 2003 and 2006, NMR was physically “restored,” with work including channel reconfiguration, the creation of pool and riffles, and bank stabilization focused primarily on hydraulic stability.

Limited data about groundwater conditions in the NMR watershed suggest that groundwater flowpaths are significantly altered from those commonly found in humid basin. The best available data for characterizing stream/groundwater interactions in Nine Mile Run result from the placement of water level elevation monitoring equipment in a well located in the floodplain of the lower portion Nine Mile Run during a Groundwater Geology class at the University of Pittsburgh (Figure 1.2). At the monitoring well, a cross section of the stream and floodplain was surveyed (Figure 1.3). Stage was recorded in this well from 3/4/2009 through 4/8/2009 and data was compared with estimated stream stage (reconstructed by applying a Manning’s roughness to the USGS discharge). Over this time period, groundwater was generally lower than stream stage at this well location. Representative data for the time period 4/2/2009 through 4/10/2009 is shown in Figure 1.3 along with the surveyed cross-section. Water levels in the monitoring well are consistently lower than that of the stream, suggesting that hydrologic flux is from the stream to the groundwater. This is in contrast to conditions generally found in humid basins, wherein groundwater contributes substantially to streamflow. Future efforts should aim to characterize groundwater-surface water interactions at additional sites within the basin, as it remains to be seen whether the trends observed at this site are similar elsewhere in the basin.

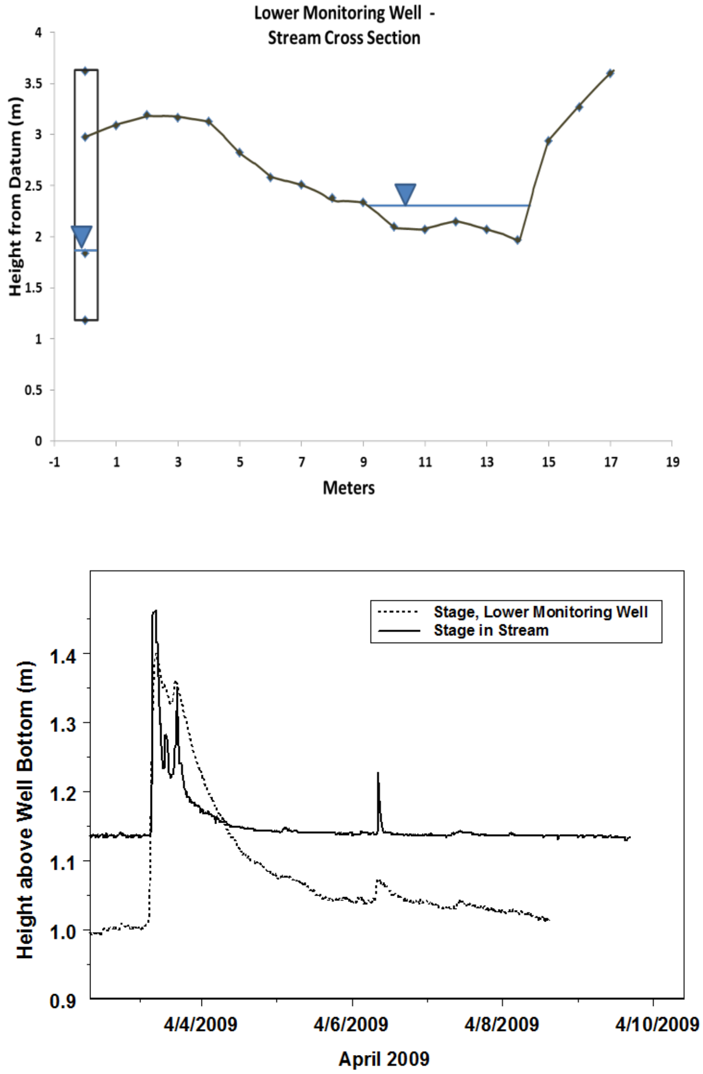


Figure 1.3 Stage and stream cross-section at Lower Monitoring Well

Top, cross section relative to well water elevations as measured during surveying. Bottom, time series of ground water elevation and stream stage during a storm event 4/3/2009.

1.1.5 Sources and dynamics of Nr to an urban watershed

This research presented in this dissertation explores sources and dynamics of Nr in the Nine Mile Run watershed through modeling, stable isotope analysis, and streamwater chemistry. The work presented in Chapter 2 was published in *Environmental Science & Technology* (Divers, Elliott et al. 2013) and uses mass balance models, coupled with Monte Carlo Simulation, to constrain inputs of leaking sewers to Nine Mile Run. Although sewer leakage is a large potential source of Nr to urban streams, previous quantification of pollution from this source is limited. Chapter 2 constrains this limitation by building, then inverting, a nitrogen budget to quantify the relative amounts of DIN that atmospheric deposition and sewage each contribute to urban streamwater concentrations.

In Chapter 3, the nutrient budget approach explored in Chapter 2 is augmented with the analysis of dual-nitrate isotopes ($\delta^{15}N$, $\delta^{18}O$), an effective indicator of nitrate sources. The work described in Chapter 3 is in review at *Environmental Science & Technology* (Divers, Elliott et al. Submitted, in Review). Streamwater nitrate is analyzed in samples from two years of bi-weekly sampling and storm events collected over a five year period. Isotopic data is used in mixing models to identify the proportional contributions of stream nitrate from each atmospheric and sewage sources at different flow regimes. Further clarification about denitrification processes is explored by analyzing and quantifying enrichment in isotopic values observed in denitrification processes, allowing the examination of the influence of denitrification on the available nitrate pool

Quantifying the nitrate from atmospheric deposition is difficult, as nitrate may be cycled through the organic N pool. Processes such as denitrification and assimilation into organic matter can change the isotopic source signature of the nitrate, and atmospheric nitrate has a wide range of isotopic values that overlap with those of other sources. Nitrate from atmospheric deposition is enriched in the least abundant oxygen isotope, ^{17}O, relative to terrestrial nitrate. In Chapter 4, this enrichment was used as a robust tracer of atmospheric deposition in the urban watershed, allowing us to unequivocally quantify this sources' impact on streamwater export, as well as gain insight into which sources of nitrate are retained in the watershed.

Although the bulk of this work has focused on nitrate, other anions can be significant indicators of human-induced contributions, particularly in urban systems. In Chapter 5, the anion chemistry of an urban stream is explored, with particular attention to seasonal patterns and sewage indicators.

Humans are the essential element in urban centers, altering, creating, polluting, and managing the ecosystems that exist in cities. As population growth in urban centers continues, residents must learn to live with and manage co-existing natural elements. To that end, Chapter 5 presents a model of a successful collaboration between University of Pittsburgh geoscientists and the Carnegie Natural History Museum. This collaboration brings educators and scientists together to serve as mentors and teachers for Pittsburgh high school students, a project termed "ENERGY-NET." The after-school sessions teach students about the connections between energy and the environment. Students then put their learning to use constructing museum exhibits for display in the Carnegie Museum of Natural History.

In closing, urban biogeochemistry is different from the natural systems upon which our understanding of these cycles is generally based. For that reason, the built environment, urban biogeochemistry, and the people who live within these environments are the focus of this dissertation.

2.0 CONSTRAINING NITROGEN INPUTS TO URBAN STREAMS FROM LEAKING SEWERS USING INVERSE MODELING: IMPLICATIONS FOR DIN RETENTION IN URBAN ENVIRONMENTS

2.1 INTRODUCTION

Sewers can be important contributors to surface and groundwater contamination; yet, quantification of pollution from this source is limited, thus constraining understanding of the biogeochemical importance of sewer-derived nutrients to urban streams. In particular, leaking sewer infrastructure can contribute multiple pathogenic, chemical, and nutrient contaminants to ground and surface waters in urban areas. Further, water introduced via leaking sewers can increase mineralization rates in near-pipe environments (Eiswirth, Hotzl et al. 1995) exacerbating existing dissolved inorganic nitrogen (DIN) loads to impaired streams. The scale of this urban problem is difficult to quantify, with over 900 thousand kilometers of sewer lines in the U.S. and many sewer systems close to one hundred years old (USEPA 2011). The potential scope of the problem is highlighted in a rare study quantifying the role of leaking sewers on groundwater degradation in Nottingham, England, where researchers estimated that leaking sewers contributed 13% of the total N load to the aquifer beneath the city (Lerner, Yang et al. 1999).

Although the U.S. EPA estimates 3 million m^3 of untreated sewage reach U.S. waterways annually (USEPA 2011), this non-point DIN source is poorly characterized in urban watershed nutrient studies (Ferreira, Matos et al. 2002; Groffman, Law et al. 2004; Wolf, Held et al. 2004). This knowledge gap results from poor estimates of sewer leakage flux, the complicated fate and transport of sewer inputs within urban hydrologic systems, and variability in sewage management systems (e.g., system age, sewer type (Eiswirth and Hotzl 1997; Bishop, Misstear et al. 1998; Rutsch, Rieckermann et al. 2008). Thus, prior studies have accounted for sewer inputs using several approaches: 1) loading rates in sewered watersheds have been estimated using per-capita nitrate excretion rates (Caraco and Cole 1999); 2) in watersheds dominated by septic systems, per-capita nitrate excretion rates have been coupled with estimates of retention of nitrogen compounds in septic systems (Valiela, Collins et al. 1997; Baker, Hope et al. 2001); 3) potential leaky sewer inputs have been acknowledged, but for purposes of analysis, have assumed that all waste is either treated or transported out of the watershed (Groffman, Law et al. 2004); 4) a combination approach utilizing water balances, water chemistry and models of water quality has been used to predict groundwater recharge from sewage systems (Cook, Vanderzalm et al. 2006; Rueedi, Cronin et al. 2009).

This work constrains the potential contribution of non-point source nutrients to surface water using inverse modeling. The role of sewage-sourced DIN in urban watersheds is quantified using data from Nine Mile Run (NMR) watershed (Pittsburgh, Pennsylvania, USA, (Figure 1.1). Sewage is a known source of nutrient pollution to this stream and region (NRC 2005), contributing both microbial and nutrient pollution to the water. A nitrogen budget was built for the NMR watershed using measured inputs/exports, as well as previously published fertilizer application, atmospheric deposition, and urban DIN retention estimates. Due to the poorly constrained nature of these sources in urban systems, four different scenarios were tested with Monte Carlo techniques to estimate sewage DIN inputs. Quantification of these sewer-sourced DIN loadings is fundamental to understanding urban ecosystems and biogeochemistry.

2.2 STUDY LOCATION AND METHODS

2.2.1 Location

Between 2003 and 2006, NMR was physically "restored," with work including channel reconfiguration, the creation of pool and riffles, and bank stabilization focused primarily on hydraulic stability. The stream drains a 1,570 ha urban watershed with 38% impervious cover (Homer, Huang et al. 2004). Bedrock in the area is composed of shale, limestone, siltstone, and sandstone (Leighton 1927). The upper portions of NMR are buried in storm sewers (Figure 1.2). NMR emerges in Frick Park (Pittsburgh, PA) and runs for 3.5 kilometers before it joins the Monongahela River.

The NMR watershed is served by two contrasting sewer systems (Figure 1.1). The eastern portion (52% of the watershed) is serviced by a sanitary sewer system whereas the western portion (36% of the watershed) is serviced by a combined sewer system. The remaining 12% is city parkland with only sewer mains running through it (Figure 1.2). Sanitary sewers are designed to direct waste from households and businesses directly to the sewage treatment plant. In dry weather, combined sewers send waste directly to the treatment facility; however during wet weather events, these systems direct overflows of sewage/storm water mixtures to surface water. Thus, both sewer systems are potential non-point sources of pollution from leakage during baseflow conditions, with point-source contributions from the combined sewers during storm events.

2.2.2 Field Sampling

Sampling was conducted bi-weekly between April 2007 and April 2009 at four sampling locations, three forming a longitudinal transect and the other a tributary stream (Figure 1.1). The upstream portion of the watershed was sampled at NMR1, NMR2 sits approximately 50 meters below a combined sewer overflow structure, and NMR3 integrates the entire watershed. A small ephemeral stream, Fern Hollow (FH1) drains a sub-watershed (Figure 1.1). Bi-weekly sampling was conducted without regard to flow, and during the course of the two-year sampling period, five high flow events (discharge exceeded 0.5 $m^3 sec^{-1}$) were captured. Additionally, storm-flow samples were collected at NMR2 on July 20, 2008 following 5 mm of precipitation during 1 hour (n=8). Stormflow samples were collected from NMR2 before the rainfall began, at 30 min intervals for the first three hours of storm flow, and at 60 min intervals until discharge returned to base flows recorded prior to the storm. Storm samples were stored on ice until filtered. Bi-weekly samples were vacuum filtered within 24 hours of collection using 0.2 μm nylon filters. Lab-filtered samples were stored in 60 mL HDPE bottles and refrigerated. Measurements of nitrate (NO_3^-) concentrations were conducted on a Dionex ICS2000 Ion Chromatograph. Analyses of ammonium (NH_4^+) and nitrite (NO_2^-) were conducted on a Thermo Scientific Evolution 60S UV-Visible Spectrophotometer (Eaton 2005).

2.2.3 Dicharge/export calculations

During sampling, area-velocity method instantaneous discharges were measured at each site. In addition, daily average discharge data (6/14/2006-9/30/2009) was obtained from USGS station 03085049 (Figure 1.1, Figure 2.1).

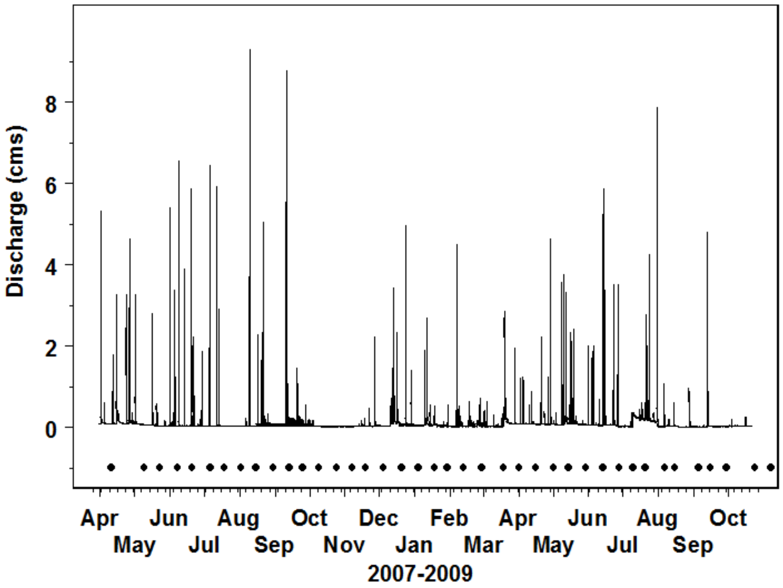


Figure 2.1 USGS continuous (black line, top) discharge data

Data points in bottom graph indicate the date sampling occurred.

The USGS program "PART" was used for hydrograph separation of the USGS discharge record for years 2007 and 2008 (Rutledge 1998). Precipitation data was obtained from 3 Rivers Wet Weather (3RWW 2010), land cover data for the region was obtained from the National Land

Cover Database (Homer, Huang et al. 2004), and watershed boundary data from the Environmental Resources Research Institute's Small Watersheds database (ERRI 1997).

Two methods were used to calculate annual DIN export (or flux) from NMR (Figure 2.2). DIN concentrations from NMR2 were used in all export calculations due to proximity to the USGS gauge location and minimal lateral inputs downstream of this point. In the first method, NO_3^--N concentrations were fit to an exponentially decreasing regression and this relationship was applied (Quilbé, Rousseau et al. 2006) to the daily average USGS discharge record (Figure 2.3). Discharge values below 0.065 m^3 sec^{-1} were not utilized when determining this relationship due to anomalously low NO_3^--N concentrations (see Discussion and Figure 2.3). In order to calculate DIN export, NO_3^--N concentrations were related to total DIN concentrations (Figure 2.3) and the resulting relationship was applied to the modeled NO_3^--N export record, hereafter termed the "*DIN/Discharge Relationship*." The second method used a linear interpolation where DIN concentrations from NMR were interpolated between sampling days (Wollheim, Pellerin et al. 2005), hereafter referred to as the "*Linear Interpolation Method*". Daily linearly interpolated concentrations were multiplied by total daily discharges to obtain daily DIN export. For both of the proceeding approaches, annual DIN export was estimated beginning in April (4/2007-4/2008, 4/2008-4/2009) based on sampling periods. Calculated export from each flux model was then used to construct a distribution of DIN exports for the Monte Carlo analysis.

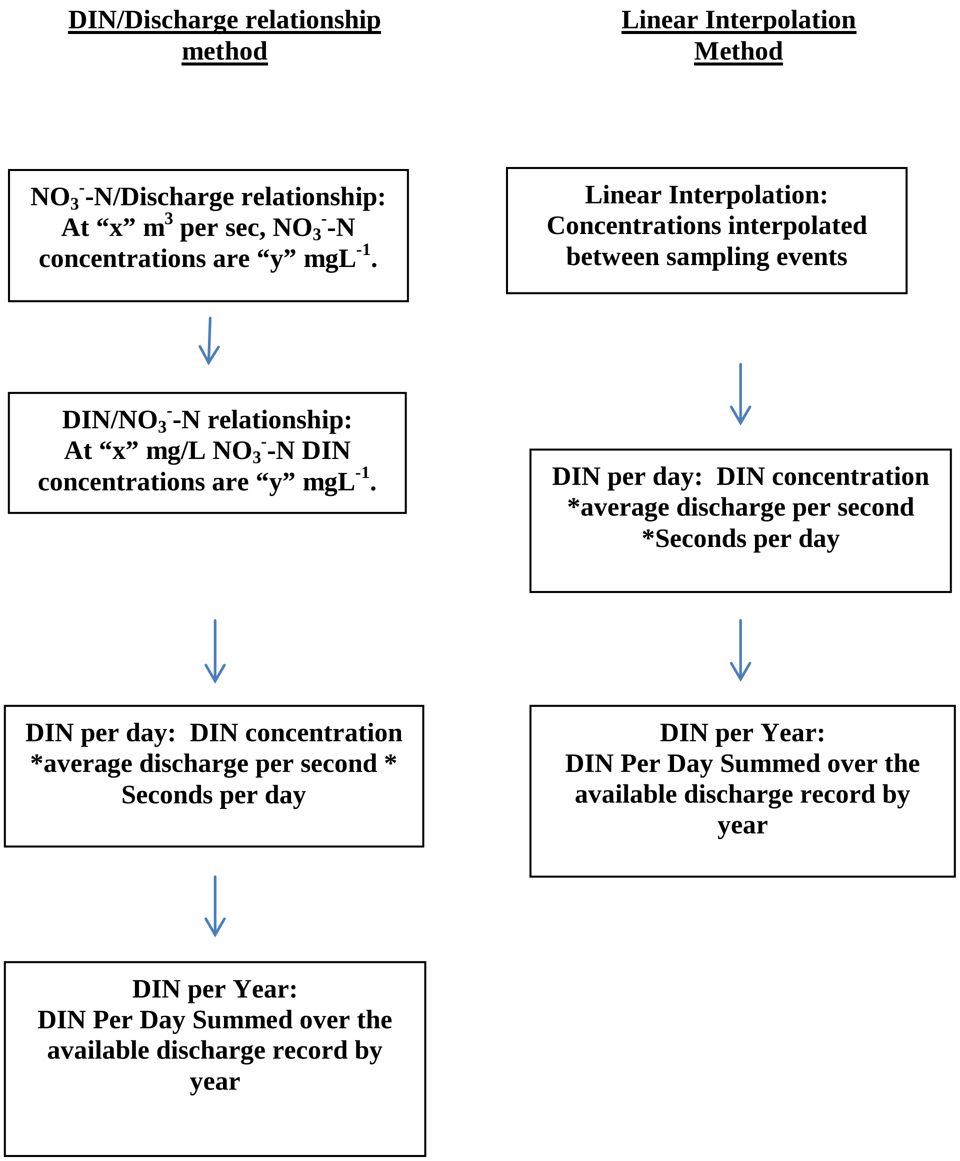


Figure 2.2 Diagram of the two methods used to calculate yearly DIN export

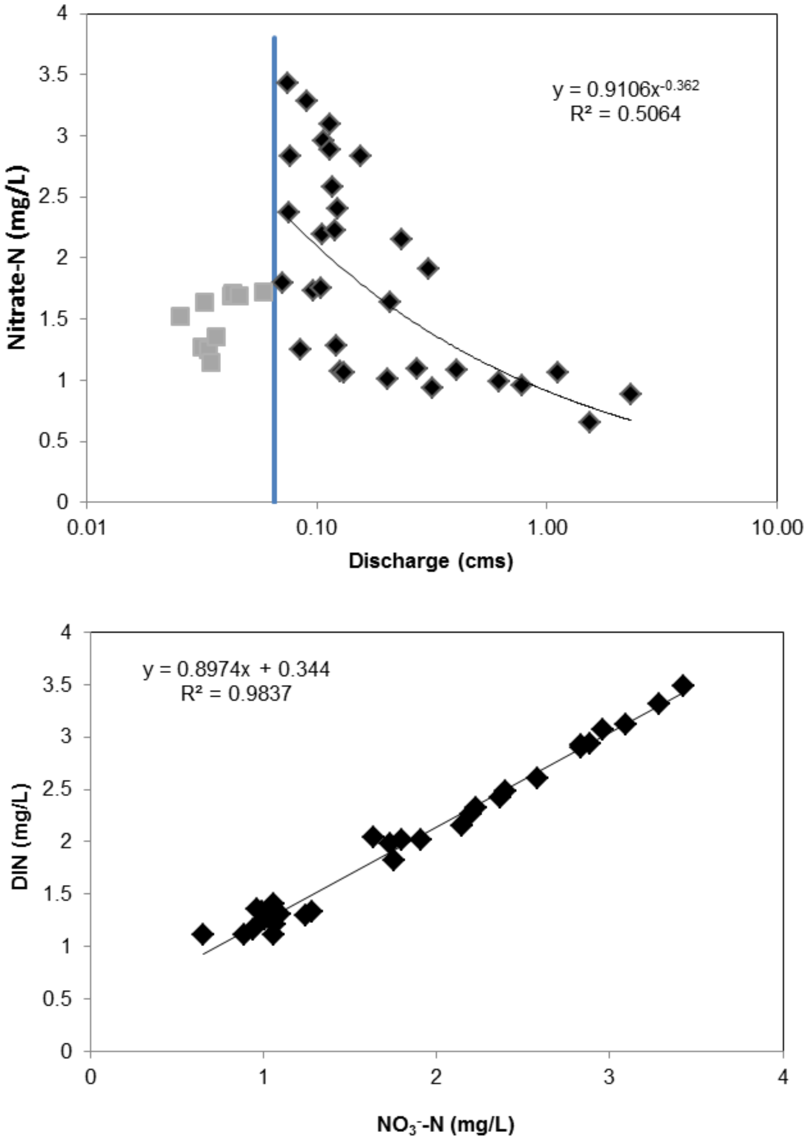


Figure 2.3 Nitrate-N/discharge Relationship & nitrate-N/DIN relationship

Top: Solid blue line and grey squares demarks cutoff point where flow drops below 0.065 m^3 sec^{-1} and low nitrate-N (1 to 1.8 mg L^{-1}) concentrations falling off the curve are observed. These points are inconsistent with concentration-discharge relationships at higher flows and were therefore removed from the nitrate-N/discharge relationship. During review and revision of this manuscript, three additional storms were sampled and results are consistent with the concentration discharge relationship shown here.

2.2.4 Sewage DIN contribution estimations

The two flux methods described above were used to construct a NMR catchment nitrogen budget (Eq. 1).

$$DIN_{export} = (DIN_{ADN} + DIN_{sewage} + DIN_{fertilizer}) \times (1 - Retention) \qquad (Eq.1)$$

Inputs to the watershed, reported in kg ha^{-1}yr^{-1}, include DIN$_{ADN}$ (where ADN is atmospherically deposited nitrogen, consisting of total atmospheric dry and wet nitrogen species), DIN$_{fertilizer}$ (DIN contributed from lawn fertilizer) and DIN$_{sewage}$ (DIN contributed from sewage). Export from the watershed, DIN$_{export}$, is the sum of observed nitrate, nitrite and ammonium concentrations (kg ha^{-1}yr^{-1}) in NMR streamwater (DIN = (NO_3^--N) + (NO_2^--N) + (NH_4^+-N)). Dry atmospheric deposition was measured at the Laurel Highlands (LRL117) dry deposition (CASTNET) monitoring site, 75 km from Pittsburgh. Wet deposition was measured at the Piney Reservoir (MD08) National Trends Network (NTN) precipitation monitoring site, 115 km from Pittsburgh. Fertilizer nitrogen inputs were calculated using an approach based on lawn care studies from suburban Baltimore (Law, Band et al. 2004). Using application rates from Baltimore, when the age of NMR neighborhoods (53% of housing stock built before 1939, and 76.9% built before 1959 (PlanPGH 2011) and the known fertilized institutional areas are accounted for, adjusted lawn fertilizer application rates distributed across the entire NMR watershed, are an estimated 4.2 ±2 kg ha^{-1}yr^{-1}.

2.2.5 Monte Carlo Simulation Implementation

To determine potential DIN from sewage, the nitrogen budget (Eq. 1) was inverted and solved for sewage (Eq. 2) using Monte Carlo simulation methods.

$$DIN_{sewage} = (DIN_{export} \div (1 - Retention)) - (DIN_{ADN} + DIN_{fertilizer}) \qquad (Eq.\ 2)$$

Distributions and data used to construct each of 4 scenarios for Monte Carlo simulation are listed in Table 1 and summarized here. All Monte Carlo simulations were implemented in R (R Development Core Team 2008), using the “mcsm” package (Robert 2009). Annual export was estimated using both methods described above, and the resulting values used to bound a distribution of export estimates (uniform distribution, 3.4 - 5.6 kg ha^{-1} yr^{-1}.). Southwestern Pennsylvania receives some of the highest rates of nitrate deposition nationwide (17- 21 kg ha^{-1} yr^{-1}) (Elliott, Kendall et al. 2007). However, ADN is expected to be even higher in urban areas such as NMR, particularly when compared to rural conditions where ADN measurements are generally made (Lovett, Traynor et al. 2000; Elliott, Kendall et al. 2007; Redling, Elliott et al. 2011). Thus, two scenarios utilizing deposition rates for rural areas likely represent a low estimate of ADN reaching urban surfaces (Hatt, Fletcher et al. 2004; Elliott, Kendall et al. 2008). While measurements of urban N deposition are scarce, measurements of dry ADN (NO_2 + HNO_3) in Pittsburgh in an ongoing study are 2.3 times higher than those measured at the nearest dry deposition monitoring locations (Redling, Elliott et al. 2011). Therefore, two scenarios use a “high” ADN distribution (Table 2.1) by assuming the same ratio of wet to dry deposition in urban and rural and multiplying CASTNET and NADP measurements of dry + wet ADN by 2.3.

Based on deposition data from CASTNET and NTN sampling sites, ADN was assumed to have a uniform distribution. Retention was assumed to have a uniform distribution in the range of published values (Table 2. 2). Fertilizer inputs were calculated as described above and a normal distribution assumed. While the first two scenarios use the range of previously reported retention estimates from other urban watersheds (65-85% total retention of nitrogen, Table 2.1, (Groffman, Law et al. 2004; Wollheim, Pellerin et al. 2005; Kaushal, Groffman et al. 2008)), the second two scenarios explore the potential effects from higher rates of retention (75-95%, with the higher end of this range similar to retention rates observed in forested systems). Sensitivity analyses for the Monte Carlo were completed. Varying the standard deviation in the normal distributions used for fertilizer by a factor of 2 did not change the MLE for Scenarios 1,2, or 4, and in Scenario 3 it raised the MLE from 7 to 8.

Table 2.1 Scenarios used in Monte Carlo simulations

All data distributions for ADN and Retention were uniform.

		Inputs					***Export (DIN from sewage)***	
Scenario Number	***Scenario Description***	***ADN [kg ha^{-1} yr^{-1}]***		***Fertilizer [kg ha^{-1} yr^{-1}]***	***Retention [%]***		***Sewage Load [kg ha^{-1} yr^{-1}]***	***Total sewage DIN [%]***
		MIN	*MAX*		*MIN*	*MAX*		
1	Low ADN, Low retention	3.6	7.8	4.2±2	65	85	6	33-43
2	High ADN, low retention	8.3	17.9	4.2±2	65	85	-2	N/A
3	High ADN, high retention	8.3	17.9	4.2±2	75	95	7	24-36
4	Low ADN high retention	3.6	7.8	4.2±2	75	95	14	53-64

Table 2.2 Characteristics and retention in urban watershed studies

For the Kaushal (2008) study, values were calculated assuming fertilizer application rates used in the rest of the study, 14.4 kg ha^{-1} yr^{-1}. Without assumed lawn fertilizer inputs, retention was 50%. Values for the forested "Pond Branch" watershed (Groffman et al, 2004) are shown for comparison between forested and urban watersheds.

Study	Watershed	Landcover/ landuse	Water-shed Size (ha)	Impervious Surface %	Population Density (per ha)	Inputs assumed	Retention %
Kaushal et al 2008[1]	Dead Run	Suburban/ Urban	1414	41	12.6	Lawn Fertilizer[2], ADN	29-84%
Groffman et al 2004	Glyndon	Suburban	81	22	9.4	Lawn Fertilizer, ADN	75%
Groffman et al 2004[4]	Pond Branch	Forested	32	0	0	ADN	95%
Wollheim 2005	Sawmill Brook	Suburban	410	25	9.81	Lawn Fertilizer, ADN, septic	78-85%
This study	NMR	Urban	1570	38	30	Lawn Fertilizer, Sewage, ADN	60-93%

2.3 RESULTS & DISCUSSION

2.3.1 Precipitation and Discharge in NMR

Over the sampling period, measured discharges ranged from 0.02 to 2.31 m^{3} sec^{-1}. Average rainfall in Pittsburgh is 936 mm (NOAA). Accordingly, 2007 was a wet year (1018 mm), 2008 an average year (963 mm), and 2009 a dry year (856 mm). The proportion of precipitation leaving the basin as surface water was 26% and 20%, respectively, for the two sampling years.

Based on PART analysis of discharge measurements at the USGS gauge station, 52% and 60% of discharge from NMR occurred during baseflow in 2007-2008 and 2008-2009, respectively. Local groundwater levels were generally 0.1 meter below stream stage over the available groundwater record (Figure 1.3). Contrary to "normal" stream conditions, this implies that flux is from the stream to groundwater in representative stream reaches.

2.3.2 DIN concentrations

Ammonium-N and nitrite-N concentrations were generally 1-2 orders of magnitude lower than nitrate concentrations at each sampling site (Figure 2.4). When concentrations were above detection limits, nitrite-N ranged from 0.01 to 0.18 mgL^{-1} and ammonium-N ranged from 0.01 to 0.63 mgL^{-1}. In comparison, nitrate-N concentrations varied from 0.58 to 4.15 mgL^{-1} during 2 years of bi-weekly sampling in NMR. The range in nitrate-N concentration at each site varied from 1.2 to 4.1 mgL^{-1} at NMR1, 0.5 to 3.6 mgL^{-1} at NMR2, and from 0.7 to 3.8 mgL^{-1} at NMR3 (Figure 2.5).

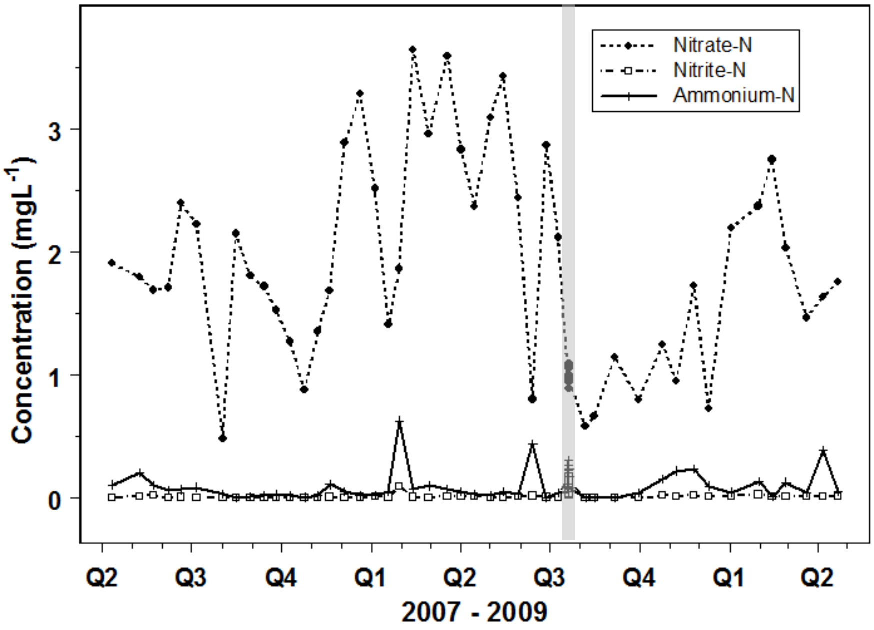


Figure 2.4 Concentrations of nitrate-N, nitrite-N, and ammonium-N

Concentrations are for the sampling time period measured at NMR2. “Q” indicates year quarters, beginning with the second quarter of 2007 (April, May, June). The shaded box indicates the storm event sampled on July 20, 2008.

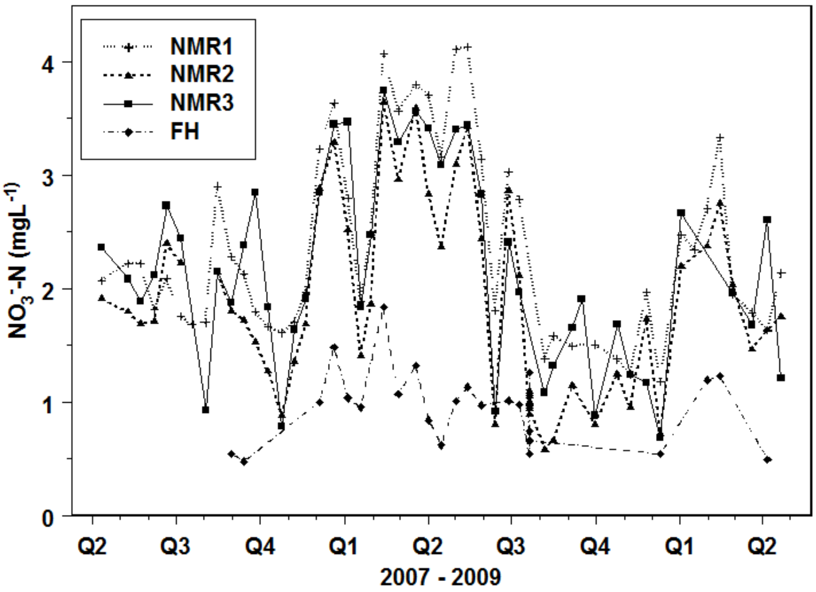


Figure 2.5 Nitrate-N (in mgL^{-1}) concentrations at each sampling location

"Q" indicates year quarters, beginning with the second quarter of 2007 (April, May, June).

These observed concentrations are comparable to nitrate concentrations reported for other urban watersheds (Groffman, Law et al. 2004; Kaushal, Groffman et al. 2008). At Fern Hollow 1 (FH1), streamwater nitrate concentrations were consistently 30-50% of those observed in NMR1, 2, and 3 (Figure 2.5). The highest nitrate-N concentration measured at FH1 was 1.3 mgL^{-1} and the lowest 0.5 mgL^{-1}. Nitrite-N at FH1 ranged from 0.01 to 0.07 mgL^{-1}; however nitrite concentrations at this site were commonly below detection (0.01 mgL^{-1}). Ammonium-N concentrations in FH were generally higher than nitrite, ranging from 0.01 to 0.09 mgL^{-1}.

2.3.3 Nitrate-N and Discharge Dynamics in a Highly Altered System

In NMR, streamwater DIN concentrations are controlled by stream/sewer interactions in the buried portion of the stream above NMR1. On most sampling days, nitrate-N concentrations were highest at NMR1 (Figure 2.5). Downstream at NMR2 and 3, nitrate-N concentrations were generally the same as or lower than those at NMR1. In the upper portions of the watershed (upstream of NMR1), the buried stream bed parallels (sanitary) sewer lines (Figure 1.2). Water from leaking sewers can therefore interact with buried stream reaches via groundwater flow paths, consequently introducing large DIN loads to the buried stream. In this highly altered hydrologic environment, the major loading of nutrients occurs in the buried streams and not through more traditional paths, such as groundwater discharge to surface water. In periods of low flow, (when flow drops below 0.065 m^3sec^{-1}), low nitrate-N (1 to 1.8 mg L^{-1}) concentrations inconsistent with concentration-discharge relationships at normal flows are observed, indicating a change in process at these low flows. In NMR, low nitrate-N concentrations may result from periods when low water tables eliminate or greatly reduce connections between stream and sewer, precluding the contribution of sewage-derived nitrate-N to the underground stream system (Figure 2.6).

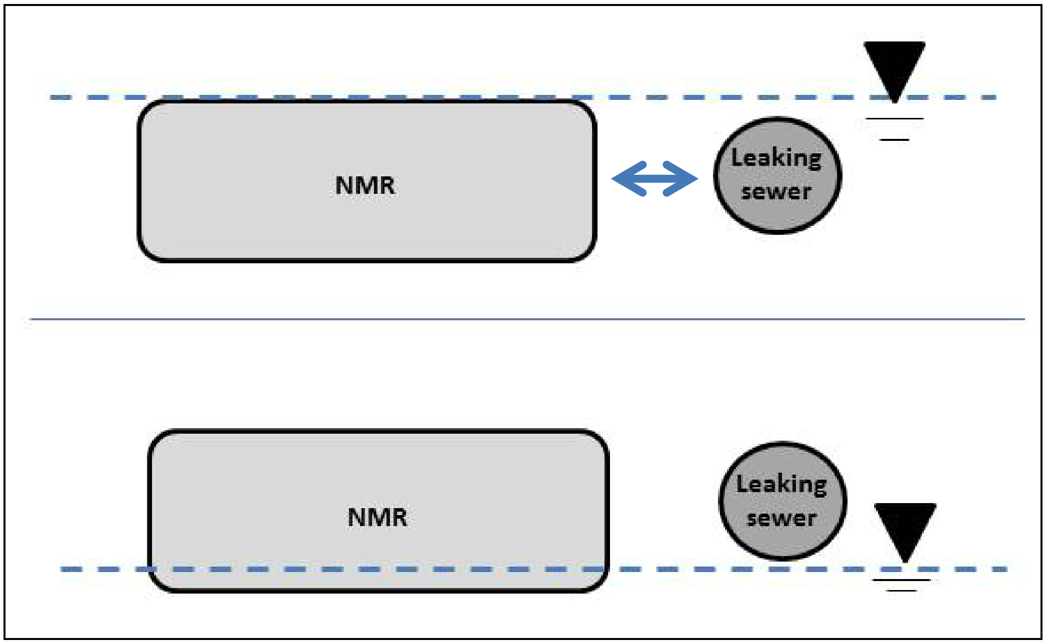


Figure 2.6 Conceptual Model of buried stream/sewer interactions

Top, groundwater allows interactions between sewer and buried stream, facilitating movement of pollutants into streamwater. Bottom, in dry periods a lower groundwater table prevents buried stream/sewer interactions.

While water table data is not available for buried stream areas, groundwater in the lower reaches of NMR is consistently ~0.1 m below stream stage (Figure 1.3). This hydraulic gradient drives water flux from the stream and further indicates that groundwater is a relatively minor contributor to stream DIN loadings in the lower, above-ground reaches of NMR. In this highly altered flow system, anomalously low nitrate-N concentrations during low flows (< 0.065 m^3 sec^{-1}) may thus be explained by interruption of stream-groundwater interactions. While we do not have sufficient data to demonstrate these dynamics completely, when these low flows were included in concentration-discharge analysis, predicted concentrations in the mid- to upper flow ranges were strongly affected by these data, resulting in underestimated total export. Therefore the nitrate-N/discharge relationship was determined while excluding flows below 0.065 m^3sec^{-1} (Figure 2.3).

The interaction between sewer and stream is further revealed by comparing sewer density with DIN export in individual NMR sub-watersheds. The FH sub-watershed is less impacted by the sewer and street network than areas draining to other portions of NMR (Figure 1.2), and therefore FH stream water nitrate-N and DIN concentrations are lower than NMR1 (Figure 2.5). The FH tributary drains a sub-watershed that includes non-sewered parkland and a city cemetery (together comprising 43% of sub-watershed). The FH sub-watershed contains a less dense sewer network, with 0.3 km ha^{-1} of sewer lines relative to 0.6 km ha^{-1} of sewer line in areas upstream of NMR1. The lower concentrations in the FH sub-basin corroborates the importance of leaking sewers to observed DIN concentrations.

2.3.4 Quantifying Contributions of Sewage to DIN Export

Estimates of yearly DIN export from the NMR watershed generated using two flux methods are similar in each of the two years. The linear interpolation method estimated higher DIN export in 2007 (5.6 kg $ha^{-1}yr^{-1}$) compared to the DIN/discharge relationship method (4.6 for 2007) but lower DIN export in 2008, (3.4 and 3.7 kg $ha^{-1}yr^{-1}$, respectively).

Four scenarios were constructed to explore potential sewage-derived DIN to NMR using inverse modeling and Monte Carol simulation (Table 2.1). At lower retention rates and lower rates of ADN (Scenario 1), the maximum likelihood estimate (MLE) of sewage-sourced DIN is 6 kg ha^{-1} yr^{-1} (Figure 2.7). At this level of inputs, the sewage input is essentially equivalent with export (3.4-5.6 kg ha^{-1}yr^{-1}), which would indicate that retention of fertilizer and ADN in the watershed would effectively be 100%. However, Scenario 1 assumes low ADN fluxes, a poor assumption for the urbanized NMR watershed.

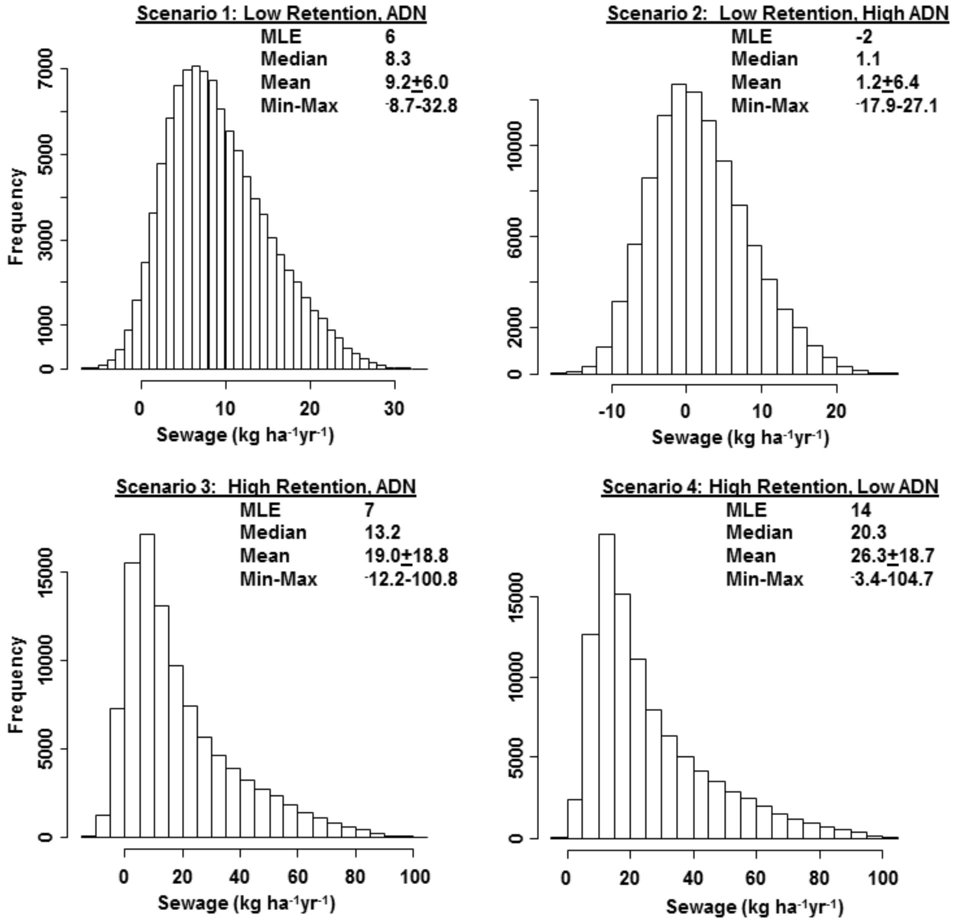


Figure 2.7 Results of MC analysis of sewage contributions to DIN export

Histograms indicating frequency distributions of values for sewage contributions to DIN export from NMR occurring after 10^5 iterations using Monte Carlo analysis of each scenario (1,2,3, & 4, shown in Table 1).

In Scenario 2, ADN is increased to a more realistic deposition rate based on observations in Pittsburgh (Redling, Elliott et al. 2011) while maintaining lower rates of retention. Monte Carlo simulations based on these higher ADN values result in a MLE of -2, a result considered infeasible (Figure 2.7). Negative values indicate one of two processes might be occurring in the watershed: 1) sewers are acting as sinks, collecting DIN from ADN and fertilizer and exporting it from the watershed at a rate far exceeding the potential contributions from the sewers, or 2) the nitrogen retention in the watershed is above the range used in the two scenarios. If sewers act as DIN sinks, this would imply that a substantial portion of "retained" DIN is actually removed from the system via export to a sewage treatment facility. While it is likely that DIN is exported in sewer systems, it is unlikely that non-point sources of DIN including fertilizer and ADN (summing to 12.5-22.1 kg ha^{-1} yr^{-1} in Scenario 2) are captured by sewers at rates equivalent to 10-16% of total DIN inputs.

In Scenario 3, assuming both high retention rates (75-95%) and high ADN inputs, the MLE for sewage contributions to DIN export is 7 kg ha^{-1} yr^{-1} (Figure 2.7). This load represents between 20-36% of the total DIN exported from NMR (Table 2.1). In Scenario 4, assuming high retention and low ADN, the maximum likelihood estimate of DIN from sewage is 14 kg ha^{-1} yr^{-1}, or between 53-64% of total DIN inputs to NMR. Based on knowledge of vehicular emission rates, the fate and transport of NO_x emission sources (Elliott, Kendall et al. 2007; Elliott, Kendall et al. 2009) and ongoing efforts in Pittsburgh to quantify rates of urban N deposition (Redling, Elliott et al. 2011), the higher deposition rates assumed in Scenarios 2 and 3 are more realistic than those used in Scenarios 1 and 4.

These results from the MC analysis illustrate two important points. 1) With reasonable estimates of fertilizer and ADN inputs in our urban DIN budget, DIN from sewage constitutes a significant proportion of total DIN inputs to NMR. Yet, these sewage inputs are often not considered in other urban and suburban watershed nutrient budgets. As a consequence of not incorporating sewage-sourced DIN into urban and suburban watershed budgets, actual DIN flux through these systems is underestimated. 2) Incorporation of substantial sewage DIN inputs observed in this study increases watershed nitrogen retention rates above previously reported values (Groffman, Law et al. 2004; Wollheim, Pellerin et al. 2005; Kaushal, Groffman et al. 2008). The following section explores urban DIN retention estimates and potential mechanisms, both important to restoration and management of urban systems.

2.3.5 Urban DIN Retention and Potential Mechanisms

To constrain the range of DIN retention rates, Monte Carlo analysis was used sampling the distribution of sewage-sourced DIN contributions to NMR export observed in the Scenarios above. This analysis assumes a range of sewage-sourced DIN inputs to NMR based on MLEs from the three scenarios with feasible sewage inputs (a uniform distribution, 6-14 kg ha^{-1} yr^{-1}), fertilizer rates previously reported, and high rates of ADN (uniform distribution 8.3-17.9 kg $ha^{-1}yr^{-1}$). Monte Carlo simulation sampling from these distributions predicts a MLE of watershed DIN retention of 84%, ranging between 57% and 92% (Figure 2.8).

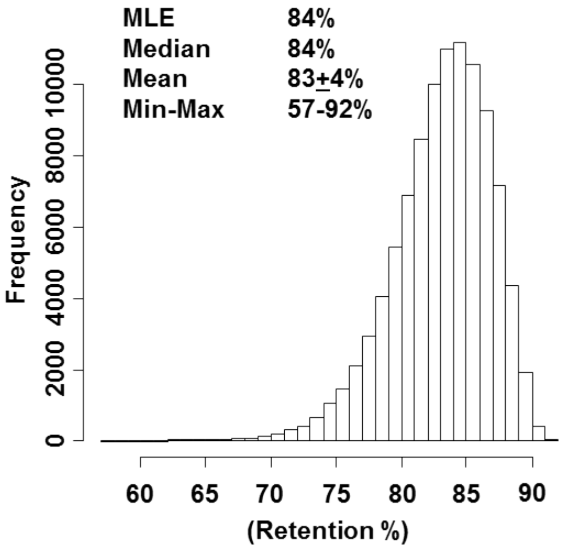


Figure 2.8 Results of MC analysis of percent watershed DIN retention.

Histograms indicating frequencies of values for percent watershed DIN retention occurring after 10^5 iterations using MC analysis of retention in the NMR watershed, calculated using a uniform distribution for sewage, with min=6 and max=14.

This retention estimate for the urbanized NMR watershed is at the high end of values reported in prior studies focusing on suburban watersheds (Table 2.2). Therefore, by incorporating sewage inputs, the NMR watershed retains even more nitrogen than previously reported for other urban watersheds. Further, if sewage inputs were incorporated into other urban nutrient budgets, retention for these systems would also be higher than reported. For example, if the loadings of DIN from sewage estimated for NMR (6 to 14 kg ha^{-1} yr^{-1}) are added to other urban watershed budgets as reported (Table 2.2), retention rates for these sites would increase between 3.5-14%.

Why does DIN retention in urbanized watersheds approach that observed in forested systems? (Table 2.2). Fundamentally, the impact of DIN on downstream systems is strongly dependent on the hydrologic connectivity between nitrogen source and surface waters (Elliott and Brush 2006). Fertilizer is generally applied to upslope residential lawns (i.e., not in riparian areas), distant from surface waters. Isotopic analysis of Baltimore streamwater suggests the absence of a fertilizer signature (Kaushal, Groffman et al. 2011), suggesting similar retention of $\text{DIN}_{\text{fertilizer}}$ within the NMR watershed. Similarly, ADN, deposited relatively uniformly across the landscape, is weakly connected to streams during dry weather. Therefore, these nitrogen sources are more likely to be retained. In contrast, sewer DIN inputs are often closely connected to surface water systems and thus readily available for export. However, leaking sewer pipes likely also create “denitrification hotspots,” moist, carbon-rich sediments (Burks and Minnis 1994) which promote denitrification (retention) of sewage-sourced nitrogen (Parkin 1986; Groffman and Crawford 2003; Groffman, Dorsey et al. 2005). Similarly, leaking sewers are sources of ammonia, ammonium and nitrite, which could retain nitrogen through processes such as anammox (anaerobic, bacterial conversion of ammonia and nitrite to nitrogen gas) (Shivaraman and Shivaraman 2003; Groffman, Dorsey et al. 2005). A network of leaking pipes may thus form a network of denitrification hotspots in near-pipe environments throughout the watershed (Eiswirth, Hotzl et al. 1995). In general, the demonstrated importance of sewer inputs highlights the need to address critical knowledge gaps including the specific fate of individual nitrogen sources and characterization of mechanisms allowing high DIN retention in urban systems.

2.3.6 DON inputs in the NMR budget

Concentrations of dissolved organic nitrogen (DON) or particulate nitrogen (PN) in the streamwater, which may contribute significantly to the total biologically available nitrogen in NMR, were not measured in this study. DON concentrations in streams have been shown to increase with increasing inputs of wastewater (Pellerin, Wollheim et al. 2004). For example, Wollheim et al (2005) observed 13% of total N exported as DON from an urban watershed (Wollheim, Pellerin et al. 2005). If DON were observed in NMR at similar proportions, annual total N export would increase, raising the lowest export estimate from 3.4 to 3.8 kg $ha^{-1}yr^{-1}$ and the highest from 5.6 to 6.4 kg $ha^{-1}yr^{-1}$. As these results indicate, accounting for DON does not dramatically change export estimates. Further, poorly characterized DON concentrations in sewage and ADN (Cornell 2011) preclude incorporation of DON into watershed budgets, yet make this an important area of future research

2.4 IMPLICATIONS

This study demonstrates the importance of sewage-contributed DIN to urban streamwater using a material budget approach. Sewer leakage rates in the NMR watershed are substantial enough that up to 12% of the N from human-generated sewage is transferred to the stream (assuming an average per-capita excretion rate of 4 kg $year^{-1}$ (Bleken and Badden 1997) and a watershed population density of 30 people ha^{-1}). Notably, this work also confirms that DIN from sewage in streamwater is clearly not a simple wet-weather problem or sewer overflow event problem. Rather, sewers in the NMR watershed streams are leaking consistently, as evidenced by high

DIN concentrations during baseflow conditions. This is an important distinction for efforts to improve urban water quality in Pittsburgh and other regions. In Pittsburgh, designs to reduce sewage contamination of surface water focus almost exclusively on combined and sanitary overflows that occur during wet weather, and do not address substantial inputs from leaking sewers.

As sewer systems across the U.S. age, sewer leakage rates will continue to increase as sewer systems reach the end of their design life (USEPA 2002). This infrastructure crisis faces a projected $180.6 billion dollar funding gap in the next 5 years alone (ASCE 2009). An improved understanding of urban nitrogen sources, retention mechanisms, and the relative influence of nitrogen sources (e.g., constraints from isotopic analysis) will be fundamental in the effort to effectively address urban nutrient pollution challenges.

3.0 PROPORTIONS OF SEWAGE AND ATMOSPHERIC DEPOSITION DERIVED NITRATE IN AN URBAN STREAM USING DUAL STABLE ISOTOPE RATIOS OF NITRATE (δ^{15}N, δ^{18}O)

3.1 INTRODUCTION

The human-built environment significantly impacts the hydrology of the landscape. Human infrastructure reroutes surface waters, grades and fills topographic variation, alters local vegetation, microclimate and atmospheric chemistry, and increases loadings of water pollutants. These affects lead to an urban landscape that is challenging to characterize with biogeochemical models developed in natural or agricultural areas (Kaye, Groffman et al. 2006; Bain, Hale et al. 2012). Surface waters in urban areas are often heavily altered by human engineering: streams are partially or completely buried, isolated from groundwater sources, and augmented by sewer and water infrastructure leaks (Lerner 2002). Impervious surfaces draining to streams compound these problems, routing pollutants directly to surface water (Walsh, Roy et al. 2005). Riparian zones, in contrast to those bordering forested streams, are significantly altered, or non-existent in urban areas. Nutrients, particularly nitrogen as nitrate (NO_3), contribute to water quality degradation, often impacting downstream areas.

Identifying the sources and dynamics of nitrate in urban streams is important to nutrient management in and downstream of urban centers and groundwater protection in areas below and down gradient of cities (Lerner, Yang et al. 1999; Wolf, Held et al. 2004; Rueedi, Cronin et al. 2009). Sewage-sourced nitrate is often assumed to be directed to streams primarily through sanitary and combined sewer overflows (USEPA 2004; USEPA 2009) or from wastewater treatment point sources (Sobota, Compton et al. 2013), yet aging, leaking sewer infrastructure also contributes potentially significant nitrate loads to urban streams (USEPA 2011; Divers, Elliott et al. 2013). Atmospherically deposited nitrate (ADN), both wet and dry, can reach the stream via precipitation and flushing of accumulated dry deposition, a process dependent on the magnitude of stormflow in a given event (Silva, Ging et al. 2002; Anisfeld, Barnes et al. 2007). However, the relative size of these nutrient sources is uncertain. In particular, the spatial pattern of inputs and proximity to drainage infrastructure likely strongly influences the retention of individual N sources. The processes retaining nitrate sources within urban watersheds are poorly constrained, thus characterization of urban contributions to regional nutrient loads are limited.

Dual nitrate isotopes have been utilized to distinguish nutrient sources to urban watersheds (Burns, Boyer et al. 2008; Kaushal, Groffman et al. 2011) (Silva, Ging et al. 2002; Fukada, Hiscock et al. 2004), however the effect of individual nitrate sources on urban surface waters is not clear. Isotopes of nitrogen and oxygen can distinguish atmospheric deposition nitrate (δ^{15}N: -11 to +3.5 ‰, δ^{18}O: +63 to +94‰) from sewage derived nitrate (δ^{15}N: 0 to +20‰, δ^{18}O: -15 to +15‰) (Kendall 1998; Kendall, Elliott et al. 2007). Not only do nitrate isotopic compositions reflect nitrate sources, they can record processes transforming nitrate during transport through the watershed. For example, increasing δ^{15}N: δ^{18}O values at a ~ 2:1 ratio can indicate denitrification, particularly when sample pool nitrate concentrations are decreasing (Bottcher, Strebel et al. 1990; Aravena and Robertson 1998; Lehmann, Reichert et al. 2003).

Results from a nutrient budget analysis in the Nine Mile Run (NMR) watershed (Pittsburgh, PA) suggest substantial sewage-sourced nitrogen inputs to stream fluxes and retention rates higher than previously assumed (Divers, Elliott et al. 2013). This study builds on the budget approach by analyzing dual-nitrate isotopic compositions to quantify nitrate sources to surface and ground waters (Kendall, Elliott et al. 2007). In particular, dual-isotopic composition data are used in mixing models incorporating Markov Chain-Monte Carlo techniques to resolve complex mixing from multiple sources. These analyses attribute nitrate to sources across flows conditions and reveal spatial patterns in retention processes.

3.2 STUDY LOCATION AND METHODS

3.2.1 Location

NMR is one of the few remaining above-ground streams in Pittsburgh, draining a 1,570 ha urban watershed with 38% impervious cover (Homer, Huang et al. 2004). The upper portions of NMR now flow through the storm sewer system (Figure 1.1), with the stream re-emerging aboveground 3.5 kilometers upstream of the Monongahela River. Human populations in the NMR watershed are served by both sanitary (52% of the total watershed area) and combined sewer systems (36%), with remaining areas (12%) in parkland. Each sewer system is designed to direct waste from households and businesses directly to the sewage treatment plant in dry weather, while in wet weather, combined sewers can direct mixed sewage and stormwater fluxes to rivers and streams.

3.2.2 Field sampling

Sampling was conducted bi-weekly between April 2007 and December 2008 at three sampling locations forming a longitudinal transect along NMR (Figure 1.1). NMR1 is approximately where the stream emerges from underground storm sewers. NMR2 is located ~50 meters below a combined sewer input. NMR3 is located at the mouth of the watershed. A small ephemeral stream, Fern Hollow (FH) was also sampled when flowing (Figure 1.1). Storm-flows were grab-sampled at NMR2 during one summer storm (Storm 1: July 20, 2008). Three subsequent storms were sampled at a location ~50 meters below NMR2 with an ISCO 6712 autosampler. Storms sampled at this site include one additional summer storm, (Storm 2: July 8, 2010) and two winter storms (Storm 3: January 1-2, 2011, Storm 4: March 22-23, 2011) (Table 3.1). Stormflow samples were collected before the rainfall began and at intervals throughout the storm. Storm samples were stored frozen until filtered in the lab.

Table 3.1 Sampling data and results for the 4 storms

Average concentrations reported are discharge-weighted, and average isotope values are flux-weighted. No discharge data is available for Storm 4, therefore just the ranges are reported.

Storm Event	***Total Rainfall Amount (mm)***	***Storm Duration***	***Sampling Frequency***	***Discharge Method***	***Sampling Begins***	***Sampling Ends***	***Avg. NO_3^--N (mgL^{-1})***	***NO_3^--N Range (mgL^{-1})***	***Avg. $\delta^{15}N$ (‰)***	***$\delta^{15}N$ Range (‰)***	***Avg. $\delta^{18}O$ (‰)***	***$\delta^{18}O$ Range (‰)***
1	9.7	1 hour 15 min	1/2 hour for 1.5 hours, then every hour	USGS gauge	7/20/2008 2:15 PM	7/20/2008 19:30	1.0 SD 0.1	0.9-1.1	5.6 SD 0.8	3.9-8.9	28.4 SD 3.0	24.69-32.78
2	25.1	6 hrs 15 min	1/2 hour for 6 hours, then once an hour	Pressure transducer	7/9/10 2:55 PM	7/10/10 7:25 AM	0.9 SD 0.05	0.4-1.4	7.3 SD 0.5	4.1-14.2	13.3 SD 1.3	1.02-25.74
3	12	6 hr 15 min	1/2 hour for 6 hours, then once an hour	pressure transducer	1/1/2011 3:44 AM	1/1/2011 6:14 PM	0.6 SD 0.02	0.3-1.5	8.0 SD 0.3	6.4-11.4	14.8 SD 1.2	-2.9 to 31.75
4	18	21 hours	once an hour	pressure transducer	3/22/2011 10:45 AM	3/23/2011 7:45 PM	*	0.3-2.3	*	5.2-10.3	*	-2.69 to 32.51

During sampling, instantaneous discharges were measured at each site using the area-velocity method. In addition, daily average and 15-minute average discharge data (6/14/2006-9/30/2009) was obtained from USGS station 03085049 (Figure 1.1). The USGS program "PART" was used for hydrograph separation of the USGS daily average discharge record for 2007 and 2008 (Rutledge 1998). During subsequent storm events, a pressure transducer was installed in a stilling well and a rating curve developed from discharges measured with the area velocity method to reconstruct discharge from the continuous stage record (Figure 3.1). The data logger was inadvertently full due to a false download and did not record discharges during Storm 4.

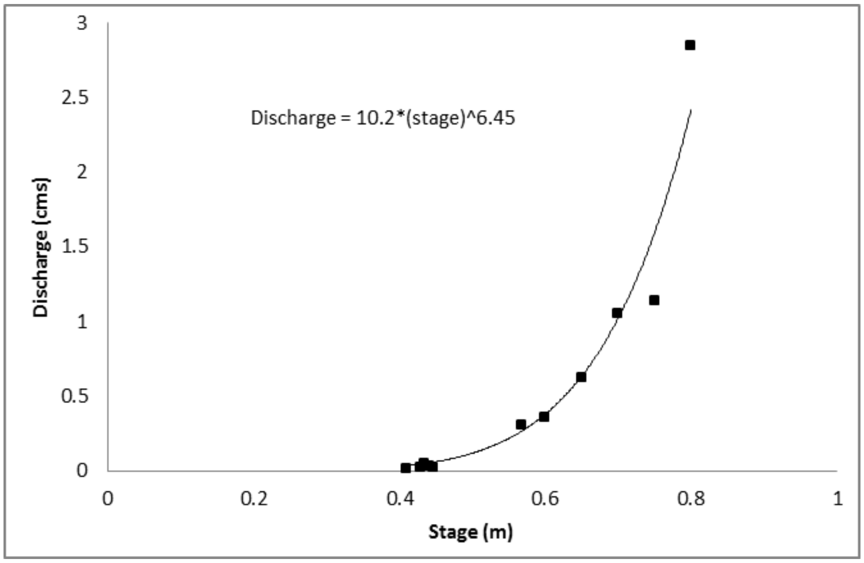


Figure 3.1 Stage/Discharge relationship developed at site NMR2

Precipitation data was obtained from the 3 Rivers Wet Weather rain gauge network, (gauge #11) (3RWW). Dry atmospheric deposition was measured at the Laurel Highlands (LRL117) dry deposition (CASTNET) monitoring site, 75 km from Pittsburgh. Wet deposition was measured at the Piney Reservoir (MD08) National Trends Network (NTN) precipitation monitoring site, 115 km from Pittsburgh.

Bi-weekly bulk anion samples were vacuum-filtered (0.2 μm nylon filters) within 24 hours of collection. Storm samples were frozen immediately and then filtered prior to subsequent analyses. Filtered samples were placed in HDPE bottles and either refrigerated (IC analyses) or frozen (isotopic analyses). Nitrate (NO_3^-) concentrations were measured on a Dionex ICS2000 Ion Chromatograph. Nitrite (NO_2^-) concentrations were measured on a Thermo Scientific Evolution 60S UV-Visible Spectrophotometer (Eaton 2005) to evaluate potential interference during isotopic measurements of nitrate.

3.2.3 Isotopic analysis

Samples for isotopic analysis were filtered in the field (0.2 μm nylon filters) into HDPE bottles triply rinsed with 18 MΩ water during bi-weekly sampling and frozen until subsequent analysis. In samples with nitrite-N concentrations >3% of total nitrate-N + nitrite-N, aliquots of the sample were pre-treated with sulfamic acid to remove nitrite, a potential interference during nitrate isotopic analysis (Granger and Sigman 2009). For isotopic analysis of $\delta^{15}N$ and $\delta^{18}O$, a denitrifying bacteria, *Pseudomonas aureofaciens*, was used to convert 20 nmoles of nitrate into $N_2O_{(g)}$, purified in a series of chemical traps and cryofocused (Sigman, Casciotti et al. 2001; Casciotti, Sigman et al. 2002). The resulting gases were analyzed using an Isoprime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) equipped with a Gilson GX271 autosampler and a Trace Gas system at the University of Pittsburgh *Regional Stable Isotope Laboratory for Earth and Environmental Science Research*.

Samples are reported relative to Standard Mean Ocean Water (SMOW) for $\delta^{18}O$ and atmospheric N_2 (for $\delta^{15}N$) using Equation 1:

$$\delta‰ = ((R_{Sample}-R_{Standard})/R_{Standard})*1000 \qquad \textit{(Eq. 1)}$$

where R indicates the ratio of the less abundant isotope to the more abundant isotope (e.g., $^{18}O/^{16}O$). Samples were corrected using international reference standards USGS-32, USGS-34, USGS-35, and IAEA-NO_3; these standards were also used to correct for linearity and instrument drift. Standard deviations for international reference standards were 0.2‰ and 0.5‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively. To evaluate the potential effect of mass-independent contributions of $\delta^{17}O$ to *m/z* 45, the increase in $\delta^{15}N$ was estimated by assuming a 1‰ increase in $\delta^{15}N$ corresponds to an 18.8‰ increase in $\delta^{17}O$ (Coplen, Bohlke et al. 2004). $\Delta^{17}O$-NO_3^- values, which were analyzed as part of a concurrent, ongoing study (n=134, $\Delta^{17}O$ range= +0.01‰ to +27.6‰) suggest $\delta^{15}N$ values were 0.0‰ to 1.5‰ lower than uncorrected values. This range of correction factors is small relative to the range of observed values for $\delta^{15}N$ (+2.5 to +19.4 ‰), thus we do not correct for mass-independent contributions of $\delta^{17}O$ to *m/z* 45.

3.2.4 Markov Chain Monte Carlo and Monte Carlo Simulation Implementation

To estimate relative contributions of known nitrate sources and denitrification occurring in NMR streamwater, Markov Chain Monte Carlo (MCMC) methods were utilized. This technique solves multiple isotope mixing models using Bayesian methods to estimate likely ranges of inputs from each source, incorporating uncertainty into the model. All MCMC simulations were implemented in R (R Development Core Team 2008) using "SIAR" (Stable Isotope Analysis in R), (Parnell and Jackson 2011). Sources of nitrate to NMR were assumed to include ADN and sewage (Divers, Elliott et al. 2013).

Distributions for ADN nitrogen and oxygen isotope values were based on nitrate in precipitation measured directly in the NMR watershed as part of this study, spanning a range of seasons (n=8). For ADN, flux-averaged δ^{15}N was +1.8 SD 0.2 ‰ (n=8), and δ^{18}O was +70.0 SD 13.4 ‰ (n=9). Distributions for sewage nitrogen and oxygen isotope values were taken from literature sources (Aravena, Evans et al. 1993; Fogg, Rolston et al. 1998). The average δ^{15}N for sewage nitrogen isotope values was +10 SD 3‰ (Fogg, Rolston et al. 1998). The average δ^{18}O isotope value for sewage was +3.5 SD 1.4‰ (Aravena, Evans et al. 1993).

As denitrification was not measured empirically, it was treated as a third end-member in the mixing model. Dual-isotope data suggest that sewage was most likely the source for nitrate undergoing denitrification. Literature values for isotopic enrichment during denitrification were used to estimate the denitrification isotopic end point (Aravena and Robertson 1998; Lehmann, Reichert et al. 2003) using large standard deviations to create an "envelope" of possible values incorporating both the 2:1 and 1:1 isotope enrichment trajectories (Aravena, Evans et al. 1993; Kendall, Elliott et al. 2007). As a result, denitrification was assigned a δ^{15}N of +25.9 SD 5‰

and a $\delta^{18}O$ of +12 SD 5‰. Lawn fertilizer is not expected to be a significant contributor of dissolved nitrogen to stream ((Elliott and Brush 2006; Raciti, Groffman et al. 2008; Kaushal, Groffman et al. 2011). Moreover, dual isotopic ratios measured do not indicate fertilizer sources or mixing with fertilizer sources (Figure 3.3). Therefore, lawn fertilizer-sourced nitrate was not considered a source for the purposes of the mixing models used here to estimate stream nitrate sources.

3.3 RESULTS AND DISCUSSION

3.3.1 Discharge and nitrate-N concentrations during storms

Discharge and nitrate-N concentration data for NMR baseflow samples are reported in Chapter 2. Discharge-weighted average nitrate-N concentrations for individual storms ranged from 0.6 mgL^{-1} (Storm 2) to 1.0 mgL^{-1} (Storm 1). Nitrate-N concentrations varied only 0.2 mg L^{-1} during Storm 1, whereas they varied 1 mg L^{-1} during Storms 2 and 3 and 2 mgL^{-1} during Storm 4 (Figure 3.2).

3.3.2 Nitrogen and oxygen isotope data during baseflow and storms

During baseflow, $\delta^{15}N$ and $\delta^{18}O$ values were similar along the longitudinal transect (Figure 3.2, Figure 3.3). The range in $\delta^{15}N$ values was +6.4 to +12.1‰, +2.5 to +14.2‰, and +3.0 to +19.4‰, at NMR1, 2, and 3, respectively (Figure 3.2).

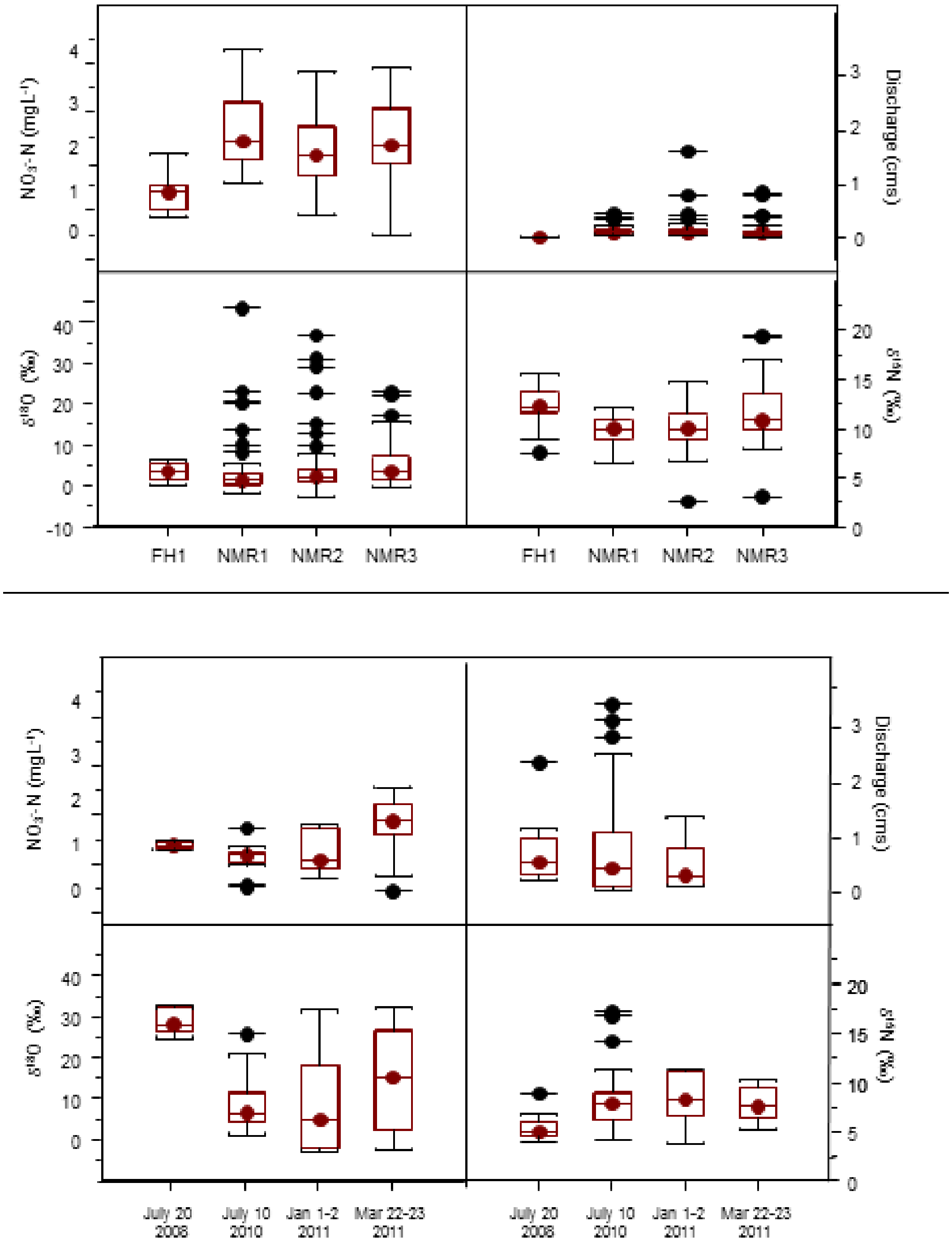


Figure 3.2 Results from sampling at each site and each storm

Boxplots indicating median, quartiles, and outliers for each site during baseflow (top) and the four storms measured at NMR2 (bottom).

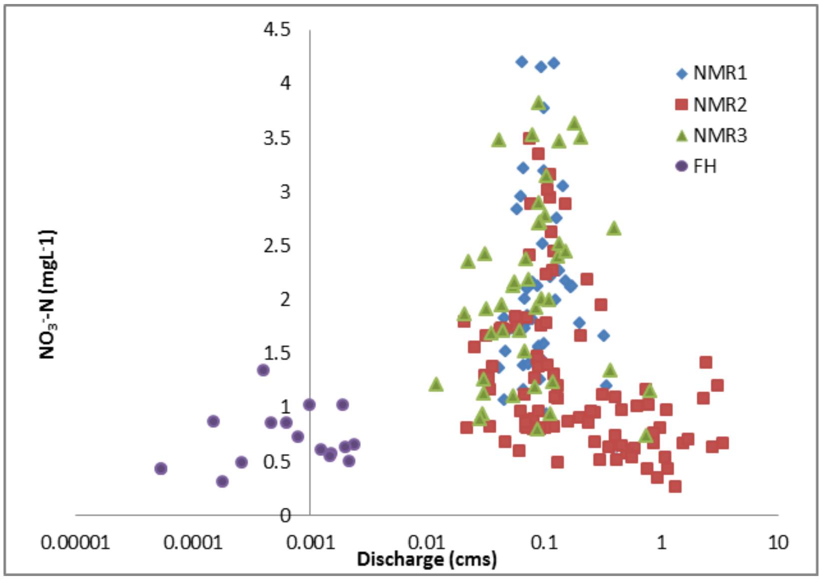


Figure 3.3 Discharge/Nitrate-N relationship including all data

Note that discharge data (x-axis) is shown on a log scale.

δ^{18}O values measured during bi-weekly sampling, which generally captured baseflows, were as low as -2.7‰ (NMR2) and as high as +43.4‰ (NMR1). δ^{18}O values ranged from -1.9 to +43.4‰, -2.7 to +36.9‰, -0.3 to +22.9‰, and +0.1 to +19.8‰ at NMR1, 2, 3, and FH, respectively (Figure 3.2).

δ^{15}N values at NMR2 varied during stormflows (Table 3.1,Figure 3.2) where the widest range of isotopic compositions was observed in Storm 2 (range =13.1 ‰) and narrowest range in Storm 1 (5.1 ‰). δ^{18}O values in stormwater nitrate ranged from +1.0 to +25.7‰ during Storm 2, -2.9 to +31.8‰ during Storm 3, and -2.7 to +32.5‰ during Storm 4. A smaller range in δ^{18}O values was observed during Storm 1, where δ^{18}O values ranged from +24.7 to +32.8‰. The flux-weighted average streamwater nitrate isotopic values measured in the two summer storms and one winter storm (with available discharge measurements) were similar (Table 3.1).

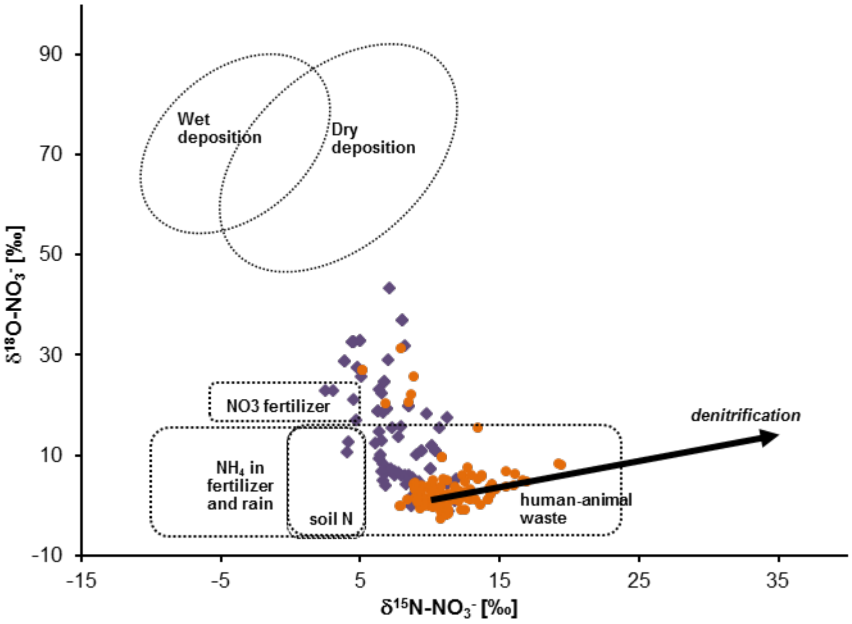


Figure 3.4 Results from dual isotope analysis of nitrate in baseflow and storms

Baseflow (n=141, black dots) and high flow (n=88, diamonds) samples. Flow regime was considered "high" as the result of precipitation events and classified by direct examination of the discharge record. Results from all sites (NMR1, 2, 3, and FH 1) are shown.

3.3.3 Sewage input of NO_3^--N during baseflow

The combination of high nitrate concentrations, high $\delta^{15}N$ values, and low $\delta^{18}O$ values indicates baseflow reactive nitrogen flux is primarily sewage-derived nitrate (Figure 3.4) at each sampling location. Baseflow samples have $\delta^{15}N$ values ranging from +6.4 to +17.3‰ and $\delta^{18}O$ values from -7 to +22.1‰. Animal waste is not considered as a significant source. Although the dogs and wildlife in Frick Park may contribute to nitrogen loads, samples show a sewage-sourced isotopic signature at all sites including NMR1, which is sampled as the stream first enters the park and before park-based animal waste would be introduced to streamwater. The SIAR mixing model estimates that sewage-sourced nitrate contributes between 83-97% of total concentrations in the mainstem of NMR and 84% in FH (Figure 3.5).

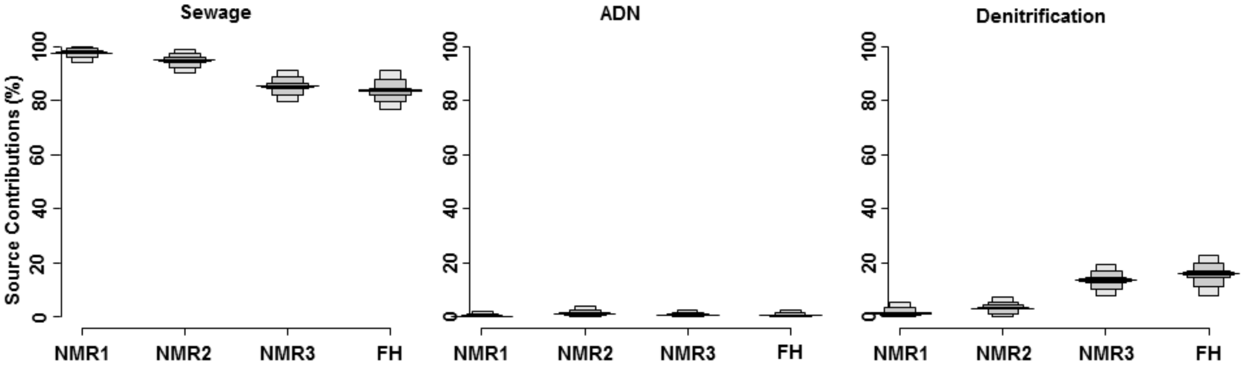


Figure 3.5 Boxplots of mixing model proportions for each site during baseflows

Results are categorized by source. Shown are the 5, 25, 75 and 95% Bayesian confidence intervals for the probability distribution calculated for each source.

In contrast, at all sites during baseflow, the nitrate contribution from ADN is minimal, 0.6 SD 0.5% at NMR1, 1.7 SD 1% at NMR2, and 0.5 SD 0.5% at NMR3 (Figure 3.5).

Although sewage contributions appear to decrease moving downstream (Figure 3.5), this apparent change in mixture instead results from increasing contributions from the denitrification end member, consistent with lower average nitrate concentrations observed at this station. Based on the observed relationship between $\delta^{15}N$ and $\delta^{18}O$, the extrapolated original isotopic composition is similar to sewage-derived nitrate (Figure 3.4). A two end-member mixing model considering only two sources (ADN and sewage) predicts sewage contributes 98-99% of nitrate sampled at all sites during baseflow.

3.3.4 Stormflows versus baseflow sources of nitrate

The nitrate in streamwater during storms is dominated by sewage sources with substantial ADN contributions. At NMR2, the stormflow samples have higher flux-weighted average $\delta^{18}O$ values and lower $\delta^{15}N$ values than those observed in baseflows (+13.3 to +28.4‰ $\delta^{18}O$ and +5.6 to +8.0‰ $\delta^{15}N$ during storms), indicating mixing between sewage and atmospheric deposition sources. The models suggest substantial influence of ADN during stormflows. Two samples from the July 2010 storm fall along the mixing line indicate a mixed sewage/atmospheric deposition source and also fall into the overlapping “soil” range (Figure 3.4). However, it is likely that these samples do represent mixing between sewage and ADN sources, not soil nitrate. For each of the two samples, concurrent concentrations of nitrate-N are 0.7 and 0.75 mgL^{-1}, concentrations that would be considered high for soil nitrate sources. Similarly, four storm samples fall in a range that could indicate a fertilizer source (Figure 3.4), however, concentrations are high in these samples, an unlikely scenario for fertilizer spread in watershed areas far from the stream (Raciti, Groffman et al. 2008; Kaushal, Groffman et al. 2011).

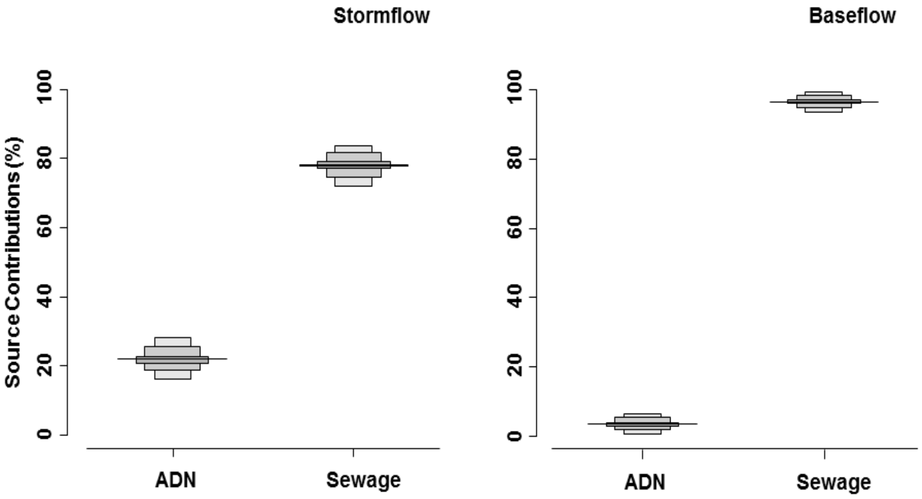


Figure 3.6 Boxplots of percent contributions at NMR2

Shown are the 5, 25, 75 and 95% Bayesian confidence intervals for the probability distribution calculated for each source during baseflows and stormflows.

Mixing models estimate that during stormflow, ADN contributes 22 SD 3% of the total nitrate load to NMR2 with sewage contributions averaging 77.9 SD 3% (Figure 3.6). Therefore, ADN comprises an average of 0.18 mgL^{-1} of the flux-weighted average 0.82 mgL^{-1} nitrate-N concentration in stormwater. This sewage contribution is likely due to leaks in the sanitary sewer system that contribute nitrogen compounds during baseflows (Divers, Elliott et al. 2013), as well as to direct inputs (during and after storms) from the combined sewer.

To inform previous mass balance analysis that inferred significant inputs of nitrate sourced from leaking sewers (Divers, Elliott et al. 2013), dual nitrate isotopes source information was combined with flux data to estimate total flux of nitrate from each source exported from the NMR watershed. In addition, the total export nitrate from each source was calculated for the years 2007 and 2008 by combining total discharge in base and storm flows, flow-weighted average nitrate concentrations during base and storm flows for each year, and the average proportion of nitrate source. By these calculations, 3.5 kg ha^{-1}yr^{-1} of sewage-sourced nitrate was exported from the NMR watershed in 2007 and, and 2.6 kg ha^{-1}yr^{-1} was exported in 2008. Total export of ADN was calculated similarly, by multiplying the total stormflow discharge for each year (Divers, Elliott et al. 2013) (in m^3) by the average nitrate concentration in streamwater observed during storms (0.18 mg L^{-1}). The estimated export of AD-sourced nitrate was 0.23 kg ha^{-1}yr^{-1} and 0.13 kg ha^{-1}yr^{-1} for 2007 and 2008, respectively. This is well below the total ADN-sourced nitrate flux measured at the closest NTN and CASTNET sites and even smaller when recognizing that these deposition estimates do not account for an estimated 2-3x higher ADN flux in urban areas (Redling, Elliott et al. 2011). Retention of ADN is likely high and retention of sewage-sourced nitrate relatively low, due to strong connectivity between sewage-sourced inputs and streamwater. However, source signatures in dual-nitrate isotopic compositions can have a large range, and can change due to biological activity such as uptake or denitrification, which may cause underestimates of ADN flux in streamwater. When total export of nitrate is calculated, export from both sewage and ADN was 3.7 and 2.7 kg ha^{-1}yr^{-1} for 2007 and 2008, respectively. Previously estimated export for total DIN (where DIN = nitrate-N + nitrite-N + ammonium-N) was slightly higher for the same years (2007: 4.5-5.6 kg ha^{-1} yr^{-1}, 2008: 3.1-3.4 kg ha^{-1}yr^{-1}) (Divers, Elliott et al. 2013), in part the discrepancy is likely due to the additional species counted for in total DIN.

Although storms hydrographs were not sampled at sites NMR1 and NMR3, several high flows were captured during bi-weekly sampling (8 at NMR1 and 7 at NMR3). During these high flow events, NMR1 has a flux-weighted average δ^{15}N value (+7.7‰ SD 0.5‰) that is lower than the flux-weighted average baseflow value (+9.1‰ SD 0.2‰), and δ^{18}O values that are higher during stormflow (+18.8‰ SD 3.8‰) than during baseflows (+5.6‰ SD 0.5‰).

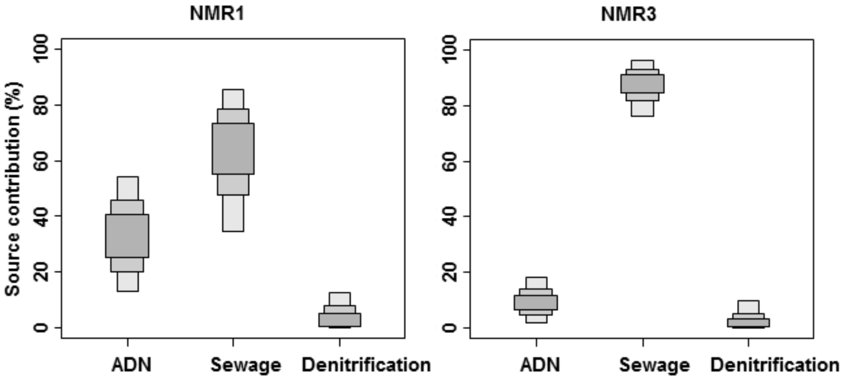


Figure 3.7 Percent source contributions from NMR1, NMR2 stormflows

During the course of bi-weekly sampling, some storm flows were captured at NMR1 and NMR3 (N=8 and N=10, respectively). Shown are the 5, 25, 75 and 95% Bayesian confidence intervals for the probability distribution calculated for each source. Note, denitrification is not a source, however here it is used as an endmember to evaluate the proportion of the nitrate pool sourced from sewage that has undergone denitrification.

The lower δ^{15}N and higher δ^{18}O value at this site during stormflow events suggest mixing between ADN and sewage. These values are indicative of ADN inputs to the stream from storm sewers. When applied to the mixing model, these results predict contributions from ADN during stormflow of up to 34 SD 10% at NMR1 (Figure 3.7). In contrast, at NMR3, storm flow flux-averaged δ^{15}N was +8.0‰ SD 0.8, and δ^{18}O was +6.9‰ SD 1.7‰, values that overlap with the baseflow values (δ^{15}N +10.3‰ SD 0.4‰, δ^{18}O +8.6‰ SD 0.4‰). The lack of clear atmospheric influence at the downstream NMR3 site during higher flow events may be due to a number of reasons: small sample size, the potential for additional inputs to streamwater with unknown isotopic constraints, and the potential for denitrification/uptake as water moves downstream.

3.3.5 Denitrification in the NMR watershed

The SIAR models suggest that as water moves downstream, denitrification occurs (Figure 3.5). Moreover, $\delta^{15}N$ and $\delta^{18}O$ values increase at downstream NMR3 further supporting a case for denitrification along the stream course (Figure 3.6, Figure 3. 8).

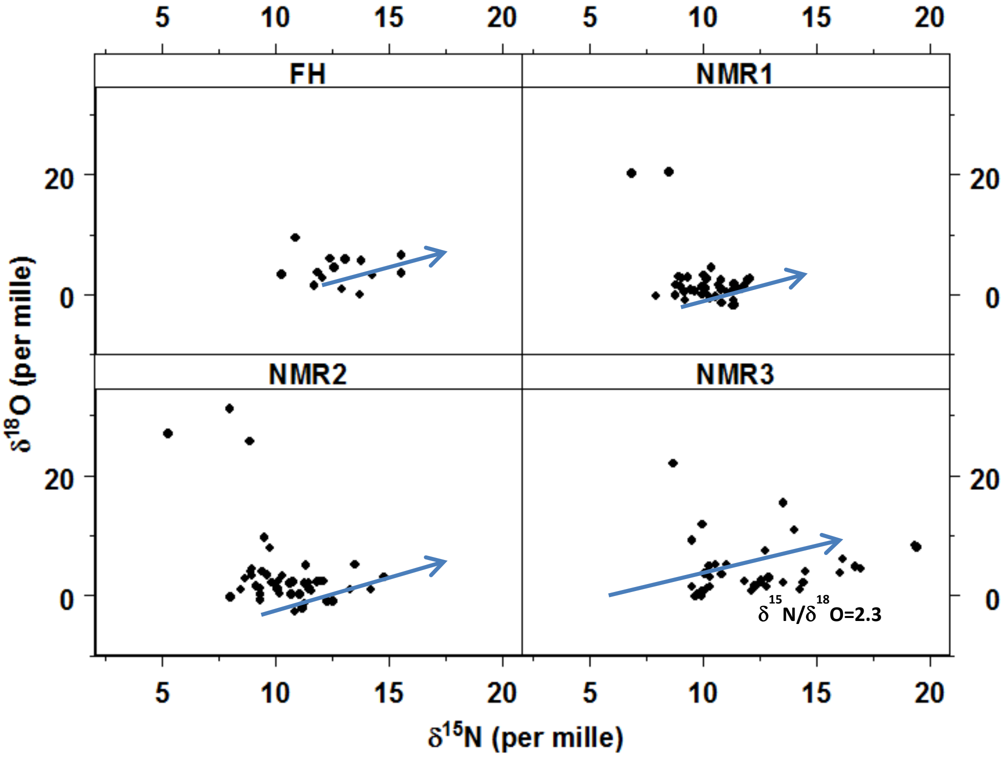


Figure 3.8 Baseflow δ^{15}N vs δ^{18}O for baseflow samples by site

As denitrification enriches the remaining nitrate pool in heavier isotopes at NMR3, the isotopes ratios move along a trajectory indicated by the line, where δ^{15}N and δ^{18}O change in a ratio of 2.3. At the other sites, the denitrification trajectory is less evident.

SIAR mixing models suggests denitrification affects 2.3 SD 1.6% of sewage-sourced nitrate at NMR1, while downstream at NMR3, denitrification affects 13.5 SD 2.8% of the nitrate pool (Figure 3.5). Significant denitrification is also predicted in the FH watershed, with 15.3 SD 3.8% of the total sewage-sourced nitrate pool arising from denitrified nitrate (Figure 3.5). The positive slope of δ^{15}N vs δ^{18}O indicates denitrification contributions at NMR3, where denitrification increases values linearly, with a ratio of 1:2.3 (Figure 3.9). The linear trend suggest systemic enrichment of the remaining nitrate pool in heavier isotopes, as lighter isotopes are removed via Rayleigh fractionation (Bottcher, Strebel et al. 1990; Kendall 1998). In the NMR watershed, the less robust linear trend observed at NMR1 may be due to a complicated mixture of leaking sewers contributing to underground portions of NMR. These sources provide variable inputs to the available nitrate pool, whereas nitrate inputs between NMR1 and NMR3 are minimal, approximating the closed system required of Rayleigh processes. This does not preclude the potential for denitrification above NMR1, rather denitrification processes are not apparent in Rayleigh analysis as the system is not closed (Mayer, Boyer et al. 2002; Anisfeld, Barnes et al. 2007).

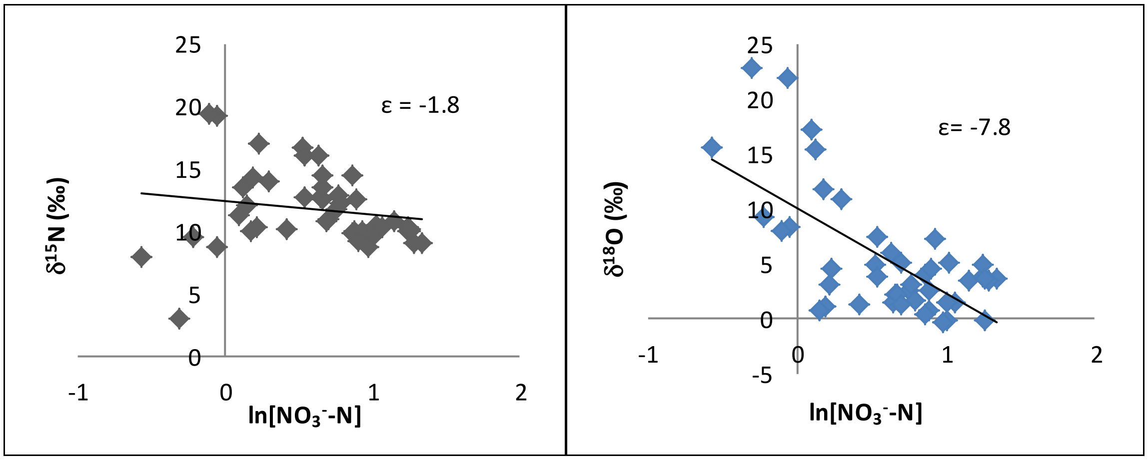


Figure 3.9 Ln[NO_3^--N] and isotope relationships

Ln[NO_3^--N] versus δ^{15}N, left, and ln[NO_3^--N] vs δ^{18}O,right, of nitrate samples from NMR3. The enrichment factor (ε) for each relationship is indicated by the slope of the line.

Confounding effects of multiple sources and inputs in urban areas are observed when the ln[NO_3^--N] is plotted versus $\delta^{15}N$ and $\delta^{18}O$ for baseflow samples at NMR3 (Bottcher, Strebel et al. 1990; Kendall 1998). Here, the resulting predicted isotopic enrichment factor for denitrification (ε) was found to be -1.8 for $\delta^{15}N$/ln[NO_3^--N] and -7.8 for the $\delta^{18}O$/ ln[NO_3^--N] (Figure 3.9). The enrichment factor for the $\delta^{15}N$/ln[NO_3^--N] is indicative of pelagic denitrification, limited by the rate of nitrate diffusion from aerobic to anaerobic waters (Lehmann, Reichert et al. 2003), whereas the value for the $\delta^{18}O$/ln[NO_3^--N] is more indicative of riparian denitrification, where fractionation during denitrification takes place in anaerobic groundwater (Sebilo, Billen et al. 2003). It is unlikely that riparian and pelagic denitrification are co-dominant, instead it is more likely that the multiple sources of nitrate are confounding the denitrification signal. The diversity of sources and dynamics present in urbanized regions makes these mixtures more complicated and therefore quantification of denitrification rates will require in-situ experiments or other approaches.

3.4 IMPLICATIONS

The application of dual-isotope analysis with MCMC techniques to urban nutrient dynamics clarifies the sources of nitrate to NMR streamwater and the fate and transport of the nitrate. Dual nitrate isotope analysis has refined inverse modeling results, attributing up to 99% of in-stream nitrate during baseflow to sewage-derived sources and an average of 78% during stormflow. Flux accounting indicates that on an annual basis, nitrate export during baseflow is higher than during storms. With dual-isotope nitrate data, precise partitioning of urban fluxes between sewage and ADN sources is possible. Therefore, assumptions about source, fate and transport can be verified, dramatically refining urban nutrient mass balance approaches. This quantification is fundamental for urban nutrient management, allowing robust accounting and clearer understanding of processes and fluxes in these human-controlled environments.

4.0 ATMOSPHERICALLY DEPOSITED NITRATE IN AN URBAN STREAM DETERMINED BY TRIPLE OXYGEN ISOTOPE ANALYSIS

4.1 INTRODUCTION

Atmospheric deposition of pollutants negatively affects water and ecological health. Atmospherically deposited nitrogen (ADN) can be concentrated in urban areas (Lovett, Traynor et al. 2000), due to increased emission source density including vehicles, industry, and power plants (Elliott, Kendall et al. 2007; Redling, Elliott et al. 2011). Atmospheric deposition, primarily in the form of nitrate (NO_3^-) has been shown to affect groundwater and surface waters in urban areas (Dejwakh, Meixner et al. 2012). Perhaps more importantly, wet and dry ADN deposited on impervious surfaces in urban areas can be directed immediately to surface waters during wet weather events through storm sewers and road drains (Walsh 2000). However, there has been a limited amount of work to quantify how much ADN contributes to loadings in urban streams due to complexities with source attribution.

Nutrient budgets and dual-nitrate isotope studies have been used to quantify inputs and export of nitrogen to urban watersheds (Mayer, Boyer et al. 2002; Homer, Huang et al. 2004; Anisfeld, Barnes et al. 2007; Burns, Boyer et al. 2008; Kaushal, Groffman et al. 2011). However, these methods do not precisely quantify atmospherically-sourced nitrogen that reaches surface water, for a variety of reasons. Fractionations from processes such as denitrification and assimilation into organic matter can influence the isotope ratios of the residual nitrate pool (Mayer, Boyer et al. 2002; Kaushal, Groffman et al. 2011). Additionally, atmospheric nitrate has a wide range of $\delta^{15}N$ and $\delta^{18}O$ values that can overlap with other nitrate sources (Kendall, Elliott et al. 2007). This overlap makes it difficult to distinguish nitrate source contributions, an important piece of information for managers and watershed groups trying to manage nitrogen pollution in their waterways.

Nitrate from atmospheric deposition is enriched in the ^{17}O atom, relative to terrestrial nitrate (Michalski, Scott et al. 2003). This enrichment is referred to by the notation "$\Delta^{17}O$", where $\Delta^{17}O=\delta^{17}O-(\delta^{18}O*0.52)$. The $\delta^{17}O$ anomaly is exclusively a photochemical effect that results from reactions with atmospheric ozone (Thiemens 1999). As a result, positive $\Delta^{17}O$ values are unambiguous indicators of atmospherically-derived nitrate (Michalski, Scott et al. 2003). In terrestrial systems, the $\delta^{17}O:\delta^{18}O$ relationship is maintained through fractionating processes, with the result that the $\Delta^{17}O$ signal will remain unchanged during denitrification reactions (Michalski, Meixner et al. 2004). This is in contrast to dual-nitrate isotopic compositions ($\delta^{15}N$, $\delta^{18}O$) in which source signature may span a large range, and are subject to fractionations during uptake or denitrification. Together, these factors complicate source apportionment of atmospheric nitrate revealed through the use of a dual isotope approach (Kendall, Elliott et al. 2007). In comparison, $\Delta^{17}O$ is robust tracer of atmospheric deposition through terrestrial systems, compared to the more widely used $\delta^{18}O$.

Few studies have employed $\Delta^{17}O$ analyses to interpret watershed-scale processes (Meixner, Huth et al. 2007; Tsunogai, Komatsu et al. 2010; Costa, Michalski et al. 2011). In general, this method has been used sparingly because of the difficulty in analysis of the low natural abundance of ^{17}O that requires large sample volumes. Recent method developments couple the bacterial denitrification method with the thermal decomposition of gaseous N_2O and thus require far less sample material (Kaiser, Hastings et al. 2006). These alterations have extended application of the $\Delta^{17}O$ technique to include studies tracking the fate and biological processing of atmospherically deposited nitrate in forested ecosystems (Tsunogai, Komatsu et al. 2010; Costa, Michalski et al. 2011) and groundwater under semi-arid urban systems (Dejwakh, Meixner et al. 2012)

In this study, the mass-independent $\Delta^{17}O$ of nitrate in an urban stream is used to quantify atmospheric contributions to streamwater nitrate concentrations. The study site, Nine Mile Run, is located in an urban watershed in Pittsburgh, PA, an industrial region with considerable potential for ADN due to local emissions sources. The $\Delta^{17}O$ anomaly was used to quantify and understand nitrate inputs both in baseflow and during storms. Previous work using dual nitrate isotopes indicates that there is little to no ADN during baseflows and approximately 22% of nitrate during stormflows is from ADN, with the remainder sourced from sewage (Divers, Elliott et al. 2013). This effort focuses on refining estimates of ADN during baseflows, quantifying ADN during stormflows, and calculating export of ADN from the watershed. Further, $\Delta^{17}O$ is used to examine potential denitrification of ADN in urban environments.

4.2 METHODS

4.2.1 Location

NMR drains a 1,570 ha urban watershed with 38% impervious cover (Homer, Huang et al. 2004). Bedrock in the area is composed of shale, limestone, siltstone, and sandstone (Leighton

1927). The upper portions of NMR are buried in storm sewers (Figure 1.2). NMR emerges in Frick Park (Pittsburgh, PA) and runs for 3.5 kilometers before it joins the Monongahela River.

The NMR watershed is served by two contrasting sewer systems (Figure 4.1). The eastern portion (52% of the watershed) is serviced by a sanitary sewer system, whereas the western portion (36% of the watershed) is serviced by a combined sewer system. The remaining 12% is city parkland with only sewer mains running through it. Sanitary sewers are designed to direct waste from households and businesses directly to the sewage treatment plant. In dry weather, combined sewers send waste directly to the treatment facility; however during wet weather events, these systems direct overflows of sewage/storm water mixtures to surface water. Thus, both sewer systems are potential non-point sources of pollution from leakage during baseflow conditions, with point-source contributions from the combined sewers during storm events.

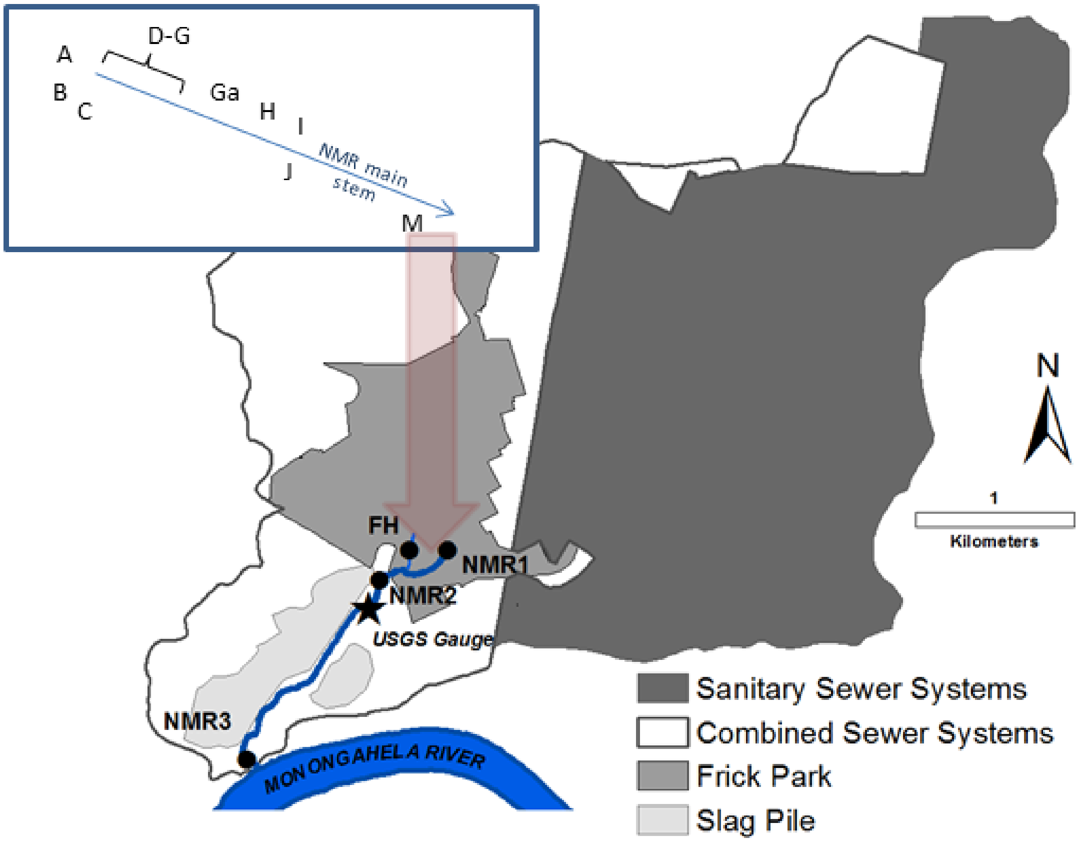


Figure 4.1 Map of the NMR watershed, with sampling locations marked

Inset map indicates the relative positions of outfalls sampled (A through G, G_a, H, I, J, M) during Storm 5 on October 18, 2012.

4.2.2 Field Sampling

Sampling was conducted bi-weekly between April 2007 and April 2009 at three sampling locations forming a longitudinal transect along Nine Mile Run (Figure 4.1). NMR1 is roughly where the stream emerges from underground storm sewers. NMR2 is located ~50 meters below a combined sewer input and below a major highway overpass. NMR3 is located at the mouth of the watershed. A small ephemeral stream, FH was also sampled when flowing (Figure 4.1). Additionally, storm-flow samples were collected at NMR2 during two summer storms (Storm 1: July 20, 2008, Storm 2: July 8, 2010), two winter storms (Storm 3: January 1-2, 2011, Storm 4: March 22-23, 2011) and a fall storm (Storm 5, October 18, 2012) (Table 4.1). Stormflow samples were collected from NMR 2 before the rainfall began and at intervals throughout the storm (Table 4.1).

Table 4.1 Results from each storm for δ^{15}N, δ^{18}O, and Δ^{17}O

NO_3^--N average concentrations are discharge weighted, and δ^{15}N, δ^{18}O, and Δ^{17}O average isotope values are flux-weighted. For Storm 4, where discharge was not measured, average NO_3^--N concentrations and isotope values were not calculated.

Storm event	***Total rainfall amount (mm)***	***Storm duration***	***Sampling frequency***	***Discharge method***	***Sampling begins***	***Sampling ends***	***NO_3^--N Avg. (mgL^{-1})***	***NO_3^--N Range (mgL^{-1})***	***δ^{15}N Avg. (‰)***	***δ^{15}N Range (‰)***	***δ^{18}O Avg. (‰)***	***δ^{18}O Range (‰)***	***Δ^{17}O Avg. (‰)***	***Δ^{17}O Range (‰)***
1	7.9	1 hour 15 min	½ hour for 1.5 hours, then every hour	USGS gauge	7/20/08 14:15	7/20/08 19:30	1.0 SD 0.1	0.9 to 1.1	5.6 SD 0.8	3.9 to 8.9	28.9 SD 3.3	24.69 to 32.78	8.6 SD 0.9	7.1 to 14.6
2	25.1	6 hrs 15 min	½ hour for 6 hours, then once an hour	pressure transducer	7/9/10 14:55	7/10/10 7:25	0.9 SD 0.05	0.4 to 1.4	7.3 SD 0.5	4.1 to 14.2	9.2 SD 6.1	1.02 to 25.74	5.3 SD 0.5	0 to 7.5
3	12	6 hr 15 min	½ hour for 6 hours, then once an hour	pressure transducer	1/1/11 15:44	1/1/11 18:14	0.6 SD 0.02	0.3 to 1.5	8.0 SD 0.3	6.4 to 11.4	14.8 SD 1.2	-2.9 to 31.75	4.2 SD 0.4	0 to 10.6
4	18	21 hours	once an hour	pressure transducer	3/22/11 10:45	3/23/11 19:45	*	0.3 to 2.3	*	5.2 to 10.3	*	-2.69 to 32.51	*	0 to 10.7
5	17.3	8 hrs 45 min	every ½ hour	pressure transducer	10/18/12 15:03	10/18/12 23:33:00	0.51 SD 0.06	0.3 to 1.1	8.3 SD 1.1	3.3 to 11.6	4.6 SD 1.3	-6.1 to 27.7	3.0 SD 0.5	0 to 9.4

Samples for isotopic analysis were filtered in the field during bi-weekly baseflow sampling using 0.2 μm nylon filters into HDPE bottles triply rinsed with 18 MΩ water. Storm samples were stored frozen then filtered (0.2 um nylon) in the lab. Sample aliquots were treated with sulfamic acid to remove nitrite, an potential interference in the nitrate isotopic analysis (Granger and Sigman 2009). All filtered and treated samples were stored frozen. Additionally, bulk precipitation was collected during each storm, stored, filtered, and analyzed in the same manner.

Samples were classified as baseflow or stormflow based on daily stream hydrographs. During storms, samples were classified as "baseflow" if they were collected before the storm began or after the discharge returned to pre-storm baseflow levels; intervening samples were classified as "storm" samples. Precipitation data was obtained from 3 Rivers Wet Weather (3RWW 2010).

During Storm 5, on October 18, 2012, both the main stem of NMR at NMR2 and 12 outfalls were sampled synoptically (referred to as A, G, G_a, H, I, J, M and shown in Figure 4.1). The origin of each inlet is unknown. Of the 12 outfalls, the five outflows with flow were sampled the day prior to the storm to compare pre- and event water at each outfall. After the storm began, each of 12 outfalls were sampled as flow began and again approximately 1 hour later. Some outfalls (B, C, J) were sampled only once during the storm due to safety concerns.

During bi-weekly sampling and Storm 1, area-velocity method instantaneous discharges were measured. In addition, daily average discharge data (6/14/2006-9/30/2009) were obtained from USGS station 03085049 (Figure 1.1). The USGS program "PART" was used for hydrograph separation of the USGS discharge record for years 2007 and 2008 (Rutledge 1998). After 9/30/2009, the USGS station was discontinued. To measure discharges during subsequent storm events, a pressure transducer was installed in the stream during the spring of 2010 and a rating curve developed (Figure 3.1). Discharge quantities for Storms 2 & 3 were obtained by applying the stage discharge relationship to the pressure transducer data. Discharge during Storm 4 was not measured due to equipment malfunction; therefore this storm was not included in analyses that required classification according to discharge.

4.2.3 Isotopic Analysis

Samples were analyzed for $\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$ at the University of Pittsburgh *Regional Stable Isotope Laboratory for Earth and Environmental Science Research*. For each isotopic analysis, a denitrifying bacteria, *Pseudomonas chlororaphis subsp. aureofaciens,* was used to convert nitrate into gaseous N_2O (Sigman, Casciotti et al. 2001; Casciotti, Sigman et al. 2002; Kaiser, Hastings et al. 2006). For $\delta^{15}N$ and $\delta^{18}O$ measurements, 20 nmoles of nitrate were converted to N_2O gas , which was purified in a series of chemical traps, cryofocused in liquid nitrogen, and analyzed in a GV Instruments Isoprime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) (Sigman, Casciotti et al. 2001; Casciotti, Sigman et al. 2002). For $\Delta^{17}O$, samples were analyzed using similar methods but with an increased sample mass of 200 nmoles of nitrate. After cryofocusing, N_2O gas enters a gold tube in a furnace heated to ~ 800 ^{0}C, where it decomposed to N_2 and O_2 gases (Kaiser, Hastings et al. 2006), followed by analysis in the CF-IRMS. International standards (IAEA-NO_3, USGS 32, USGS 34, and USGS 35 for $\delta^{15}N$ and $\delta^{18}O$, and USGS 34 and USGS 35 for $\Delta^{17}O$) were processed and analyzed concurrently with samples, and the samples were corrected based on these standards. Sample values were reported relative to Standard Mean Ocean Water (for $\delta^{18}O$) and atmospheric N_2 (for $\delta^{15}N$) using Equation 1:

$$\delta\text{‰} = ((R_{Sample}-R_{Standard})/R_{Standard})*1000 \qquad \text{(Eq. 1)}$$

where R indicates the ratio of the less abundant isotope to the more abundant (e.g., ^{18}O /^{16}O) in the sample versus the standard, respectively. The mass-independent $\Delta^{17}O$ is calculated using the relationship in Equation 2:

$$\Delta^{17}O = \delta^{17}0 - 0.52 * \delta^{18}O \qquad \text{(Eq. 2)}$$

Precision was 0.2‰, 0.5‰, and 0.5‰ for $\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$, respectively.

4.3 RESULTS

4.3.1 $\Delta^{17}O$ during baseflow and storms:

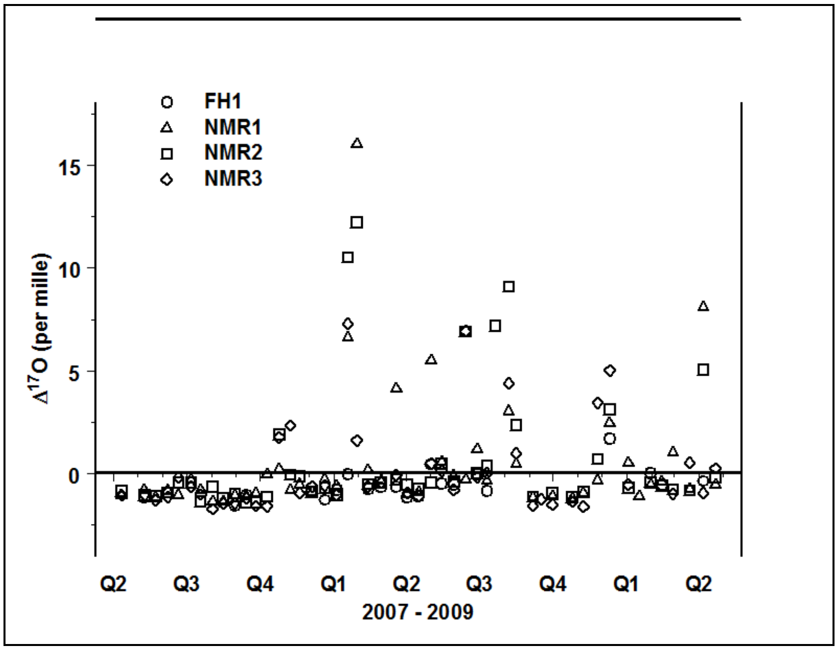


Figure 4.2 Baseflow $\Delta^{17}O$ from biweekly sampling April 2007-2009

$\Delta^{17}O$ values greater than 0‰ indicate the presence of ADN.

Dual isotope results for nitrate evaluated during baseflows are reported in Chapter 3. Positive $\Delta^{17}O$ values, indicative of the presence of ADN, were measured in 40 of 164 (24%) of samples collected during bi-weekly sampling (Figure 4.2). For these biweekly samples, $\Delta^{17}O$ values ranged from +0.12 to +16‰, with a flow-weighted average value of 1.3 SD 0.04‰. In general, these values indicate small contributions of ADN to streamwater nitrate during baseflow conditions.

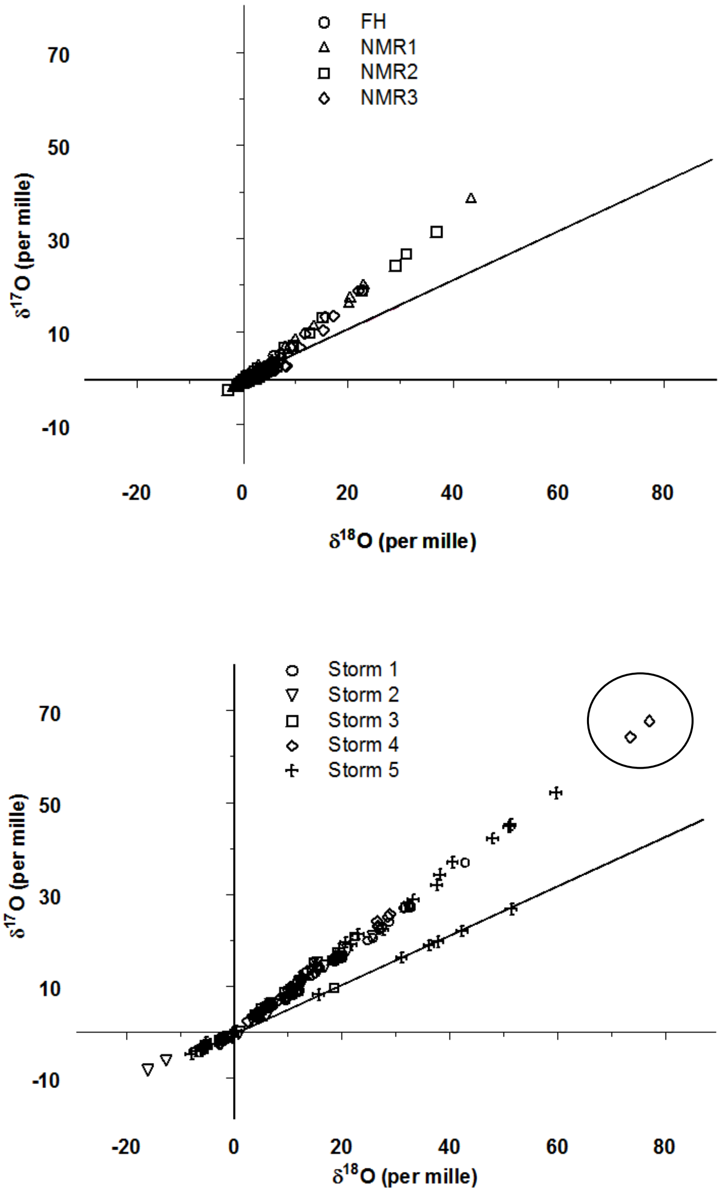
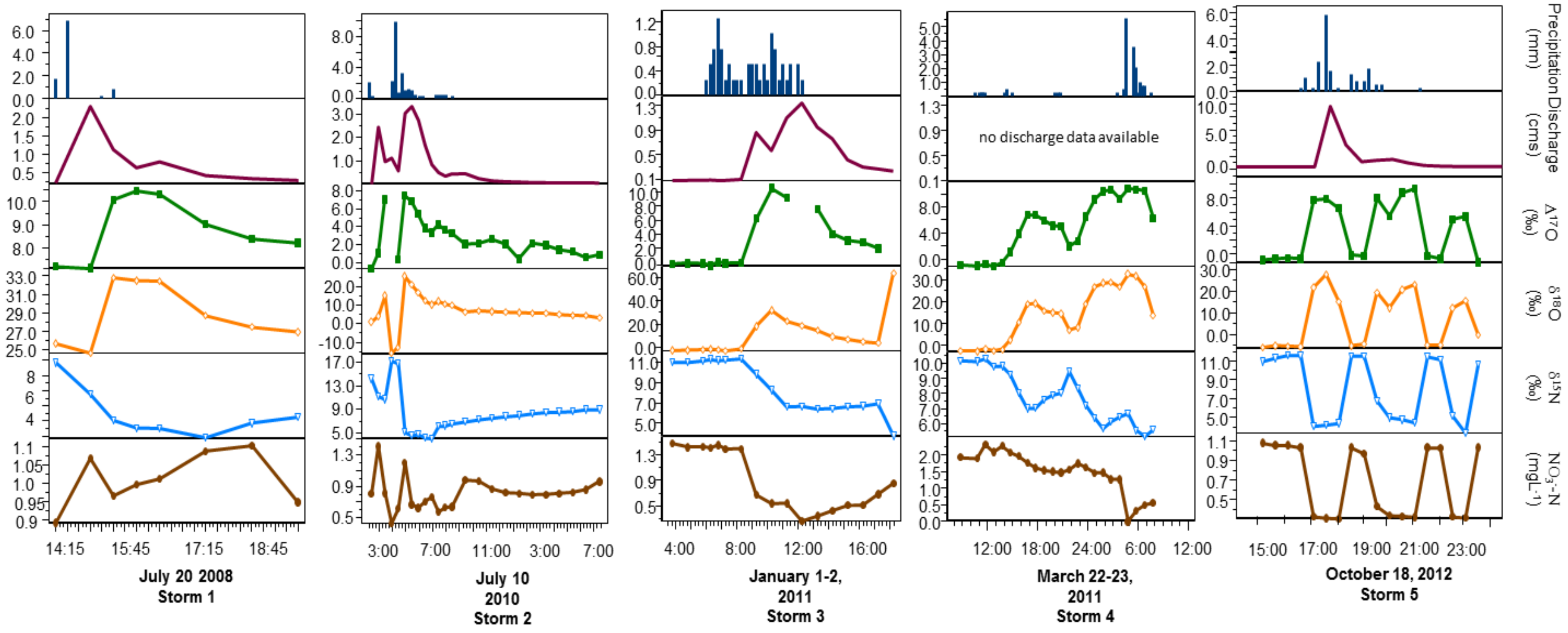


Figure 4.3 Triple isotope plot of NMR samples during baseflow and storms at NMR2

Solid black line in each plot indicates the Terrestrial Fractionation Line, or TFL, (TFL=δ^{18}O*0.52-δ^{17}O). In the bottom panel, data points that fall along the TFL include samples taken from the stream before the storm began (Storms 3 & 5), as well as 12 outfalls draining to the stream (Storm 5). Circled data points indicate two precipitation samples from Storm 2, with Δ^{17}O values of +26.0 and +27.6 ‰.

Dual isotope results for nitrate evaluated during storm flows are reported in Chapter 3 (Table 4.1,Figure 3.4). Positive $\Delta^{17}O$ values, indicative of the presence of ADN, were measured in 67 of 91 (73%) of samples collected before and during storms, with a flux weighted average $\Delta^{17}O$ value for the storms of 4.8 SD 0.18‰. Samples taken before the onset of storms generally did not contain ADN with the exception of Storm 1 (see discussion). Similarly, samples taken from outfalls before the storm began had negative $\Delta^{17}O$ values indicating a non-ADN source. These samples instead have dual nitrate isotope values indicative of nitrate from sewage ($\delta^{15}N$ from +10.9 to +11.6‰, $\delta^{18}O$ from -6.1 to -5.3‰) (Figure 3.4).



July 20 2008
Storm 1

July 10
2010
Storm 2

January 1-2,
2011
Storm 3

March 22-23,
2011
Storm 4

October 18, 2012
Storm 5

Figure 4.4 Results from sequential sampling of stream at NMR2 during each storm

Note the change in scale for each storm event.

4.4 DISCUSSION

4.4.1 Changes in nitrate source between baseflow and stormflows

There was little ADN-sourced nitrate observed (Figure 4.3) during baseflows, with a flux-weighted average $\Delta^{17}O$ of 1.3 SD 0.04‰, compared to 4.8 SD 0.18‰ in storms. The primary transport vectors for ADN into streamwater are runoff of dissolved nitrate in rainwater and transport of dry deposition from impervious surfaces through storm sewers and into streams. Field observations about weather conditions during sampling indicate that samples with detectable ADN were collected on days with precipitation in the 24-36 h preceding sampling. $\Delta^{17}O$ generally increased with increasing discharge for storms although the relationship was not strong. There was no relationship between discharge and $\Delta^{17}O$ during bi-weekly sampling. Stream samples collected from the main stem of NMR (NMR1, 2, 3) did not contain measurable $\Delta^{17}O$ at discharges below 0.023 cms. This suggests a potential "threshold" discharge for the influence of ADN on streamwater. At discharges lower than this threshold, there may not be enough flow to deliver ADN to stream water.

Hysteresis loops during storm flows can be used to investigate mixing between sources (Evans and Davies 1998). The hysteresis in dual isotope space of samples collected through each of the storms indicates a consistent temporal change in nitrate source contributions to NMR (Figure 4.6). Nitrogen and oxygen isotopic values measured at the beginning of storm flow for Storms 2, 3, 4, and 5 each are typical of sewage-derived sources. During Storms 2, 3, and 4 isotopic values shift towards a mix of ADN and sewage-derived nitrate before returning to values typical of sewage-derived nitrate (Figure 4.5).

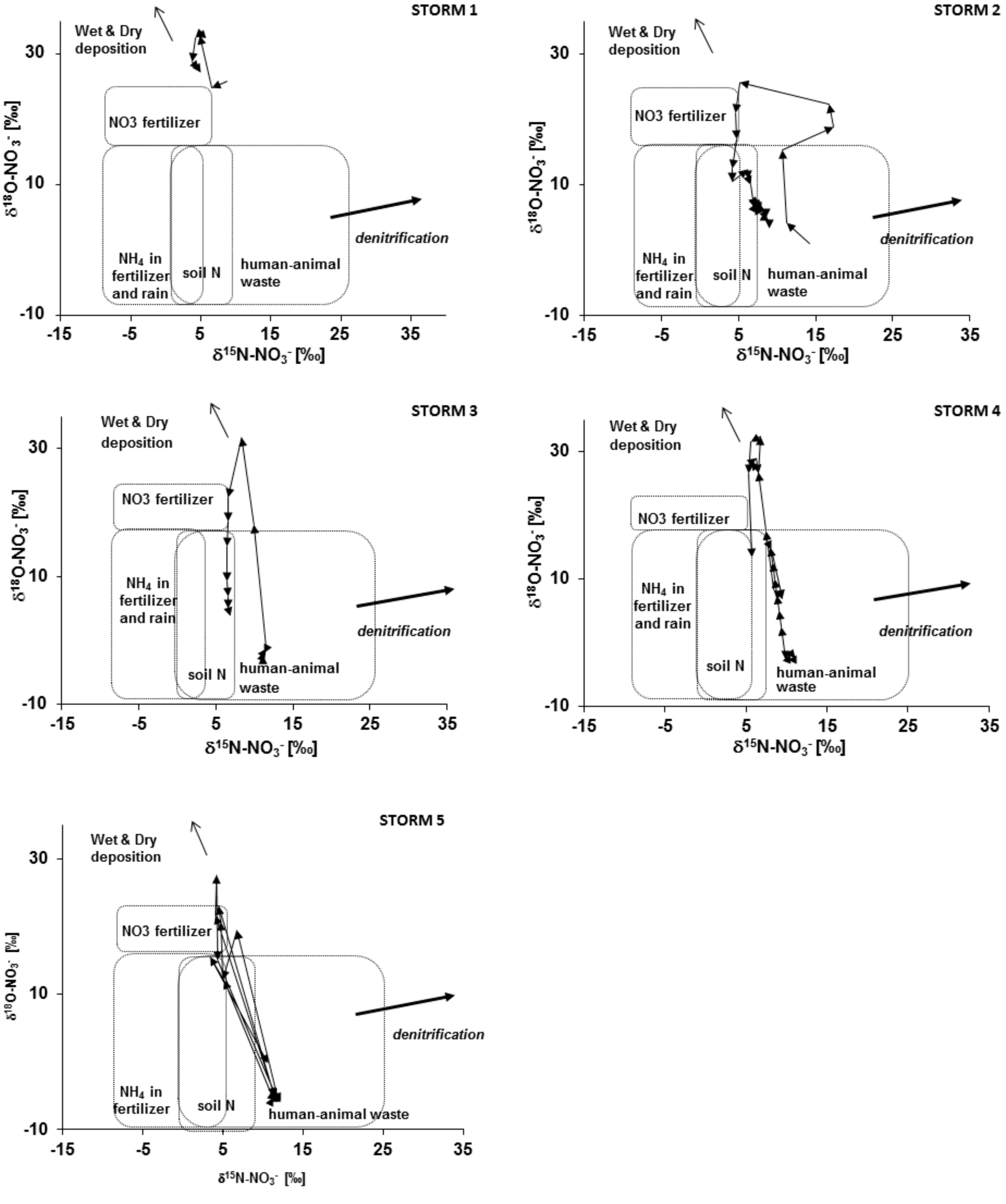


Figure 4.5 Hysteresis analyses of dual nitrate isotope values for individual storms

Isotopic values for every storm showed a counter-clockwise hysteresis, except for Storm 5. During Storm 2, two isotopic values measure along the trajectory indicating denitrification of the available nitrate pool.

Pre-storm samples taken before Storm 1 showed evidence of ADN in the streamwater. On the day Storm 1 was sampled, 1.5 mm of precipitation fell at 7:30 in the morning (sampling began at 2:30 pm). This amount of rainfall is perhaps enough to transport the ADN into streamwater, or simply transport it closer to the stream, so that a large flux of ADN is observed when the second storm came through in the afternoon. Storm 1 isotope values do not return to typical sewage values observed during baseflow conditions; this likely results from a shorter sampling duration for this storm that may not have captured the full extent of the stream hydrograph.

4.4.2 Timing of response with storms

The amount of ADN, its frequency, and persistence in streamwater vary during each storm, as indicated by $\Delta^{17}O$ values > 0 (Table 4.1). As mentioned previously for dual nitrate isotopes, Storm 1 shows evidence of ADN prior to the first sample collection. This is also the case with $\Delta^{17}O$ values, as they range from +7.1 to +14.6 ‰ prior to the onset of Storm 1 (Figure 4.4). During the two summer storms (Storms 1 and 2) each peak in $\Delta^{17}O$ follows an intense period of rainfall and trails the subsequent peak in discharge by approximately 30 minutes (Figure 4.4). During the winter storms (Storms 3 and 4), there is a longer delay in the response time between initial rainfall and positive $\Delta^{17}O$ value (3 hours for Storm 3 and 4.5 hours for Storm 4). For these winter storm events, precipitation volume was low (less than 1.5 mm in 15 minutes) during the first 3 and 4 hours, respectively. In comparison, during the summer storms, rainfall intensity was greater earlier in the storm. This suggests that the observed increase in rainfall intensity resulted in flow from impervious surfaces to the stream, and this intensity was required to mobilize and transport ADN to streamwater. In contrast, during the two winter storms, precipitation increased steadily and did not show the dramatic intensity exhibited in the summer storms. As further comparison, during the fall storm (Storm 5) the Δ^{17}O peak followed a period of intense rainfall, but preceded the discharge peak (Figure 4.4). During this storm, two peaks in Δ^{17}O were observed, with one following a second period of intense precipitation by an hour; the other did not show any correspondence to peaks in discharge or precipitation intensity. These three periods of high Δ^{17}O, as well as the first peak of Δ^{17}O that precedes the discharge peak, suggest that the rainfall may not have been uniform across the NMR watershed during Storm 5, so that timing of delivery of run-off from impervious surfaces was distributed throughout the storm event.

4.4.3 Quantification of ADN in streamwater and implications for retention

The use of Δ^{17}O in mixing models for storm events allows precise quantification of ADN inputs during storms. To determine the Δ^{17}O of the wet deposition endmember, bulk precipitation was analyzed from two samples taken during Storm 4. (Other precipitation samples did not contain sufficient nitrate to analyze for Δ^{17}O without pre-concentration). The Δ^{17}O values in precipitation samples was +27.6 and +26‰, and are within the range (~+25 to +30‰) reported for Δ^{17}O of atmospheric nitrate based on seasonal differences in photochemical oxidation pathways (Michalski, Scott et al. 2003). Accordingly, the ADN endmember in mixing models was conservatively estimated at +25‰. This endmember was used in mixing models along with discharge data, concentration-weighted nitrate-N data, and the flux-weighted Δ^{17}O to calculate the total export of nitrate-N (in kg) from each source during each storm. Results from this calculation are shown in Table 4.2. ADN exported during individual storms varied with amounts ranging from 2.3 kg total nitrate-N (Storm 2) to 6.6 kg total nitrate-N (Storm 1). As a percentage of the total exported nitrate-N during each storm, ADN varied from 17 to 39%, with an average of 25%. This average is only slightly higher than the 22% average calculated from nitrate dual-isotope analysis without analysis of the mass-independent $\Delta^{17}O$, although each analysis employed two different mixing model formulations.

Table 4.2 Flux of NO_3^--N calculated during each storm from ADN and sewage sources

No flux data is shown for Storm 4, because of the lack of discharge data.

	Total NO_3^--N exported (kg)	***ADN exported (kg)***	***Sewage exported (kg)***	***ADN (%) of total NO_3^--N***	***Sewage (%) of total NO_3--N***	***Precipitation (mm)***	***Discharge (m^3)***
Storm 1	16.9	6.6	10.2	39	61	7.9	15,359
Storm 2	29.8	5.1	24.7	17	83	25.1	37,861
Storm 3	13.1	2.3	10.7	18	82	12.0	25,629
Storm 5	15.3	2.5	12.8	16	84	17.3	33,511

The use of $\Delta^{17}O$ as a tracer in streamwater can be applied to prior watershed N budgets results. If this 25% average of ADN export during stormflow is applied to estimates of total export for sampling years 2007 and 2009 (see Chapter 2), estimates of total export of ADN for each year rise from 0.25 to 0.32 kg ha^{-1} (2007) and from 0.15 to 0.19 kg ha^{-1} (2008). Total ADN flux is not correlated with total precipitation or total discharge (Table 4.2), instead the largest flux of ADN was observed during Storm 1, a summer thunderstorm that rained 7.9 mm in 45 minutes (Figure 4.4). Accordingly, future analyses of this data will address whether any thresholds in cumulative precipitation or antecedent moisture conditions are correlated with export of ADN.

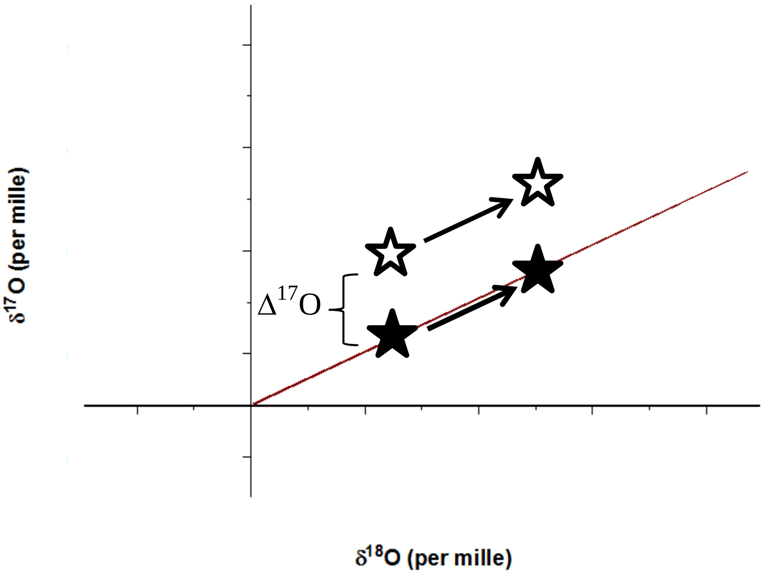


Figure 4.6 Denitrification effects on Δ^{17}O

Hypothetical representation of the effects of denitrification processes on δ^{17}O, δ^{18}O, and Δ^{17}O values. Denitrification will increase δ^{17}O and δ^{18}O values proportionally, such that values will follow the trajectory of the TFL as indicated by "A" that moves along arrow to "B". Samples with a positive Δ^{17}O will behave in the same fashion, with δ^{17}O and δ^{18}O increasing proportionally (C to D), such that they follow a parallel trajectory as the TFL, while maintaining the original Δ^{17}O.

Using dual-nitrate isotope data, isotopic fractionations characteristic of denitrification have been observed in NMR, particularly at NMR3 (Chapter 3) and potentially during Storm 2 (Figure 4.4). Denitrification in the Δ^{17}O data from baseflow samples would be observable as samples with a higher δ^{17}O that trends parallel to, but falls above, both the TFL and the main data cluster (Figure 4.6), as the mass-independent isotope would be unaffected by denitrification processes (Michalski, Scott et al. 2003). While denitrification of ADN may occur in NMR, it is not evident from examination of Δ^{17}O data (Figure 4.3). This likely results from the slower, consistent delivery of leaky-sewer sourced nitrate to the stream and anaerobic zones where denitrification occurs. In comparison, ADN is transported to the stream during higher flows and thus may not remain in the system long enough for denitrification processes to take place, and/or may not be directed through saturated soil/groundwater zones where conditions are conducive to denitrification. This suggests that when management goals of removing nitrate from a watershed are evaluated, directing storm run-off into Best Management Practices, such as retention ponds and rain gardens, may be an effective solution in reducing ADN that is transported to receiving waters.

4.4.4 Synoptic sampling of flows into NMR during October 2012 storm

Results from samples collected before and during the October 18, 2012 storm elucidate sources and dynamics of ADN as it is washed into NMR. Of the 5 outfalls with flow into the main NMR stream channel, three had sufficient nitrate concentrations to measure Δ^{17}O. No Δ^{17}O was present in any of the samples from pre-storm sampling (Figure 4.7), indicating these pre-storm flows are likely sourced from groundwater or buried stream sections. Shortly after the storm began, the main flow of NMR emerging from underground storm sewers (outfall “A”) had a Δ^{17}O of +0.5‰, indicating that very little nitrate-N was ADN. A second sample taken ~30 minutes later had a Δ^{17}O of +14.4‰, indicating that 58% of the nitrate load was from ADN. Other sites were sampled as they began flowing (D, F, C, G, G_a, H, I, and M). With the exception of M, water samples from each site had significant Δ^{17}O ranging from +11.5 to +21‰ (Figure 4.7). Mixing models applied to these isotope measurements indicate ADN contributed from 17 to 84% of the total nitrate to outflow from these piped inputs, with the remainder sourced from sewage (as indicated by dual-isotope analysis). These proportions of ADN, particularly from sites D, F, G, G_a, H and I are strongly indicative of a direct connection between stream and impervious surfaces. As the stormwater reached the stream, the FH sub-watershed, (referred to in Figure 5 as site "M") showed the effects of ADN to a lesser degree, with streamwater Δ^{17}O of +5.3‰.

As the storm progressed, many sites showed the effects of dilution, with water NO_3^--N concentrations very low, precluding further Δ^{17}O analysis. Sites D, I, and J, with sufficient concentrations for analysis, showed Δ^{17}O values of +4.3, +5.7, and +5.3 ‰ respectively, much lower than values originally observed coming from these outfalls earlier in the storm, indicative of a flushing effect of ADN from the land surfaces into streamwater with the first rush of high-intensity rainfall. Future analysis of these stormflow samples and data will include pre-concentration of samples where nitrate was too dilute, and thus allow the analysis of these samples for Δ^{17}O. Additionally, more specific spatial analysis using GIS software will help to determine contributing areas for each outfall.

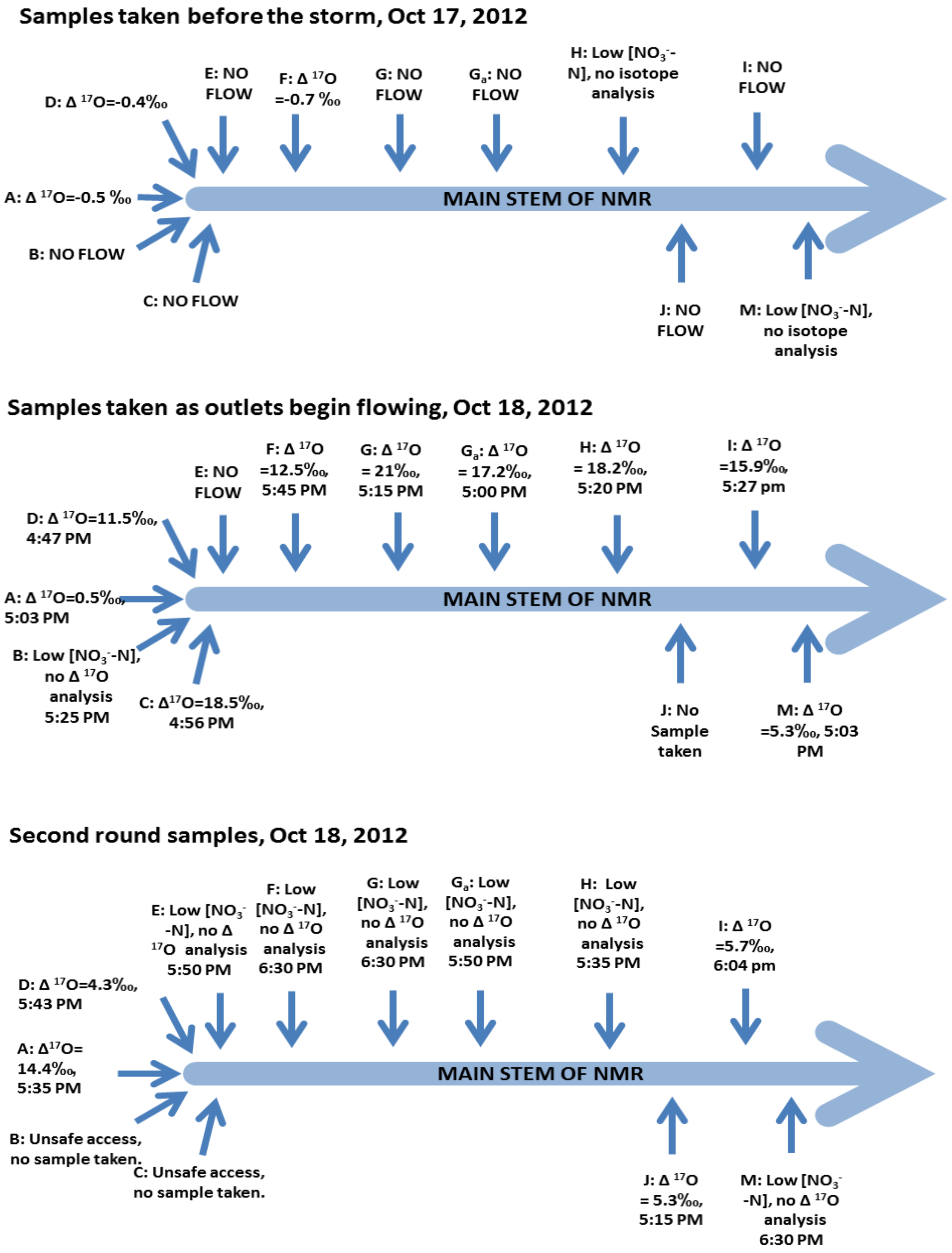


Figure 4.7 Results from synoptic sampling, October 18, 2012

Δ^{17}O values of samples collected from 12 outfalls draining into NMR and taken during synoptic sampling conducted Oct 17-18, 2012.

4.5 CONCLUSIONS

The $\Delta^{17}O$ of oxygen in nitrate is used to document the amounts and dynamics of atmospheric N in urban streamwater. These estimates have refined and contributed significantly to an understanding of the presence and persistence of ADN in urban streamwater. ADN is contributed to streamwater during storm flows, with little to no ADN evident in streamwater 24-36 hours after a storm has passed. On average during storms, 25% of total N is sourced from ADN, whereas little to no ADN is observed during baseflows. Future work includes combining this analysis with ongoing efforts to quantify the ADN deposited on land surfaces within the NMR watershed. This quantification would help to determine the overall retention of ADN, an important factor in determining the retention capabilities of urban watersheds.

5.0 ANION CHEMISTRY OF URBAN STREAM WATER

5.1 INTRODUCTION

Human engineering significantly alters many aspects of urban streams, even at lower levels of land use change. For example, urban progression (including land use change and population growth) have been observed to affect ecosystem processes, hydrology, geomorphology, species diversity, and invertebrate communities (Rutledge 1998; Paul and Meyer 2001). It is likely that no single urban process is responsible for the degradation of urban waters as a whole, rather, the combination of stressors from nutrient pollution to altered hydrologic flows all contribute to reduced ecological quality in urban streams (Walsh, Roy et al. 2005). For this reason, studies that explore a range of factors can provide a more comprehensive picture of stream health.

In this study, anion chemistry from Nine Mile Run (NMR), a stream impacted by human activity, is explored. This information adds to our understanding of nutrient sources and dynamics investigated during previous research in NMR. Anion analyses were conducted on biweekly samples taken from spring 2007 through the spring of 2009, plus five storms. Indicators of altered anion chemistry in streamwater are presented and discussed below.

To measure anion concentrations, aliquots were taken of lab-filtered bulk samples (n=262). Aliquots were bottled with zero headspace in HDPE bottles and refrigerated. Precipitation samples (n=11) were also lab-filtered and aliquots treated in the same manner as stream water samples. Analysis of major anion concentrations (Br^-, F^-, Cl^-, SO_4^-) were conducted on a Dionex ICS2000 Ion Chromatograph. Averages reported are straight averages, unless stated specifically that they are flow -weighted.

5.2 RESULTS

Table 5.1 Average anion concentrations during baseflows and storms

Concentrations observed during baseflows (left) and each individual storm, reported in mgL^{-1}. During baseflows, FH water did not contain measurable [Br-], nor did water from Storms 3 &4. One sample during Storm 1 had measurable Br^- and the value for that sample is shown.

	Average Baseflow (mgL^{-1})				***Precip***	***Storm Events (mgL^{-1})***				
	FH	***NMR1***	***NMR2***	***NMR3***	***(n=11)***	***1***	***2***	***3***	***4***	***5***
Br^-	n/a	1.5	1.4	1.3	n/a	0.89	0.88	n/a	n/a	0.05
Cl^-	162	582	468	400	0.7	94	140	586	314	190
F^-	0.29	0.6	0.57	0.6	0.04	0.37	0.35	0.28	0.32	0.24
SO_4^-	156	166	173	172	2.1	50	48	86	109	114

5.2.1 Bromide

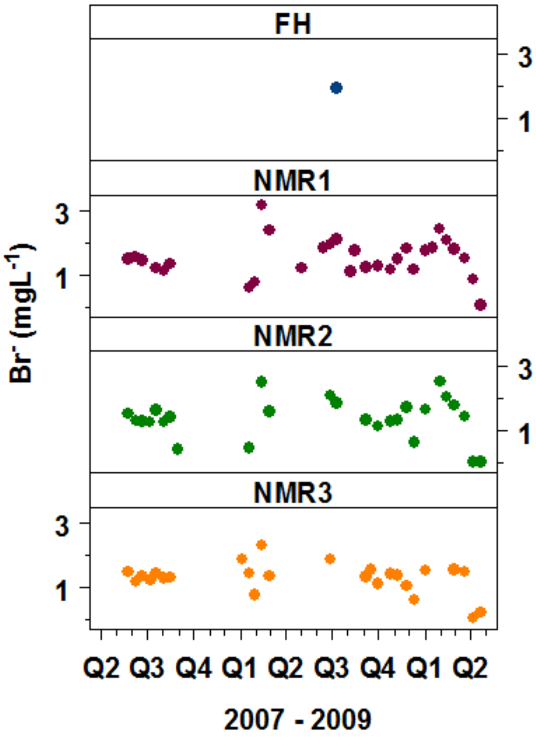


Figure 5.1 Bromide concentrations over time in the NMR watershed

Concentrations measured during bi-weekly sampling from 2007-2009. “Q” refers to year quarters.

During baseflow sampling, average bromide (Br-) concentrations decreased slightly downstream from NMR1 to NMR3 (1.3 to 1.5 mgL^{-1}), potentially due to dilution effects. Of all samples taken at FH, only 1 had measurable Br- (1.9 mgL^{-1}, Figure 5.1). Br- concentrations varied more during winter months, (Dec, Jan, Feb), with the highest concentration measuring 3.2 mgL^{-1}

(Figure 5.1). Overall, concentrations are higher than those observed in the Monongahela River (Wilson and VanBriesen 2013). During storm sampling, Br- concentrations were below detection limits throughout Storms 3 and 4 (Table 5.1). During Storm 1, the only sample with measurable concentrations of Br- was taken from streamwater before the storm began, and therefore is likely indicative of baseflow concentrations. Storm 2 and Storm 5 had average concentrations of 0.88 and 0.05 mgL^{-1}, respectively (Table 5.1).

5.2.2 Chloride

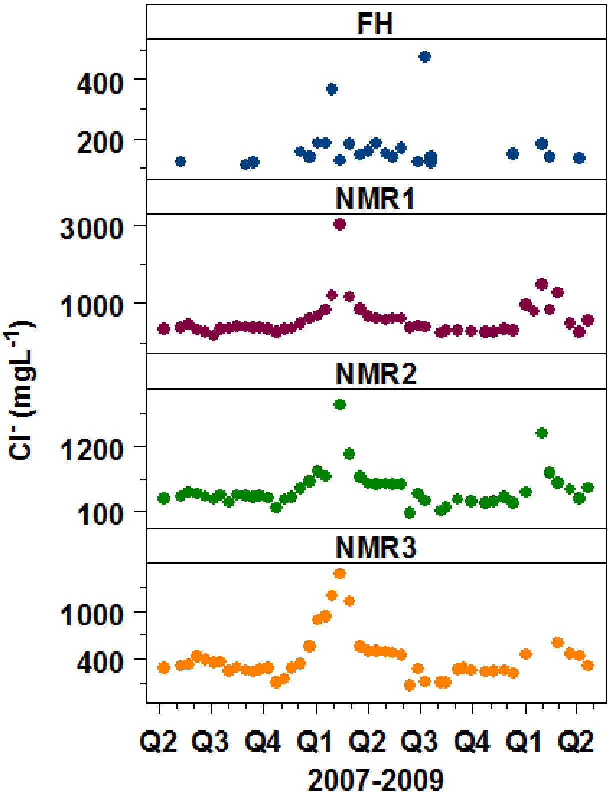


Figure 5.2 Cl^- concentrations over time in the NMR watershed, during bi-weekly sampling

Cl^- concentrations are shown on a log scale, and the scale for each section is variable. It should be noted that these samples had concentrations higher than standards used for the IC analysis and therefore the highest measured concentrations are not likely accurate. For more precise determination, diluted samples will need to be analyzed.

Average chloride concentration between sites were similar (Table 5.1) except for FH, where average Cl^- concentrations were at least 50% lower than those observed at main-stem NMR sites. Seasonal changes in Cl^- concentrations were observed in NMR stream water. Winter average Cl^-

concentrations exceed 740 mgL^{-1}, with individual measurements exceeding 3,000 mgL^{-1}. It should be noted that these samples had concentrations higher than standards used for the IC analysis and therefore the measured concentration is likely not accurate. For more precise determination, diluted samples should be analyzed in the future. During the spring, summer, and fall months, average Cl^- concentrations decrease steadily to an average of 278 mgL^{-1} (Figure 5.2). Similarly, storm concentrations of Cl^- varied greatly with average concentrations ranging from 94-190 mgL^{-1} in the summer and fall storms (Storms 1, 2, and 5) to 586 mgL^{-1} in the winter storm (Storm 3). Cl^- concentrations observed in precipitation samples averaged 0.7 mgL^{-1}.

5.2.3 Fluoride

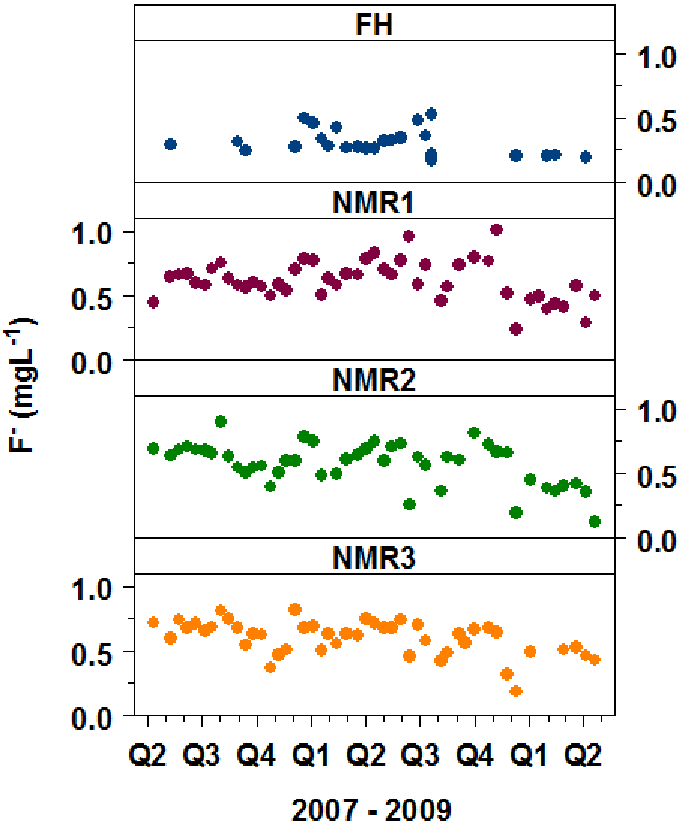


Figure 5.3 Fluoride concentrations during bi-weekly sampling in the NMR watershed

Fluoride (F^-) concentrations at NMR1, 2, and 3 were similar throughout baseflows, with lower concentrations observed at FH (Figure 5.3). Baseflow concentrations in NMR averaged between 0.57 to 0.6 mgL^{-1}. In contrast, during storms, average F^- concentrations at each site were lower with concentrations that ranged from 0.24 to 0.37 mgL^{-1} (Table 5.1).

5.2.4 Sulfate

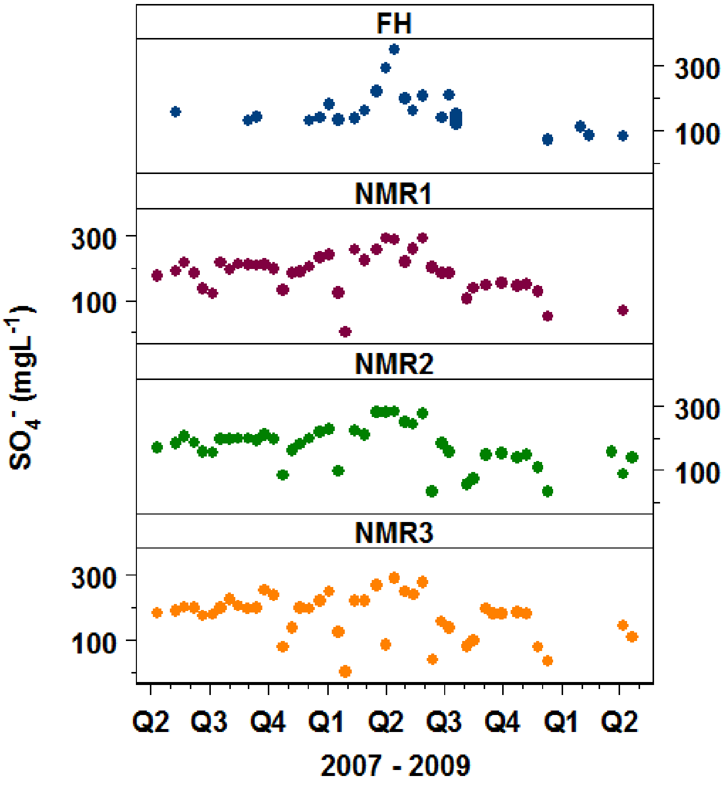


Figure 5.4 Sulfate concentrations over time, during bi-weekly baseflow sampling

Sulfate (SO_4^-) concentrations in baseflow samples varied similarly between sites, with average concentrations in the main stem ranging from 166-173 mgL^{-1}, and concentrations in FH slightly lower at 156 mgL^{-1} (Figure 5.4). During storms, SO_4^- concentrations decreased (Table 5.1) with concentrations ranging from 50 to 114 mgL^{-1}. The lower concentrations observed during storms (Table 5.1) is likely indicative of dilution from incoming precipitation, as average precipitation SO_4^- concentrations averaged 2.1 + 1.8 mgL^{-1}.

5.3 DISCUSSION

5.3.1 Chloride and bromide in streamwater

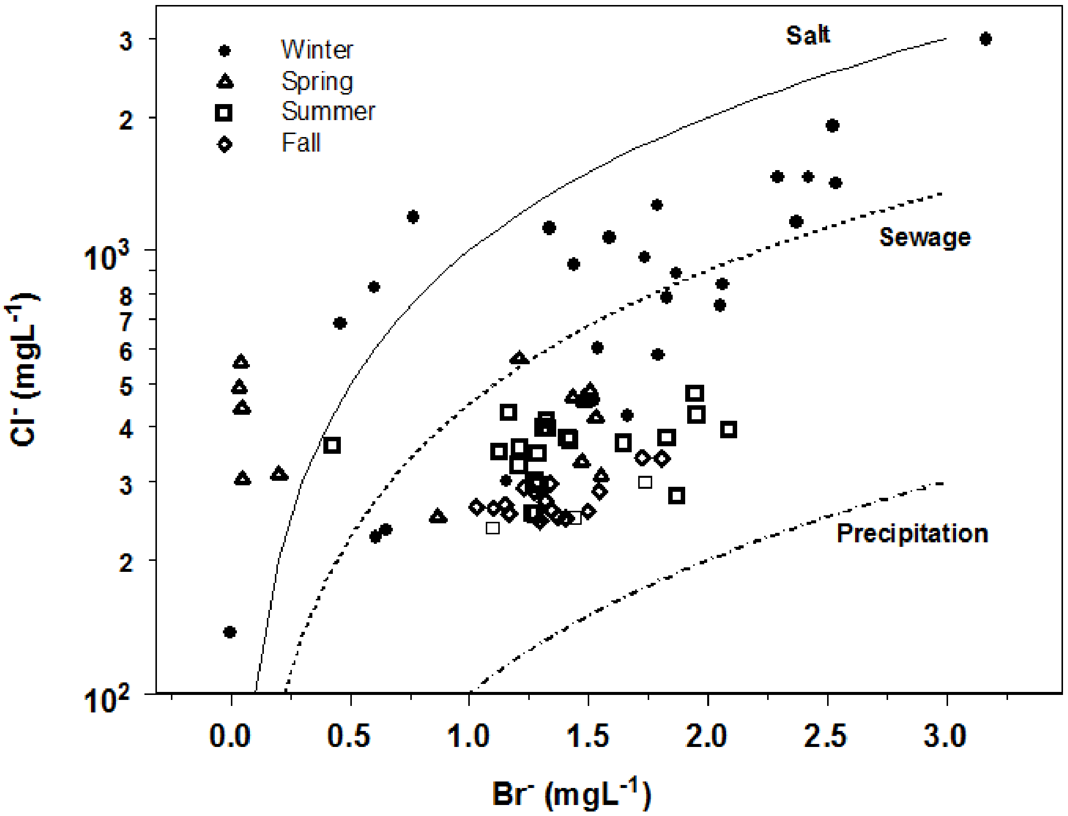


Figure 5.5 Cl^- and Br^- concentrations, classified by season

Winter=December, January, February; Spring=March, April, May; Summer=June, July, August; Fall=September, October, November. Lines indicating ratios of Cl/Br for sewage, salt, and precipitation are also plotted. Note: Cl^- concentrations are shown on a log scale.

Br^- and Cl^- concentrations are both higher in the winter months. Br^- concentrations in NMR streamwater exhibit a greater range of values in the winter than the summer. The only measurable Br^- value observed at FH co-occurs with a Cl^- concentration of 475 mgL^{-1}, well above the average Cl^- concentrations observed at this site (Table 5.1). Chloride and bromide are both found in the various sources that influence NMR streamwater, including sewage, evaporite deposits in local rocks, de-icing road salts, and road run-off (Davis, Whittemore et al. 1998). In the winter months, therefore, it is likely that increased concentrations of both are indicative of road salt (Figure 5.5). In the summer months, higher Cl^- and Br^- ratios may be indicative of drier conditions in the watershed. There is little correspondence between Cl^- and Br^- observed in spring (Figure 5.5).

Cl^- inputs to the watershed include road salt and leaking sewers, where Cl^- is sourced from cleaning products, disinfectant used in public drinking water, and urine. The seasonality evident in changing Cl^- concentrations through the year is expected due to road salt application in the winter, with relatively small inputs from rainwater (Figure 5.2). Further, the slow, sequential decrease in average concentrations observed in spring, summer, and fall seasons suggests that road salt has a chronic, as well seasonally intense effect on water chemistry. NMR Cl^- concentrations observed in winter (in these samples and other studies, e.g. (Koryak, Stafford et al. 2001) and succeeding months are comparable to the maximum concentrations observed in an urban watershed that is part of the Baltimore Ecosystem Study (Kaushal, Groffman et al. 2005), potentially due to increased use of salt in the colder Pittsburgh climate. Cl^- can be toxic to aquatic life in higher concentrations. EPA National Aquatic Life Criteria for Cl^- is 860mgL^{-1} for acute (short-term) exposure and 230 mgL^{-1} for chronic (long-term) exposure (EPA 1988). Cl^-

concentrations observed in NMR may have substantial impacts on ecological quality and aquatic diversity (EPA 1988; Bain, Hale et al. 2012).

5.3.2 Fluoride

Potential fluoride (F^-) sources to NMR include municipal water (measured in Pittsburgh tap water at 1 SD 0.1 mgL^{-1} for this study), the dissolution of evaporite deposits in rock, and from industrial pollution including slag. Due to the sewer leaks and CSO inputs to NMR (Divers, Elliott et al. 2013), it is likely that leaky sewers contribute to F^- concentrations observed in streamwater, however it is not known how much each source contributes. The unchanging average concentrations along the main channel suggest there may be little lateral flow from groundwater into the stream between NMR1 and 3 (Figure 5.3).

5.3.3 Sulfate

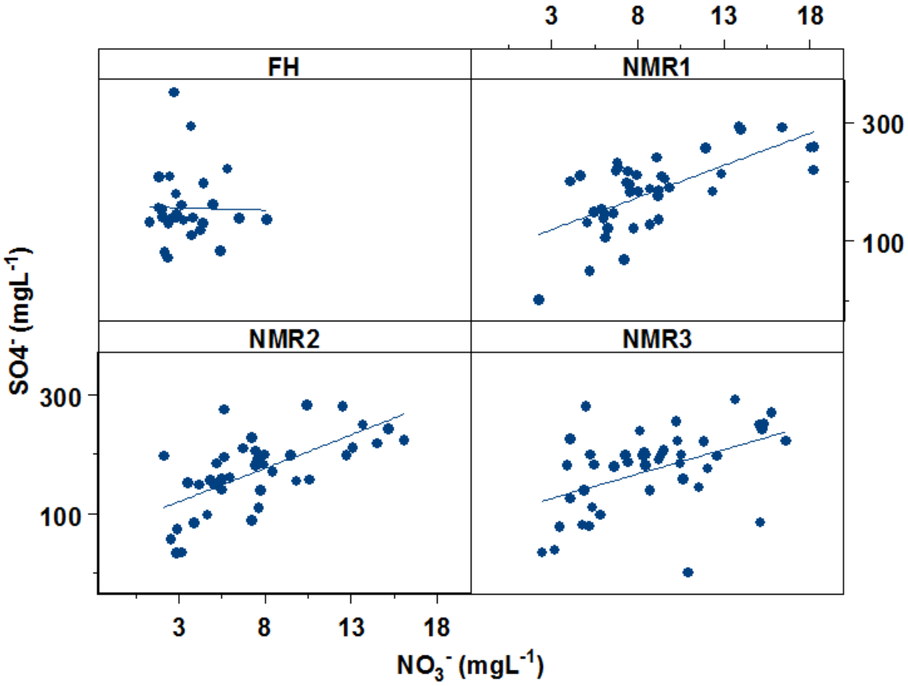


Figure 5.6 Nitrate and Sulfate concentrations for biweekly samples during baseflows

SO_4^-, particularly in a stream such as NMR that is heavily impacted by human activity, can be contributed from a variety of sources such as atmospheric deposition (wet and dry), sewage, and dissolution of sulfate-bearing rock. In NMR, there is a significant correlation between SO_4^- and nitrate (NO_3^-) concentrations at each site except FH, indicating that a mix of sewage and atmospheric deposition may each contribute both solutes to main-stem NMR sites (Figure 5.6). Average SO_4^- concentrations in NMR are higher when compared to those observed in Dead Run, a stream draining an urban watershed that is part of the Baltimore Ecosystem Study, a Long-Term Ecological Research network site. Average SO_4^- concentrations in Dead Run are 31.4

mgL^{-1} for approximately the same sampling time period as presented in NMR (April 2007-March 2009) (Welty and Cole 2013). The NMR watershed bedrock includes sedimentary rock and evaporite deposits, which potentially contain gypsum (Leighton 1927), the dissolution of which can contribute to SO_4^- concentrations in streamwater.

5.4 CONCLUSIONS

Analysis of anion water chemistry in urban streams provides basic information about the influence of the urban environment on streamwater chemistry. Here, the correlation between Br- and Cl- is particularly strong in seasons where road salt is applied to melt snow/ice. Fluoride concentrations indicate the influence of municipally treated water, likely the result of leaking sewers during baseflow. Additionally, SO_4^- and NO_3^- concentrations are likely from the same sources (ADN and sewage), and therefore show a positive correlation. These conclusions illustrate how stream chemistry can be affected by a number of contamination sources contributed to surface waters by urban watersheds.

6.0 EXPLORING THE ENERGY-ENVIRONMENT-SOCIETY NEXUS THROUGH EXPERIENTIAL LEARNING: A UNIVERSITY-MUSEUM COLLABORATIVE MODEL

6.1 INTRODUCTION

Increasing participation, achievement, and graduation rates in the STEM fields are recognized goals for U.S. educators. A corollary objective is to diversify these fields by increasing the number of minorities, including women and ethnic groups, that continue to be under-represented in these fields (NAS 2011). Additionally, there is a growing demand for students that pursue careers specifically in the geoscience-focused STEM fields. Current projections indicate that the number of university students pursuing geoscience studies is not sufficient to fill future workforce needs (Gonzales and Keane 2010). Further, there is a critical need to improve public literacy about environmental and energy connections (Coyle 2005). To pursue these multiple objectives, collaborators at the University of Pittsburgh and the Carnegie Museum of Natural History, in Pittsburgh, PA developed an afterschool program designed to promote inquiry-based learning for underserved teens in informal (out-of-classroom) environments. Presented here is a description of an ongoing, effective partnership between University and Museum affiliates including geoscientists, learning researchers, and Natural History Museum educators that could be adopted by other Universities with access to such expertise.

6.1.1 Project Description

ENERGY-NET is three-year, NSF-funded program designed to introduce Pittsburgh (Pennsylvania, USA) city high school students ("GeoSquad" members) to energy/environment/society connections. The goal of the ENERGY-NET project is use to use an Earth systems science framework to guide experiential learning focused on the intersecting lenses of energy, the environment, and society (Figure 6.1). The program aims to expose underserved students to the large diversity of geoscience-related STEM careers, professionals, and educational opportunities, as well as give them the opportunity to teach museum visitors through the creation of public exhibits that showcase what they have learned. The program takes place after school and utilizes the rich diversity of local businesses, experts, and industries that work in both energy and the environmental professions, as well as emphasizing the importance of out-of-classroom learning to overall education. Scientist guest speakers and interactions with professionals provide GeoSquad members with models and mentors at a critical time in their high school careers, as they begin to make future plans. GeoSquad members not only learn about energy/environmental issues, they then take this learning and apply it to create a museum exhibit that is displayed on the museum floor for visitors.

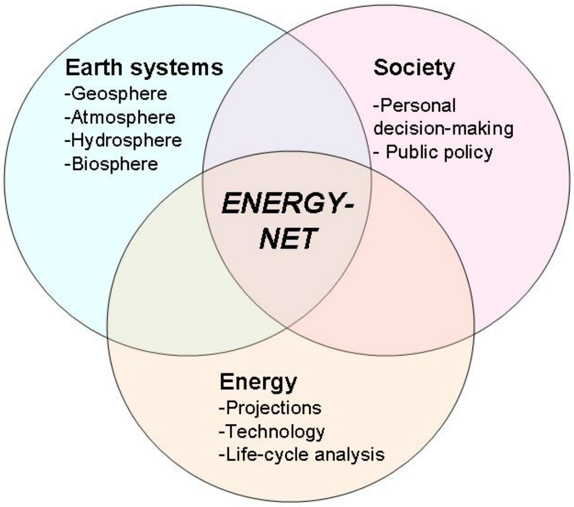


Figure 6.1 Conceptual model of the energy, environmental, and societal nexus

This collaborative effort leverages available resources at the University of Pittsburgh (Pitt) and the Carnegie Museum of Natural History (CMNH). From the Pitt Department of Geology and Planetary Science, undergraduate Environmental Interns (“EI’s”), required to complete an 160-hour internship as part of their Environmental studies majors, are managed by a graduate student “Geoscience Fellow” who also serves as a science advisor for the program. Also involved is the University of Pittsburgh Center for Learning in Out of School Environments (UPCLOSE). An “UPCLOSE Fellow”, a graduate student fellow from UPCLOSE, conducts pre- and post-session evaluations of EI’s and GeoSquad participants to judge their growth and learning, and provides feedback to EI’s and staff members focused on best-practices teaching and learning. From CMNH, the Teen Programs manager and the head of Public Programs help to coordinate Museum resources, space, supplies, and training of GeoSquad to interact with the public. They also manage the exhibit-building process, including keeping the GeoSquad informed about design standards at the Museum and building logistics.

6.2 OUTCOMES

Table 6.1 Participants and themes from first two cohort sessions

Session	***E.I. Partici-pants***	***GeoSquad Partici-pants***	***GeoSquad Average Hours***	***Session Theme***	***Exhibit Title/Theme***	***Exhibit Duration***
Cohort 1, Spring	5	11	70	Personal Energy	"Make Choices Market," Energy and Food choices	April 2013-August 2013
Cohort 2, Summer	3	17	40	Water & Energy	"The Water-Energy Nexus: Watt about it?"	August 2013 Through December 2013

6.2.1 GeoSquad and E.I. Participation

In total, 17 teens participated in ENERGY-NET for the first and second semesters (Table 6.1). In total, 77% teen participants identify as African American/Black students and 47% are women, thereby achieving the desired mix of participants. Five undergraduate interns worked with the GeoSquad members, and three of the EIs chose to stay on to work more intensively during the summer semester.

6.2.2 Learning experiences and exhibit results

For the first cohort, (Spring, 2013) GeoSquad members began by discovering the energy in their lives (Table 6.1). Workshops began with food or "human energy" and later explored the energy, and environmental costs, of daily living and household energy use. Focus moved outward to local fossil fuels through interviews with Museum scientists, Pitt scientists, and energy industry professionals. After a sequence of labs, field trips and meetings with researchers from the University of Pittsburgh and local energy industry professionals, GeoSquad members participated in exhibit development workshops to bring all the ideas into the context of our visitors and their interests. The result of this process was an exhibit, titled the "Make Choices Market: What energy goes into making your food?" which opened on April 20, 2013 and remained open to the public until August 2013. The "Make Choices Market" offered a display of meal options, offered in a cafeteria style. After picking their meals, visitors sit at tables and compare their food choices to cards outlining the amount of water used to produce the food, as well as equivalent CO_2 emissions. Visitors are also encouraged to seek out local food choices with "takeout menus" highlighting environmental organizations and large map pin-pointing local farmers.

Figure 6.2 The ENERGY-NET team with the first exhibit

The exhibit was titled “Make Choices Market” and explored the energy and resources used to produce food.

For Cohort 2, the second session (Summer, 2013) GeoSquad and EI’s focused on the connections between water and energy (Table 6.1). The Western Pennsylvania region has long been home to energy-intensive and related extraction including coal mining and electrical generation, natural gas production, and steel production. The regions’ rivers were treated as part of this industrial infrastructure, which led to degradation of water quality, with recent improvements due to changing resource use and industry (Tarr 2004). The activities in the summer 2013 focused specifically on the ways water is involved in the production of energy and how energy is used to clean and transport water. The team began by learning about watersheds and how water and land surfaces interact. They then explored city systems for managing water and energy, visiting water treatment and sewage plants, they sampled water at an acid mine drainage site, in city creeks. The ENERGY-NET team also visited the Department of Geology

& Planetary Science at Pitt to tour the hydrology and biogeochemistry labs, learn about associated instrumentation in these labs, and to work with the Department's stream table. Historical water-energy connections were made during an overnight trip to the museum's Powdermill Nature Reserve, where the team learned about early coke production, water wheels, and the potential energy savings involved in alternative insulation and water treatment systems. The result of these explorations was an exhibit "The Water-Energy Nexus: WATT about it?" that opened August 31, 2013 and remained open to visitors through November 2013.

The exhibit featured water-energy connections in various contexts. Flip-up panels compared the amount of water required to extract coal, gas, and oil resources, and the water needed to produce biofuels. Diagrams and puzzles followed the path of water through drinking water treatment plants and coal fired power plants. Posters highlighted innovative solutions for regions of the world where energy or clean water, or both, are limited. GeoSquad members designed an interactive game modeled after the water distribution system and a water filtration demonstration.

Figure 6.3 Water Testing with ENERGY-NET

Pictures of GeoSquad members testing water from a pristine stream (left) and sampling water from an acid mine drainage treatment pool (right).

6.2.3 Evaluation products

A distinct aspect of this program is the emphasis on evaluation of the learning and experiences of the students (Geosquad members and EI's), as well as on the part of the Museum visitors who visit the exhibit created by ENERGY-NET participants. Evaluations were conducted by the UPCLOSE Fellow.

For each cohort, a series of evaluation tools were implemented by the UPCLOSE Fellow. These included before and after "Interest and Understanding Surveys" and interviews of the EI's and GeoSquad members. Additional evaluative elements included journal assignments and observations of museum visitor habits.

Evaluation of interviews and journal entries indicate that students generally report an enhanced interest and understanding of environmental issues. Additionally, the quotes below excerpted from interviews conducted by the UPCLOSE Fellow describe the welcoming, supportive tone that was maintained through the program.

"[I liked] the social interaction and being part of a team: working together. There is that whole mentality that there are no bad ideas here and a lot of times you don't get that in a lot of places." - GeoSquad Member

"[I got better at] public speaking in the sense of presenting to a large audience and drawing people in. I know more about the food choices I should be making, and I can better share that." – GeoSquad Member

"The [teens] were a pretty mixed up crowd as well: probably not people they're usually used to hanging out with. It was cool. I think they realized if they all have a common goal then they can all get along. I feel like they realized the importance of hard work and hard work can lead to a positive result if everybody puts their heads together." - EI

The EI's and GeoSquad Members developed a working mentorship that benefited both groups of students. Quotes illustrating this are listed below.

"[Working with the EIs] was great. They had a lot of information to share with us, and they were really knowledgeable about what they were teaching us, and they were really nice people too." - GeoSquad Member

"[Working with the EIs] felt like I was working with brothers and sisters I've never had. It felt comfortable talking with them. It made it a little bit more comfortable because they're not teenagers, but they're also not 'adult, adults' yet because they are still in school. So, if you have a problem with school or if I want to know how to study for this they can give you that." - GeoSquad Member

"I learned that teens are a lot more interested in what we were doing and what we were talking about than I thought they would be. They're willing to come to this program to learn about this stuff. I just learned how interested they were in learning about college life in general; they'd ask about it, 'What's college like?'" -EI

During the second session, the evaluation process was composed of pre and post "Interest and Understanding" stations that assessed GeoSquad members' understanding of watersheds and energy/water connections. Further, on the exhibit opening day, interviews were conducted with Museum visitors to evaluate their response to the exhibit. ENERGY-NET participants showed significant gains in understanding over the summer. For example, during pre-session conversations with teams about energy and water, the teens focused on hydroelectric dams. However, the exhibit that opened at the end of the summer session included information on energy use in water treatment and transportation, water use in energy production, and simple solutions to water or energy problems.

6.3 CONCLUSION AND IMPLICATIONS FOR THE ENERGY-NET PROGRAM

There have been considerable, measurable successes during the first year of ENERGY-NET. In particular, evaluation of gains in teen understanding is a quantifiable result of this program. In this context, evaluations are not only quantifying learning gains that are important for meeting program goals, they are also allowing feedback to ENERGY-NET staff on a regular basis throughout the process, so that teaching can be adjusted accordingly to meet teen needs. Further, integrated evaluation of the museum visitor experience teaches the teens how to create effective learning experiences for others. Making sure that the teens "get it", and relate that information in an effective manner to the visitors through exhibits is a particular challenge. The feedback/response portions of the exhibit have proven valuable in helping to make sure that visitors understand the connections the exhibit highlights. Additionally, evaluations offer information on more qualitative aspects of the ENERGY-NET program. For example, comments from Geosquad members indicate that the program is successful at creating a learning community, where “geeky talk” is encouraged and learning is not relegated to the school/lecture/notes and homework realm.

Through ENERGY-NET, teens are exposed to new ideas, career options, and are able to view scientists as real people and potential mentors. Exposure to scientists and professions through speakers and field trips provides information about professional opportunities and jobs in STEM fields beyond simple information given out by guidance counselors at school. Many teens have simply expressed that they have had a general exposure to things they might otherwise never have seen. These “out-of-classroom” experiences, such as testing water quality on the rivers, seeing the countryside, touring a water treatment plant or coal-fired power plant, are beneficial on many levels. The program is further strengthened by the exhibit creation process, through which the students are given ownership of their learning, and the process of teaching that understanding to museum visitors.

7.0 CONCLUSIONS

This dissertation has documented the sources, retention, and dynamics of nitrate in an urban stream. These observations have important implications for urban surface water quality and management decisions. Quantifying and understanding the source and fate of nitrogen sources that impact urban waters is important in developing coherent strategies to mitigate these sources.

In Chapter 2, we quantified the contribution of sewage-sourced DIN at urban catchment scales, an important area of research. Aging infrastructure is a problem that cities will continue to face. Leaking sewers can potentially have detrimental human and environmental health affects as a source of both nutrient and microbiological contamination. In Chapter 3, dual nitrate isotope analyses quantified the proportions of sewage and atmospherically deposited nitrate in streamwater. This approach combined MCMC techniques with dual nitrate isotope analysis for source apportionment, and is one of the most extensive analyses of nitrate sources to urban streams using a dual isotope approach. Further, we gained insight into retention of atmospherically deposited nitrate, which may be retained at high rates. These estimates of atmospheric deposition-sourced nitrate were further refined in Chapter 4, using the mass-independent ^{17}O in nitrate and is one of the most extensive quantifications to date of ADN contributions to urban streamwater.

Understanding the sources and fate of nitrate pollution in urban waterways has important implications for efforts to plan effective management of these sources. With future population and industrial growth in urban areas, they will continue to contribute nitrogen to downstream waters, and mitigation efforts will likely need to approach the problem from multiple angles (Coles, McMahon et al. 2012). For example, removing sewage-sourced nitrate from the stream may entail the digging up of entire streets. On the other hand, removal may also be accomplished by increasing soil moisture, thereby increasing overall denitrification rates. Different strategies may be required to remove atmospherically deposited nitrate from streamwater, such as filtration through rain gardens or permeable paving. This work provides vital information about the source and dynamics of reactive nitrogen in streamwater, an important first step towards achieving any management goals.

In the future, follow-up projects could help to answer questions raised in this study. For example, quantification of the amount and distribution of atmospheric nitrogen deposition in Nine Mile Run (rather than a remote rural location) will constrain input estimates and thus further refine retention estimates from this source. Measurements of soil-based denitrification will contribute to our understanding of where and when retention occurs. Is it in the riparian zones, “denitrification hotspots” around sewer pipes, or through biomass uptake? Answering some of these questions will help city managers to plan for reducing nitrogen loads to receiving waters.

APPENDIX A

DATA TABLES

Table A-1 DIN species, concentrations, and measured discharge

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR07-01	NMR 1	4/10/07 3:45 PM	9.2	2.1	0.01	0.00	0.336	0.26	0.1700	
NMR07-02	NMR 2	4/10/07 4:15 PM	8.5	1.9	0.00	0.00	0.139	0.11	0.3070	
NMR07-03	NMR 3	4/10/07 5:15 PM	10.5	2.4	0.19	0.06	0.227	0.18	0.1330	
NMR07-04	NMR 1	5/9/07 9:30 AM	9.8	2.3	0.09	0.03	0.172	0.13	0.1340	
NMR07-05	FH 1	5/9/07 10:45 AM	1.8	0.4	0.00	0.00	0	0.00	0.0001	
NMR07-06	NMR 2	5/9/07 11:15 AM	8.0	1.8	0.05	0.02	0.262	0.20	0.0710	
NMR07-07	NMR 3	5/9/07 12:30 PM	9.2	2.1	0.29	0.09	0.21	0.16	0.0550	
NMR07-	NMR 1	5/23/07	9.8	2.3	0.08	0.02	0.043	0.03	0.0900	

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
08		9:30 AM								
NMR07-09	NMR 2	5/23/07 10:30 AM	7.5	1.7	0.07	0.02	0.131	0.10	0.0460	
NMR07-10	NMR 3	5/23/07 11:30 AM	8.4	1.9	0.23	0.07	0.213	0.17	0.0860	
NMR07-11	NMR 1	6/7/07 8:30 AM	8.0	1.8	0.03	0.01	0.093	0.07	0.0720	
NMR07-12	NMR 2	6/7/07 9:15 AM	7.6	1.7	0.01	0.00	0.084	0.07	0.0430	
NMR07-13	NMR 3	6/7/07 9:30 AM	9.4	2.2	0.27	0.08	0.15	0.12	0.0560	
NMR07-14	NMR 1	6/20/07 3:15 PM	9.2	2.1	0.04	0.01	0.25	0.19	0.0890	
NMR07-15	NMR 2	6/20/07 4:00 PM	10.6	2.4	0.03	0.01	0.09	0.07	0.1230	
NMR07-16	NMR 3	6/20/07 4:30 PM	12.1	2.8	0.12	0.04	0.14	0.11	0.1030	
NMR07-17	NMR 1	7/6/07 7:15 AM	7.8	1.8	0.02	0.01	0.16	0.12	0.0700	
NMR07-18	NMR 2	7/6/07 7:45 AM	9.9	2.3	0.01	0.00	0.11	0.09	0.1190	
NMR07-19	NMR 3	7/6/07 8:15 AM	10.8	2.5	0.14	0.04	0.16	0.13	0.0690	
NMR07-20	NMR 1	7/18/07 7:30 AM	7.4	1.7	0.04	0.01	0.08	0.06	0.0430	
NMR07-21	NMR 2	7/18/07 8:30 AM	7.8	1.8	0.00	0.00	0.00	0.00	0.0210	
NMR07-22	NMR 3	7/18/07 9:00 AM	0.2	0.0	0.00	0.00	0.00	0.00	0.0120	
NMR07-23	NMR 1	8/2/07 8:00 AM	7.5	1.7	0.03	0.01	0.07	0.06	0.0690	
NMR07-24	NMR 2	8/2/07 9:00 AM	2.1	0.5	0.00	0.00	0.04	0.03	0.1330	

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR07-25	NMR 3	8/2/07 10:45 AM	4.1	0.9	0.14	0.04	0.11	0.08	0.0300	
NMR07-26	NMR 1	8/15/07 9:30 AM	12.9	3.0	0.02	0.00	0.05	0.04	0.0640	
NMR07-27	NMR 2	8/15/07 10:00 AM	9.5	2.2	0.00	0.00	0.00	0.00	0.2330	
NMR07-28	NMR 3	8/15/07 11:30 AM	9.5	2.2	0.21	0.06	0.04	0.03	0.0730	
NMR07-31	NMR 3	8/30/07 7:15 AM	8.3	1.9	0.24	0.07	0.09	0.07	0.0324	
NMR07-32	NMR 2	8/30/07 7:45 AM	8.0	1.8	0.00	0.00	0.02	0.01	0.0575	
NMR07-30	FH 1	8/30/07 8:00 AM	2.4	0.6	0.00	0.00	0.00	0.00		
NMR07-29	NMR 1	8/30/07 8:30 AM	10.1	2.3	0.00	0.00	0.02	0.01	0.0455	
NMR07-36	NMR 3	9/13/07 10:45 AM	10.5	2.4	0.28	0.09	0.09	0.07	0.0315	
NMR07-34	NMR 2	9/13/07 11:00 AM	7.6	1.8	0.00	0.00	0.03	0.02	0.0583	
NMR07-33	NMR 1	9/13/07 12:00 PM	9.4	2.2	0.00	0.00	0.05	0.04	0.0786	
NMR07-35	FH 1	9/13/07 12:15 PM	2.1	0.5	0.00	0.00	0.02	0.02	0.0003	
NMR07-39	NMR 3	9/25/07 7:45 AM	12.6	2.9	0.38	0.12	0.30	0.24	0.0227	
NMR07-38	NMR 2	9/25/07 8:15 AM	6.8	1.6	0.00	0.00	0.04	0.03	0.0254	
NMR07-37	NMR 1	9/25/07 8:30 AM	7.9	1.8	0.07	0.02	0.11	0.08	0.0452	
NMR07-42	NMR 3	10/9/07 7:45 AM	8.1	1.9	0.34	0.10	0.35	0.27	0.0211	
NMR07-41	NMR 2	10/9/07 8:15 AM	5.6	1.3	0.00	0.00	0.03	0.02	0.0316	

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR07-40	NMR 1	10/9/07 8:45 AM	7.4	1.7	0.10	0.03	0.18	0.14	0.0480	
NMR07-45	NMR 3	10/24/07 3:45 PM	3.5	0.8	0.07	0.02	0.00	0.00	0.0871	
NMR07-44	NMR 2	10/24/07 4:15 PM	3.9	0.9	0.00	0.00	0.01	0.01	0.0809	
NMR07-43	NMR 1	10/24/07 4:45 PM	7.1	1.6	0.01	0.00	0.01	0.01	0.0666	
NMR07-48	NMR 3	11/7/07 8:00 AM	7.2	1.7	0.32	0.10	0.14	0.11	0.0305	
NMR07-47	NMR 2	11/7/07 8:30 AM	6.0	1.4	0.00	0.00	0.03	0.02	0.0365	
NMR07-46	NMR 1	11/7/07 9:00 AM	7.6	1.7	0.00	0.00	0.03	0.02	0.0545	
NMR07-51	NMR 3	11/19/07 8:30 AM	8.5	1.9	0.18	0.06	0.14	0.11	0.0433	
NMR07-50	NMR 2	11/19/07 9:15 AM	7.5	1.7	0.03	0.01	0.14	0.11	0.0424	
NMR07-49	NMR 1	11/19/07 9:30 AM	8.7	2.0	0.03	0.01	0.09	0.07	0.0675	
NMR07-54	NMR 3	12/4/07 1:30 PM	12.6	2.9	0.10	0.03	0.11	0.08	0.0910	
NMR07-53	NMR 2	12/4/07 2:30 PM	12.8	2.9	0.01	0.00	0.07	0.05	0.1134	
NMR07-55	FH 1	12/4/07 2:45 PM	4.4	1.0	0.00	0.00	0.06	0.05	0.0010	
NMR07-56	FH 2	12/4/07 2:45 PM	3.0	0.7	0.03	0.01	0.03	0.02		
NMR07-52	NMR 1	12/4/07 3:15 PM	14.3	3.3	0.04	0.01	0.12	0.09	0.1125	
NMR07-58	NMR 2	12/20/07 11:15 AM	14.6	3.3	0.02	0.01	0.03	0.02	0.0898	
NMR07-60	FH 1	12/20/07 11:20 AM	6.6	1.5	0.00	0.00	0.02	0.01		

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR07-57	NMR 1	12/20/07 11:45 AM	16.1	3.7	0.03	0.01	0.12	0.09	0.0891	
NMR07-59	NMR 3	12/20/07 1:00 PM	15.3	3.5	0.08	0.02	0.05	0.04	0.0702	
NMR08-01	NMR 3	1/4/08 10:30 AM	15.4	3.5	0.29	0.09	0.02	0.01	0.0792	
NMR08-02	NMR 2	1/4/08 11:00 AM	11.1	2.6	0.03	0.01	0.03	0.02	0.0325	
NMR08-03	FH 1	1/4/08 11:30 AM	4.6	1.1	0.00	0.00	0.00	0.00	0.0024	
NMR08-04	NMR 1	1/4/08 11:45 AM	12.4	2.8	0.05	0.02	0.17	0.13	0.0712	
NMR08-06	NMR 3	1/18/08 8:00 AM	8.2	1.9	0.04	0.01	0.14	0.11	0.1119	
NMR08-07	NMR 1	1/18/08 8:45 AM	8.4	1.9	0.05	0.01	0.07	0.06	0.0968	
NMR08-08	NMR 2	1/18/08 9:45 AM	6.2	1.4	0.03	0.01	0.07	0.05	0.1302	
NMR08-05	FH 1	1/18/08 10:15 AM	4.2	1.0	0.00	0.00	0.02	0.02	0.0002	
NMR08-09	NMR 3	1/29/08 9:30 AM	10.9	2.5	0.14	0.04	0.39	0.30	0.1335	
NMR08-11	NMR 2	1/29/08 9:30 AM	8.3	1.9	0.32	0.10	0.81	0.63	0.7454	
NMR08-12	FH 1	1/29/08 9:45 AM	3.8	0.9	0.00	0.00	0.00	0.00	0.0006	
NMR08-10	NMR 1	1/29/08 10:15 AM	10.9	2.5	0.13	0.04	0.55	0.43	0.4142	
NMR08-13	NMR 3	2/12/08 1:15 PM	16.6	3.8	0.18	0.05	0.17	0.13	0.0894	
NMR08-15	FH 1	2/12/08 1:45 PM	8.1	1.9	0.00	0.00	0.00	0.00		
NMR08-14	NMR 2	2/12/08 2:15 PM	16.1	3.7	0.02	0.01	0.09	0.07		

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR08-16	NMR 1	2/12/08 2:45 PM	18.0	4.1	0.06	0.02	0.10	0.08	0.0954	
NMR08-17	NMR 1	2/28/08 12:45 PM	15.8	3.6	0.04	0.01	0.28	0.22	0.1006	
NMR08-20	FH 1	2/28/08 1:15 PM	4.7	1.1	0.00	0.00	0.09	0.07	0.0008	
NMR08-18	NMR 2	2/28/08 1:30 PM	13.1	3.0	0.02	0.00	0.13	0.10	0.1068	
NMR08-19	NMR 3	2/28/08 2:00 PM	14.6	3.4	0.11	0.03	0.16	0.13	0.0932	
NMR08-21	NMR 1	3/18/08 12:45 PM	16.8	3.9	0.14	0.04	0.44	0.34	0.1269	
NMR08-24	FH 1	3/18/08 1:30 PM	5.8	1.3	0.00	0.00	0.08	0.06	0.0004	
NMR08-22	NMR 2	3/18/08 1:45 PM	15.9	3.7	0.05	0.01	0.09	0.07	0.1542	
NMR08-23	NMR 3	3/18/08 2:15 PM	15.8	3.6	0.09	0.03	0.14	0.11	0.1838	
NMR08-26	NMR 2	4/1/08 12:45 PM	12.5	2.9	0.04	0.01	0.07	0.05	0.0766	
NMR08-28	FH 1	4/1/08 1:00 PM	3.7	0.9	0.00	0.00	0.12	0.09	0.0005	
NMR08-25	NMR 1	4/1/08 1:30 PM	16.4	3.8	0.10	0.03	0.14	0.11	0.0993	
NMR08-27	NMR 3	4/1/08 2:00 PM	15.1	3.5	0.17	0.05	0.13	0.10	0.0410	
NMR08-30	NMR 2	4/15/08 12:45 PM	10.5	2.4	0.05	0.02	0.04	0.03	0.0752	
NMR08-32	FH 1	4/15/08 1:15 PM	2.7	0.6	0.00	0.00	0.05	0.04	0.0020	
NMR08-29	NMR 1	4/15/08 1:45 PM	14.0	3.2	0.11	0.03	0.13	0.10	0.0668	
NMR08-31	NMR 3	4/15/08 2:15 PM	13.7	3.1	0.21	0.06	0.18	0.14	0.1042	

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR08-33	GW 1	4/18/08 1:00 PM	0.4	0.1	0.00	0.00	0.00	0.00		
NMR08-34	GW 2	4/18/08 1:30 PM	0.3	0.1	0.00	0.00	0.85	0.66		
NMR08-36	NMR 2	5/1/08 9:45 AM	13.7	3.2	0.01	0.00	0.03	0.02	0.1138	
NMR08-38	FH 1	5/1/08 10:15 AM	4.5	1.0	0.00	0.00	0.05	0.04	0.0019	
NMR08-35	NMR 1	5/1/08 10:45 AM	18.2	4.2	0.11	0.03	0.72	0.56	0.1217	
NMR08-37	NMR 3	5/1/08 11:15 AM	15.1	3.5	0.10	0.03	0.10	0.08	0.1360	
NMR08-39	NMR 1	5/14/08 9:30 AM	18.3	4.2	0.08	0.02	0.11	0.08	0.0642	
NMR08-42	FH 1	5/14/08 9:45 AM	5.0	1.2	0.00	0.00	0.04	0.03		
NMR08-40	NMR 2	5/14/08 10:15 AM	15.2	3.5	0.01	0.00	0.07	0.06	0.0747	
NMR08-41	NMR 3	5/14/08 11:00 AM	15.2	3.5	0.06	0.02	0.24	0.19	0.2063	
NMR08-43	NMR 1	5/29/08 9:15 AM	13.9	3.2	0.09	0.03	0.08	0.06	0.1009	
NMR08-46	FH 1	5/29/08 10:00 AM	4.3	1.0	0.00	0.00	0.05	0.04	0.0001	
NMR08-44	NMR 2	5/29/08 10:15 AM	10.8	2.5	0.04	0.01	0.04	0.03	0.1210	
NMR08-45	NMR 3	5/29/08 10:45 AM	12.5	2.9	0.15	0.05	0.22	0.17	0.7970	
NMR08-47	NMR 1	6/13/08 8:00 AM	8.0	1.8	0.08	0.02	0.03	0.02	0.1044	
NMR08-48	NMR 2	6/13/08 1:45 PM	3.6	0.8	0.06	0.02	0.56	0.44	1.5469	
NMR08-49	NMR 3	6/13/08 2:30 PM	4.0	0.9	0.06	0.02	0.58	0.45	0.7478	

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR08-52	NMR 3	6/27/08 2:45 PM	10.7	2.5	0.08	0.02	0.05	0.04	0.1532	
NMR08-51	NMR 2	6/27/08 3:15 PM	12.7	2.9	0.03	0.01	0.00	0.00	0.1327	
NMR08-53	FH 1	6/27/08 3:30 PM	4.5	1.0	0.00	0.00	0.08	0.06	0.0013	
NMR08-50	NMR 1	6/27/08 4:00 PM	13.4	3.1	0.05	0.01	0.08	0.06	0.1748	
NMR08-54	NMR 1	7/9/08 5:45 PM	12.4	2.8	0.05	0.01	0.09	0.07	0.0592	
NMR08-57	FH 1	7/9/08 6:30 PM	4.3	1.0	0.00	0.00	0.00	0.00	0.0015	
NMR08-55	NMR 2	7/9/08 6:45 PM	9.4	2.2	0.03	0.01	0.06	0.04	0.0843	
NMR08-56	NMR 3	7/9/08 7:15 PM	8.7	2.0	0.25	0.08	0.11	0.09	0.0941	
NMR08-58	NMR 2	7/20/08 2:15 PM	3.9	0.9	0.59	0.18	0.07	0.05	0.2020	1
NMR08-88	FH 1	7/20/08 2:30 PM	2.4	0.6	0.23	0.07	0.00	0.00		
NMR08-59	NMR 2	7/20/08 3:00 PM	4.7	1.1	0.40	0.12	0.29	0.22	2.3103	1
NMR08-89	FH 1	7/20/08 3:00 PM	3.3	0.8	0.00	0.00	0.00	0.00		
NMR08-60	NMR 2	7/20/08 3:30 PM	4.2	1.0	0.45	0.14	0.34	0.26	1.1204	1
NMR08-90	FH 1	7/20/08 3:30 PM	5.6	1.3	0.01	0.00	0.02	0.02		
NMR08-61	N	7/20/08 3:45 PM	4.2	1.0	0.95	0.29	0.17	0.13		
NMR08-62	NMR 2	7/20/08 4:00 PM	4.4	1.0	0.14	0.04	0.39	0.31	0.6186	1
NMR08-91	FH 1	7/20/08 4:00 PM	4.3	1.0	0.01	0.00	0.00	0.00		

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR08-63	NMR 2	7/20/08 4:30 PM	4.4	1.0	0.09	0.03	0.30	0.23	0.7822	1
NMR08-92	FH 1	7/20/08 4:30 PM	2.4	0.6	0.00	0.00	0.00	0.00		
NMR08-64	NMR 2	7/20/08 5:30 PM	4.8	1.1	0.13	0.04	0.23	0.18	0.4031	1
NMR08-93	FH 1	7/20/08 5:30 PM	2.9	0.7	0.00	0.00	0.00	0.00		
NMR08-65	NMR 2	7/20/08 6:30 PM	4.8	1.1	0.44	0.13	0.10	0.08	0.3175	1
NMR08-94	FH 1	7/20/08 6:30 PM	2.9	0.7	0.00	0.00	0.00	0.00		
NMR08-66	NMR 2	7/20/08 7:30 PM	4.2	1.0	0.46	0.14	0.10	0.08	0.2706	1
NMR08-95	FH 1	7/20/08 7:30 PM	2.9	0.7	0.00	0.00	0.00	0.00		
NMR08-69	NMR 3	8/6/08 10:45 AM	4.8	1.1	0.26	0.08	0.00	0.00	0.0538	
NMR08-67	NMR 1	8/6/08 11:30 AM	6.1	1.4	0.05	0.01	0.03	0.03	0.0905	
NMR08-68	NMR 2	8/6/08 12:30 PM	2.6	0.6	0.01	0.00	0.00	0.00	0.0621	
NMR08-70	NMR 1	8/15/08 9:45 AM	7.0	1.6	0.06	0.02	0.00	0.00	0.0664	
NMR08-71	NMR 2	8/15/08 10:15 AM	2.9	0.7	0.01	0.00	0.00	0.00	0.0467	
NMR08-72	NMR 3	8/15/08 10:45 AM	5.9	1.3	0.41	0.12	0.00	0.00	0.3675	
NMR08-73	NMR 1	9/5/08 10:30 AM	6.6	1.5	0.22	0.07	0.03	0.03	0.0465	
NMR08-74	NMR 2	9/5/08 10:45 AM	5.1	1.2	0.00	0.00	0.00	0.00	0.0343	
NMR08-75	NMR 3	9/5/08 11:15 AM	7.3	1.7	0.34	0.10	0.19	0.15	0.0359	

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR08-78	NMR 3	9/15/08 5:00 PM	8.5	1.9	0.20	0.06	0.00	0.00	0.0436	
NMR08-81	NMR 3	9/29/08 4:00 PM	3.9	0.9	0.21	0.06	0.47	0.37	0.0282	
NMR08-79	NMR 1	9/29/08 4:45 PM	6.7	1.5	0.36	0.11	0.08	0.06	0.0411	
NMR08-80	NMR 2	9/29/08 5:15 PM	3.5	0.8	0.00	0.00	0.06	0.05	0.0344	
NMR08-82	NMR 1	10/24/08 10:30 AM	6.1	1.4	0.24	0.07	0.24	0.19	0.0740	
NMR08-83	NMR 2	10/24/08 10:45 AM	5.5	1.3	0.07	0.02	0.20	0.16	0.0337	
NMR08-84	NMR 3	10/24/08 11:30 AM	7.4	1.7	0.28	0.09	0.44	0.34	0.0442	
NMR08-85	NMR 1	11/7/08 10:30 AM	5.5	1.3	0.12	0.04	0.22	0.17	0.0918	
NMR08-86	NMR 2	11/7/08 11:00 AM	4.2	1.0	0.05	0.01	0.29	0.22	0.0893	
NMR08-87	NMR 3	11/7/08 11:30 AM	5.5	1.3	0.23	0.07	0.52	0.40	0.0303	
NMR08-96	NMR 1	11/25/08 9:15 AM	8.7	2.0	0.25	0.08	0.50	0.39	0.1240	
NMR08-97	NMR 2	11/25/08 9:45 AM	7.7	1.8	0.07	0.02	0.30	0.23	0.0960	
NMR08-98	NMR 3	11/25/08 10:15 AM	5.2	1.2	0.10	0.03	0.11	0.09	0.0832	
NMR08-100	NMR 1	12/10/08 10:45 AM	5.2	1.2	0.05	0.01	0.17	0.13	0.3417	
NMR08-99	FH 1	12/10/08 11:15 AM	2.4	0.5	0.00	0.00	0.06	0.04	0.0015	
NMR08-101	NMR 2	12/10/08 11:45 AM	3.2	0.7	0.03	0.01	0.13	0.10	0.4038	
NMR08-102	NMR 3	12/10/08 12:00 PM	3.0	0.7	0.05	0.01	0.22	0.17		

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR09-01	NMR 1	1/2/09 10:45 AM	11.0	2.5	0.13	0.04	0.25	0.19	0.0969	
NMR09-02	NMR 2	1/2/09 11:00 AM	9.7	2.2	0.06	0.02	0.06	0.05	0.1049	
NMR09-03	NMR 3	1/2/09 11:30 AM	11.8	2.7	0.20	0.06	0.06	0.05	0.0893	
NMR09-04	NMR 1	1/16/09 8:30 AM	10.4	2.4	0.08	0.02	0.16	0.13	0.1345	
NMR09-05	NMR 1	1/30/09 8:45 AM	12.0	2.8	0.13	0.04	0.17	0.13		
NMR09-07	FH 1	1/30/09 9:15 AM	5.3	1.2	0.00	0.00	0.00	0.00	0.0002	
NMR09-06	NMR 2	1/30/09 9:30 AM	10.5	2.4	0.10	0.03	0.18	0.14		
NMR09-08	NMR 1	2/13/09 8:30 AM	14.7	3.4	0.08	0.02	0.14	0.11	0.1461	
NMR09-11	FH 2	2/13/09 9:00 AM	4.9	1.1	0.00	0.00	0.00	0.00		
NMR09-10	FH 1	2/13/09 9:15 AM	5.4	1.2	0.00	0.00	0.00	0.00		
NMR09-09	NMR 2	2/13/09 9:30 AM	12.2	2.8	0.05	0.01	0.02	0.01	0.1167	
NMR09-12	NMR 1	2/27/09 8:30 AM	8.6	2.0	0.21	0.06	0.44	0.34	0.2024	
NMR09-13	NMR 2	2/27/09 9:00 AM	9.0	2.1	0.03	0.01	0.17	0.13	0.1266	
NMR09-14	NMR 3	2/27/09 9:30 AM	8.7	2.0	0.24	0.07	0.21	0.17	0.1102	
NMR09-26	GW 1	3/4/09 4:30 PM	0.1	0.0	0.00	0.00	0.62	0.48		
NMR09-27	GW 2	3/4/09 4:40 PM		0.0	0.00	0.00	0.30	0.23		
NMR09-15	NMR 1	3/20/09 8:30 AM	7.9	1.8	0.12	0.04	0.18	0.14	0.0798	

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR09-16	NMR 2	3/20/09 9:00 AM	6.5	1.5	0.05	0.01	0.05	0.04	0.0691	
NMR09-17	NMR 3	3/20/09 9:30 AM	7.4	1.7	0.34	0.10	0.14	0.11	0.0621	
NMR09-18	NMR 1	4/6/09 8:30 AM	7.2	1.7	0.05	0.02	0.48	0.37	0.3272	
NMR09-21	FH 1	4/6/09 9:00 AM	2.2	0.5	0.00	0.00	0.07	0.05	0.0022	
NMR09-19	NMR 2	4/6/09 9:15 AM	7.2	1.7	0.05	0.02	0.50	0.39	0.2072	
NMR09-22	FH 2	4/6/09 9:15 AM	1.7	0.4	0.00	0.00	0.01	0.01		
NMR09-20	NMR 3	4/6/09 9:45 AM	11.5	2.7	0.03	0.01	0.25	0.20	0.3978	
NMR09-28	GW 1	4/8/09 4:00 PM	0.3	0.1	0.00	0.00	0.64	0.50		
NMR09-29	GW 2	4/8/09 4:30 PM		0.0	0.00	0.00	0.35	0.27		
NMR09-23	NMR 1	4/21/09 8:45 AM	9.5	2.2	0.07	0.02	0.19	0.14	0.1517	
NMR09-24	NMR 2	4/21/09 9:15 AM	7.8	1.8	0.05	0.01	0.07	0.06	0.1040	
NMR09-25	NMR 3	4/21/09 9:45 AM	5.4	1.2	0.14	0.04	0.19	0.14	0.1188	
NMR10-37	Precip	7/9/10 8:30 AM	0.8	0.2	0.00	0.00	0.49	0.38		
NMR10-37	Precip	7/9/10 8:30 AM	0.8	0.2	0.00	0.00	0.49	0.38		
NMR10-37	Precip	7/9/10 8:30 AM	0.8	0.2	0.00	0.00	0.49	0.38		
NMR10-38	NMR 2	7/9/10 2:25 PM	3.5	0.8	0.00	0.00	0.38	0.30	0.0218	2
NMR10-39	NMR 2	7/9/10 2:55 PM	6.2	1.4	0.13	0.04	0.45	0.35	2.4625	2

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR10-40	NMR 2	7/9/10 3:25 PM	3.5	0.8	1.16	0.35	0.30	0.23	0.9750	2
NMR10-41	NMR 2	7/9/10 3:55 PM	0.4	0.1	1.69	0.51	0.13	0.10	1.1360	2
NMR10-42	NMR 2	7/9/10 4:25 PM	3.3	0.8	1.69	0.51	0.13	0.10	0.5910	2
NMR10-43	NMR 2	7/9/10 4:55 PM	0.5	0.1	0.13	0.04	0.07	0.05	3.0654	2
NMR10-44	NMR 2	7/9/10 5:25 PM	2.9	0.7	0.10	0.03	0.09	0.07	3.3557	2
NMR10-45	NMR 2	7/9/10 5:55 PM	2.7	0.6	0.09	0.03	0.07	0.05	2.7604	2
NMR10-46	NMR 2	7/9/10 6:25 PM	3.1	0.7	0.07	0.02	0.09	0.07	1.6922	2
NMR10-47	NMR 2	7/9/10 6:55 PM	3.3	0.8	0.07	0.02	0.08	0.06	0.8571	2
NMR10-48	NMR 2	7/9/10 7:25 PM	2.5	0.6	0.03	0.01	0.07	0.06	0.5117	2
NMR10-49	NMR 2	7/9/10 7:55 PM	2.8	0.6	0.04	0.01	0.05	0.04	0.3600	2
NMR10-50	NMR 2	7/9/10 8:25 PM	2.8	0.6	0.03	0.01	0.08	0.06	0.4570	2
NMR10-51	NMR 2	7/9/10 9:25 PM	4.3	1.0	0.04	0.01	0.05	0.04	0.4608	2
NMR10-52	NMR 2	7/9/10 10:25 PM	4.2	1.0	0.04	0.01	0.00	0.00	0.2511	2
NMR10-53	NMR 2	7/9/10 11:25 PM	3.8	0.9	0.03	0.01	0.01	0.01	0.1591	2
NMR10-54	NMR 2	7/10/10 12:25 AM	3.6	0.8	0.03	0.01	0.03	0.02	0.1206	2
NMR10-55	NMR 2	7/10/10 1:25 AM	3.5	0.8	0.03	0.01	0.03	0.02	0.1032	2
NMR10-56	NMR 2	7/10/10 2:25 AM	3.5	0.8	0.03	0.01	0.03	0.02	0.0924	2

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR10-57	NMR 2	7/10/10 3:25 AM	3.5	0.8	0.03	0.01	0.02	0.02	0.0821	2
NMR10-58	NMR 2	7/10/10 4:25 AM	3.5	0.8	0.03	0.01	0.01	0.01	0.0724	2
NMR10-59	NMR 2	7/10/10 5:25 AM	3.6	0.8	0.03	0.01	0.00	0.00	0.0708	2
NMR10-60	NMR 2	7/10/10 6:25 AM	3.7	0.9	0.03	0.01	0.00	0.00	0.0708	2
NMR10-61	NMR 2	7/10/10 7:25 AM	4.2	1.0	0.03	0.01	0.04	0.03	0.0632	2
NMR11-03	NMR 2	1/1/11 3:44 AM	6.4	1.5	0.05	0.02	0.15	0.12	0.0872	3
NMR11-04	NMR 2	1/1/11 4:44 AM	6.2	1.4	0.06	0.02	0.22	0.17	0.0906	3
NMR11-05	NMR 2	1/1/11 5:44 AM	6.2	1.4	0.06	0.02	0.18	0.14	0.0906	3
NMR11-06	NMR 2	1/1/11 6:14 AM	6.1	1.4	0.05	0.01	0.10	0.08	0.0942	3
NMR11-07	NMR 2	1/1/11 6:44 AM	6.3	1.4	0.06	0.02	0.12	0.10	0.0889	3
NMR11-08	NMR 2	1/1/11 7:14 AM	6.0	1.4	0.06	0.02	0.13	0.10	0.0906	3
NMR11-09	NMR 2	1/1/11 8:14 AM	6.1	1.4	0.05	0.02	0.14	0.11	0.1070	3
NMR11-10	NMR 2	1/1/11 9:14 AM	2.9	0.7	0.24	0.07	0.26	0.20	0.8571	3
NMR11-11	NMR 2	1/1/11 10:14 AM	2.3	0.5	0.16	0.05	0.30	0.24	0.5653	3
NMR11-01	Precip	1/1/11 10:45 AM	0.2	0.1	0.00	0.00	0.15	0.12		3
NMR11-12	NMR 2	1/1/11 11:14 AM	2.4	0.5	0.09	0.03	0.23	0.18	1.0888	3
NMR11-13	NMR 2	1/1/11 12:14 PM	1.2	0.3	0.05	0.01	0.21	0.17	1.3285	3

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR11-14	NMR 2	1/1/11 1:14 PM	1.5	0.3	0.03	0.01	0.17	0.13	0.9421	3
NMR11-15	NMR 2	1/1/11 2:14 PM	1.9	0.4	0.00	0.00	0.00	0.00	0.7565	3
NMR11-16	NMR 2	1/1/11 3:14 PM	2.2	0.5	0.02	0.01	0.13	0.10	0.4161	3
NMR11-17	NMR 2	1/1/11 4:14 PM	2.2	0.5	0.02	0.01	0.14	0.11	0.3047	3
NMR11-02	Precip	1/1/11 5:00 PM	0.6	0.1	0.01	0.00	0.24	0.19		3
NMR11-18	NMR 2	1/1/11 5:14 PM	3.0	0.7	0.01	0.00	0.16	0.13	0.2714	3
NMR11-19	NMR 2	1/1/11 6:14 PM	3.7	0.9	0.02	0.01	0.16	0.12	0.2399	3
NMR11-46	Precip	3/9/11 12:00 PM	0.3	0.1	0.00	0.00	not measured	not measured		
NMR11-47	B	3/9/11 2:30 PM	1.7	0.4	0.00	0.00	not measured	not measured		
NMR11-48	M	3/9/11 2:47 PM	5.5	1.3	0.00	0.00	not measured	not measured		
NMR11-49	F	3/9/11 3:47 PM	11.7	2.7	0.00	0.00	not measured	not measured		
NMR11-50	N	3/9/11 3:48 PM	10.0	2.3	0.00	0.00	not measured	not measured		
NMR11-51	O	3/9/11 4:07 PM	9.4	2.2	0.00	0.00	not measured	not measured		
NMR11-53	Precip	3/10/11 8:00 AM	0.3	0.1	0.00	0.00	not measured	not measured		
NMR11-20	NMR 2	3/22/11 8:45 PM	8.4	1.9	0.03	0.01	0.09	0.07		4
NMR11-21	NMR 2	3/22/11 10:45 PM	8.2	1.9	0.03	0.01	0.16	0.12		4
NMR11-22	NMR 2	3/22/11 11:45 PM	10.1	2.3	0.03	0.01	0.11	0.08		4

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR11-24	NMR 2	3/23/11 12:45 AM	9.1	2.1	0.00	0.00	0.00	0.00		4
NMR11-23	NMR 2	3/23/11 1:45 AM	9.9	2.3	0.05	0.02	0.14	0.11		4
NMR11-25	NMR 2	3/23/11 2:45 AM	9.1	2.1	0.06	0.02	0.12	0.10		4
NMR11-26	NMR 2	3/23/11 3:45 AM	8.6	2.0	0.08	0.02	0.29	0.23		4
NMR11-27	NMR 2	3/23/11 4:45 AM	7.7	1.8	0.10	0.03	0.22	0.17		4
NMR11-28	NMR 2	3/23/11 5:45 AM	7.0	1.6	0.10	0.03	0.20	0.16		4
NMR11-29	NMR 2	3/23/11 6:45 AM	6.7	1.5	0.09	0.03	0.15	0.12		4
NMR11-30	NMR 2	3/23/11 7:45 AM	6.6	1.5	0.08	0.02	0.16	0.13		4
NMR11-43	Precip	3/23/11 8:00 AM	3.7	0.8	0.00	0.00	0.00	0.00		4
NMR11-31	NMR 2	3/23/11 8:45 AM	6.4	1.5	0.09	0.03	0.23	0.18		4
NMR11-32	NMR 2	3/23/11 9:45 AM	6.8	1.6	0.33	0.10	0.25	0.20		4
NMR11-33	NMR 2	3/23/11 10:45 AM	7.6	1.8	0.08	0.03	0.25	0.20		4
NMR11-34	NMR 2	3/23/11 11:45 AM	7.1	1.6	0.10	0.03	0.32	0.25		4
NMR11-35	NMR 2	3/23/11 12:45 PM	6.4	1.5	0.11	0.03	0.36	0.28		4
NMR11-36	NMR 2	3/23/11 1:45 PM	6.4	1.5	0.12	0.04	0.31	0.24		4
NMR11-44	Precip	3/23/11 2:00 PM	3.5	0.8	0.00	0.00	0.00	0.00		4
NMR11-37	NMR 2	3/23/11 2:45 PM	5.5	1.3	0.11	0.03	0.27	0.21		4

Sample Name	*Station Name*	*Sample Date*	*Nitrate (mgL^{-1})*	*Nitrate-N (mgL^{-1})*	*Nitrite (mgL^{-1})*	*Nitrite-N (mgL^{-1})*	*Ammonium (mgL^{-1})*	*Ammonium-N (mgL^{-1})*	*Discharge (cms)*	*Storm Event Number*
NMR11-38	NMR 2	3/23/11 3:45 PM	5.5	1.3	0.11	0.03	0.23	0.18		4
NMR11-39	NMR 2	3/23/11 4:45 PM	0.0	0.0	0.16	0.05	0.32	0.25		4
NMR11-40	NMR 2	3/23/11 5:45 PM	1.4	0.3	0.12	0.04	0.26	0.20		4
NMR11-41	NMR 2	3/23/11 6:45 PM	2.2	0.5	0.05	0.01	0.23	0.18		4
NMR11-42	NMR 2	3/23/11 7:45 PM	2.4	0.5	0.02	0.01	0.15	0.12		4
NMR11-45	Precip	3/24/11 12:00 AM	0.8	0.2	0.00	0.00	not measured	not measured		4
NMR12-01	A	10/17/12 4:15 PM	5.0	1.1	0.01	0.00	not measured	not measured		5
NMR12-02	D	10/17/12 4:30 PM	8.2	1.9	0.00	0.00	not measured	not measured		5
NMR12-03	F	10/17/12 4:40 PM	13.5	3.1	0.45	0.14	not measured	not measured		5
NMR12-05	H	10/17/12 5:00 PM	0.0	0.0	0.00	0.00	not measured	not measured		5
NMR12-04	M	10/17/12 5:10 PM	0.4	0.1	0.00	0.00	not measured	not measured		5
NMR12-27	Precip	10/18/12 2:33 PM	0.5	0.1	0.00	0.00	not measured	not measured		5
NMR12-28	NMR 2	10/18/12 3:03 PM	4.7	1.1	0.00	0.00	not measured	not measured	0.0189	5
NMR12-29	NMR 2	10/18/12 3:33 PM	4.6	1.1	0.00	0.00	not measured	not measured	0.0185	5
NMR12-30	NMR 2	10/18/12 4:03 PM	4.6	1.1	0.00	0.00	not measured	not measured	0.0184	5
NMR12-31	NMR 2	10/18/12 4:33 PM	4.5	1.0	0.00	0.00	not measured	not measured	0.0199	5
NMR12-25	F	10/18/12 4:45 PM	4.2	1.0	0.40	0.12	not measured	not measured		5

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR12-12	D	10/18/12 4:47 PM	5.0	1.2	0.40	0.12	not measured	not measured		5
NMR12-22	J	10/18/12 4:54 PM	6.2	1.4	0.04	0.01	not measured	not measured		5
NMR12-07	C	10/18/12 4:56 PM	2.7	0.6	0.14	0.04	not measured	not measured		5
NMR12-08	Ga	10/18/12 5:00 PM	4.1	0.9	0.48	0.14	not measured	not measured		5
NMR12-20	M	10/18/12 5:03 PM	0.4	0.1	0.0000	0.00	not measured	not measured		5
NMR12-32	NMR 2	10/18/12 5:03 PM	1.4	0.3	0.04	0.01	not measured	not measured	0.0211	5
NMR12-11	A	10/18/12 5:05 PM	5.0	1.2	0.04	0.01	not measured	not measured		5
NMR12-09	G	10/18/12 5:15 PM	2.3	0.5	0.25	0.08	not measured	not measured		5
NMR12-19	H	10/18/12 5:20 PM	1.6	0.4	0.10	0.03	not measured	not measured		5
NMR12-06	B	10/18/12 5:25 PM	0.8	0.2	0.00	0.00	not measured	not measured		5
NMR12-10	I	10/18/12 5:27 PM	1.6	0.4	0.02	0.01	not measured	not measured		5
NMR12-33	NMR 2	10/18/12 5:33 PM	1.4	0.3	0.02	0.01	not measured	not measured	0.0237	5
NMR12-14	A	10/18/12 5:35 PM	1.3	0.3	0.00	0.00	not measured	not measured		5
NMR12-18	F	10/18/12 5:35 PM	0.9	0.2	0.00	0.00	not measured	not measured		5
NMR12-23	H	10/18/12 5:35 PM	0.7	0.2	0.00	0.00	not measured	not measured		5
NMR12-24	D	10/18/12 5:43 PM	4.2	1.0	0.00	0.00	not measured	not measured		5
NMR12-16	Ga	10/18/12 5:45 PM	1.1	0.3	0.00	0.00	not measured	not measured		5

Sample Name	***Station Name***	***Sample Date***	***Nitrate (mgL^{-1})***	***Nitrate-N (mgL^{-1})***	***Nitrite (mgL^{-1})***	***Nitrite-N (mgL^{-1})***	***Ammonium (mgL^{-1})***	***Ammonium-N (mgL^{-1})***	***Discharge (cms)***	***Storm Event Number***
NMR12-15	E	10/18/12 5:50 PM	0.9	0.2	0.00	0.00	not measured	not measured		5
NMR12-21	G	10/18/12 5:50 PM	0.6	0.1	0.003	0.00	not measured	not measured		5
NMR12-17	J	10/18/12 6:00 PM	1.6	0.4	0.01	0.00	not measured	not measured		5
NMR12-34	NMR 2	10/18/12 6:03 PM	1.3	0.3	0.00	0.00	not measured	not measured	10.1437	5
NMR12-13	I	10/18/12 6:04 PM	1.4	0.3	0.00	0.00	not measured	not measured		5
NMR12-26	M	10/18/12 6:30 PM	1.5	0.3	0.03	0.01	not measured	not measured		5
NMR12-35	NMR 2	10/18/12 6:33 PM	4.5	1.0	0.06	0.02	not measured	not measured	3.7129	5
NMR12-36	NMR 2	10/18/12 7:03 PM	4.2	1.0	0.00	0.00	not measured	not measured	0.8956	5
NMR12-37	NMR 2	10/18/12 7:33 PM	1.9	0.4	0.03	0.01	not measured	not measured	1.1230	5
NMR12-38	NMR 2	10/18/12 8:03 PM	1.5	0.3	0.05	0.02	not measured	not measured	1.2619	5
NMR12-39	NMR 2	10/18/12 8:33 PM	1.4	0.3	0.04	0.01	not measured	not measured	0.6718	5
NMR12-40	NMR 2	10/18/12 9:03 PM	1.4	0.3	0.04	0.01	not measured	not measured	0.2792	5
NMR12-41	NMR 2	10/18/12 9:33 PM	4.5	1.0	0.09	0.03	not measured	not measured	0.1454	5
NMR12-42	NMR 2	10/18/12 10:03 PM	4.5	1.0	0.09	0.03	not measured	not measured	0.0959	5
NMR12-43	NMR 2	10/18/12 10:33 PM	1.4	0.3	0.04	0.01	not measured	not measured	0.0702	5
NMR12-44	NMR 2	10/18/12 11:03 PM	1.4	0.3	0.00	0.00	not measured	not measured	0.0580	5
NMR12-45	NMR 2	10/18/12 11:33 PM	4.5	1.0	0.05	0.02	not measured	not measured	0.0488	5

Table A-2 δ^{15}N, δ^{18}O, and Δ^{17}O isotope data

No data entry indicates nitrate concentrations were too low for isotopic analysis without prior preconcentration. Precision was 0.2‰, 0.5‰, and 0.5‰ for δ^{15}N, δ^{18}O, and Δ^{17}O, respectively.

Sample Name	***Station Name***	***Sample Date***	***δ^{15}N (‰)***	***δ^{18}O (‰)***	***Δ^{17}O (‰)***
NMR07-01	NMR 1	4/10/07 3:45 PM	9.0	1.3	-1.0
NMR07-02	NMR 2	4/10/07 4:15 PM	9.3	1.2	-0.8
NMR07-03	NMR 3	4/10/07 5:15 PM	10.0	0.7	-1.1
NMR07-04	NMR 1	5/9/07 9:30 AM	10.0	1.3	-0.8
NMR07-05	FH 1	5/9/07 10:45 AM	13.8	5.6	-1.1
NMR07-06	NMR 2	5/9/07 11:15 AM	10.6	2.1	-1.1
NMR07-07	NMR 3	5/9/07 12:30 PM	11.8	2.5	-1.0
NMR07-08	NMR 1	5/23/07 9:30 AM	10.8	0.8	-1.1
NMR07-09	NMR 2	5/23/07 10:30 AM	11.5	1.1	-1.1
NMR07-10	NMR 3	5/23/07 11:30 AM	12.6	2.3	-1.3
NMR07-11	NMR 1	6/7/07 8:30 AM	11.4	1.8	-0.8
NMR07-12	NMR 2	6/7/07 9:15 AM	11.5	2.2	-0.9
NMR07-13	NMR 3	6/7/07 9:30 AM	12.9	3.0	-1.1
NMR07-14	NMR 1	6/20/07 3:15 PM	10.1	1.1	-1.0
NMR07-15	NMR 2	6/20/07 4:00 PM	9.8	2.2	-0.4
NMR07-16	NMR 3	6/20/07 4:30 PM	10.5	5.1	-0.2
NMR07-17	NMR 1	7/6/07 7:15 AM	10.7	1.7	-0.3
NMR07-18	NMR 2	7/6/07 7:45 AM	10.1	2.5	-0.4
NMR07-19	NMR 3	7/6/07 8:15 AM	10.2	1.3	-0.7
NMR07-20	NMR 1	7/18/07 7:30 AM	11.3	0.7	-0.8
NMR07-21	NMR 2	7/18/07 8:30 AM	14.8	3.1	-1.3
NMR07-22	NMR 3	7/18/07 9:00 AM	14.3	1.1	-1.0
NMR07-23	NMR 1	8/2/07 8:00 AM	11.7	0.9	-1.3
NMR07-24	NMR 2	8/2/07 9:00 AM	13.5	5.3	-0.6
NMR07-25	NMR 3	8/2/07 10:45 AM	19.3	8.3	-1.7
NMR07-26	NMR 1	8/15/07 9:30 AM	10.8	2.5	-1.3
NMR07-27	NMR 2	8/15/07 10:00 AM	11.9	2.5	-1.2
NMR07-28	NMR 3	8/15/07 11:30 AM	12.3	1.6	-1.5
NMR07-31	NMR 3	8/30/07 7:15 AM	12.8	1.4	-1.5
NMR07-32	NMR 2	8/30/07 7:45 AM	11.8	2.3	-1.0
NMR07-30	FH 1	8/30/07 8:00 AM	14.7	2.8	-1.6
NMR07-29	NMR 1	8/30/07 8:30 AM	11.0	0.5	-1.0

Sample Name	***Station Name***	***Sample Date***	$\delta^{15}N$ ***(‰)***	$\delta^{18}O$ ***(‰)***	$\Delta^{17}O$ ***(‰)***
NMR07-36	NMR 3	9/13/07 10:45 AM	12.5	2.6	-1.2
NMR07-34	NMR 2	9/13/07 11:00 AM	12.1	2.5	-1.4
NMR07-33	NMR 1	9/13/07 12:00 PM	12.1	2.7	-1.1
NMR07-35	FH 1	9/13/07 12:15 PM	15.5	3.6	-1.0
NMR07-39	NMR 3	9/25/07 7:45 AM	14.5	4.1	-1.6
NMR07-38	NMR 2	9/25/07 8:15 AM	11.9	2.5	-1.4
NMR07-37	NMR 1	9/25/07 8:30 AM	11.8	1.5	-0.9
NMR07-42	NMR 3	10/9/07 7:45 AM	16.1	6.1	-1.6
NMR07-41	NMR 2	10/9/07 8:15 AM	11.3	2.1	-1.1
NMR07-40	NMR 1	10/9/07 8:45 AM	11.5	0.8	0.0
NMR07-45	NMR 3	10/24/07 3:45 PM	9.5	9.2	1.8
NMR07-44	NMR 2	10/24/07 4:15 PM	9.5	9.7	1.9
NMR07-43	NMR 1	10/24/07 4:45 PM	10.4	4.5	0.2
NMR07-48	NMR 3	11/7/07 8:00 AM	13.5	15.4	2.3
NMR07-47	NMR 2	11/7/07 8:30 AM	11.3	5.0	-0.1
NMR07-46	NMR 1	11/7/07 9:00 AM	12.0	2.5	-0.8
NMR07-51	NMR 3	11/19/07 8:30 AM	13.5	2.2	-1.0
NMR07-50	NMR 2	11/19/07 9:15 AM	11.6	0.8	-0.1
NMR07-49	NMR 1	11/19/07 9:30 AM	11.6	0.9	-0.5
NMR07-54	NMR 3	12/4/07 1:30 PM	10.3	1.5	-0.6
NMR07-53	NMR 2	12/4/07 2:30 PM	10.1	1.2	-0.9
NMR07-55	FH 1	12/4/07 2:45 PM	11.7	1.6	-0.9
NMR07-52	NMR 1	12/4/07 3:15 PM	10.0	0.1	-0.9
NMR07-58	NMR 2	12/20/07 11:15 AM	9.3	0.2	-0.7
NMR07-60	FH 1	12/20/07 11:20 AM	11.7	0.6	-1.3
NMR07-57	NMR 1	12/20/07 11:45 AM	9.5	0.9	-0.2
NMR07-59	NMR 3	12/20/07 1:00 PM	9.8	0.3	-0.6
NMR08-01	NMR 3	1/4/08 10:30 AM	9.9	-0.2	-1.0
NMR08-02	NMR 2	1/4/08 11:00 AM	10.2	0.3	-1.1
NMR08-03	FH 1	1/4/08 11:30 AM	14.3	3.3	-0.8
NMR08-04	NMR 1	1/4/08 11:45 AM	10.2	0.0	-0.6
NMR08-06	NMR 3	1/18/08 8:00 AM	8.7	22.1	7.3
NMR08-07	NMR 1	1/18/08 8:45 AM	8.5	20.4	6.7
NMR08-08	NMR 2	1/18/08 9:45 AM	8.0	31.1	10.5
NMR08-05	FH 1	1/18/08 10:15 AM	13.1	6.0	0.0
NMR08-09	NMR 3	1/29/08 9:30 AM	10.1	7.2	1.6
NMR08-11	NMR 2	1/29/08 9:30 AM	8.1	36.9	12.2
NMR08-12	FH 1	1/29/08 9:45 AM	14.5	3.9	
NMR08-10	NMR 1	1/29/08 10:15 AM	7.1	43.4	16.1
NMR08-13	NMR 3	2/12/08 1:15 PM	9.0	3.6	-0.6

Sample Name	*Station Name*	*Sample Date*	*δ^{15}N (‰)*	*δ^{18}O (‰)*	*Δ^{17}O (‰)*
NMR08-15	FH 1	2/12/08 1:45 PM	10.2	3.5	-0.7
NMR08-14	NMR 2	2/12/08 2:15 PM	8.7	3.6	-0.5
NMR08-16	NMR 1	2/12/08 2:45 PM	8.3	4.0	0.2
NMR08-17	NMR 1	2/28/08 12:45 PM	8.8	1.6	-0.3
NMR08-20	FH 1	2/28/08 1:15 PM	12.1	2.7	-0.7
NMR08-18	NMR 2	2/28/08 1:30 PM	8.9	4.1	-0.4
NMR08-19	NMR 3	2/28/08 2:00 PM	9.5	1.5	-0.5
NMR08-21	NMR 1	3/18/08 12:45 PM	7.8	13.5	4.2
NMR08-24	FH 1	3/18/08 1:30 PM	11.9	5.3	-0.6
NMR08-22	NMR 2	3/18/08 1:45 PM	8.8	1.9	-0.3
NMR08-23	NMR 3	3/18/08 2:15 PM	9.1	3.5	-0.1
NMR08-26	NMR 2	4/1/08 12:45 PM	9.4	4.0	-0.5
NMR08-28	FH 1	4/1/08 1:00 PM	13.8	5.9	-1.2
NMR08-25	NMR 1	4/1/08 1:30 PM	8.9	3.0	-1.0
NMR08-27	NMR 3	4/1/08 2:00 PM	10.1	3.8	-1.0
NMR08-30	NMR 2	4/15/08 12:45 PM	10.3	3.3	-0.7
NMR08-32	FH 1	4/15/08 1:15 PM	15.5	6.6	-1.1
NMR08-29	NMR 1	4/15/08 1:45 PM	9.6	0.6	-0.9
NMR08-31	NMR 3	4/15/08 2:15 PM	10.8	3.5	-1.1
NMR08-36	NMR 2	5/1/08 9:45 AM	9.6	3.5	-0.4
NMR08-38	FH 1	5/1/08 10:15 AM	12.4	6.0	0.5
NMR08-35	NMR 1	5/1/08 10:45 AM	6.9	20.2	5.5
NMR08-37	NMR 3	5/1/08 11:15 AM	10.3	4.9	0.5
NMR08-39	NMR 1	5/14/08 9:30 AM	9.1	2.9	0.6
NMR08-42	FH 1	5/14/08 9:45 AM	11.8	3.7	-0.5
NMR08-40	NMR 2	5/14/08 10:15 AM	9.6	3.5	0.5
NMR08-41	NMR 3	5/14/08 11:00 AM	10.1	3.6	0.1
NMR08-43	NMR 1	5/29/08 9:15 AM	10.1	2.7	-0.1
NMR08-46	FH 1	5/29/08 10:00 AM	12.9	1.0	-0.5
NMR08-44	NMR 2	5/29/08 10:15 AM	11.1	0.2	-0.4
NMR08-45	NMR 3	5/29/08 10:45 AM	12.1	0.8	-0.8
NMR08-47	NMR 1	6/13/08 8:00 AM	10.5	-0.3	-0.3
NMR08-48	NMR 2	6/13/08 1:45 PM	2.5	22.8	6.9
NMR08-49	NMR 3	6/13/08 2:30 PM	3.0	22.9	6.9
NMR08-52	NMR 3	6/27/08 2:45 PM	9.3	4.6	-0.2
NMR08-51	NMR 2	6/27/08 3:15 PM	9.1	1.1	0.0
NMR08-53	FH 1	6/27/08 3:30 PM	11.8	0.7	0.0
NMR08-50	NMR 1	6/27/08 4:00 PM	9.0	3.1	1.2
NMR08-54	NMR 1	7/9/08 5:45 PM	10.0	3.3	-0.3
NMR08-57	FH 1	7/9/08 6:30 PM	13.7	0.1	-0.8

Sample Name	*Station Name*	*Sample Date*	*$\delta^{15}N$ (‰)*	*$\delta^{18}O$ (‰)*	*$\Delta^{17}O$ (‰)*
NMR08-55	NMR 2	7/9/08 6:45 PM	10.7	2.3	0.4
NMR08-56	NMR 3	7/9/08 7:15 PM	11.0	5.1	0.0
NMR08-58	NMR 2	7/20/08 2:15 PM	8.9	25.7	7.2
NMR08-88	FH 1	7/20/08 2:30 PM	12.6	4.5	0.8
NMR08-59	NMR 2	7/20/08 3:00 PM	6.8	24.7	7.1
NMR08-89	FH 1	7/20/08 3:00 PM	8.5	19.8	5.9
NMR08-60	NMR 2	7/20/08 3:30 PM	5.0	32.8	10.1
NMR08-90	FH 1	7/20/08 3:30 PM	6.9	19.3	6.2
NMR08-61	NMR 2	7/20/08 3:45 PM	2.0	42.8	14.6
NMR08-62	NMR 2	7/20/08 4:00 PM	4.5	32.5	10.5
NMR08-91	FH 1	7/20/08 4:00 PM	6.3	18.6	5.8
NMR08-63	NMR 2	7/20/08 4:30 PM	4.5	32.4	10.3
NMR08-92	FH 1	7/20/08 4:30 PM	9.4	10.8	2.7
NMR08-64	NMR 2	7/20/08 5:30 PM	3.9	28.7	9.0
NMR08-93	FH 1	7/20/08 5:30 PM	10.2	11.8	2.9
NMR08-65	NMR 2	7/20/08 6:30 PM	4.9	27.5	8.4
NMR08-94	FH 1	7/20/08 6:30 PM	10.5	10.8	2.8
NMR08-66	NMR 2	7/20/08 7:30 PM	5.2	27.0	8.2
NMR08-95	FH 1	7/20/08 7:30 PM	10.9	9.6	2.3
NMR08-69	NMR 3	8/6/08 10:45 AM	11.3	17.3	4.4
NMR08-67	NMR 1	8/6/08 11:30 AM	9.1	10.0	3.1
NMR08-68	NMR 2	8/6/08 12:30 PM	7.0	29.1	9.1
NMR08-70	NMR 1	8/15/08 9:45 AM	10.8	1.2	0.5
NMR08-71	NMR 2	8/15/08 10:15 AM	9.7	7.9	2.4
NMR08-72	NMR 3	8/15/08 10:45 AM	14.0	10.9	1.0
NMR08-73	NMR 1	9/5/08 10:30 AM	11.3	-1.9	-1.1
NMR08-74	NMR 2	9/5/08 10:45 AM	12.5	-0.9	-1.1
NMR08-75	NMR 3	9/5/08 11:15 AM	16.7	4.8	-1.6
NMR08-78	NMR 3	9/15/08 5:00 PM	14.4	2.2	-1.3
NMR08-81	NMR 3	9/29/08 4:00 PM	19.4	8.0	-1.5
NMR08-79	NMR 1	9/29/08 4:45 PM	10.8	-1.4	-1.1
NMR08-80	NMR 2	9/29/08 5:15 PM	13.3	0.9	-0.9
NMR08-82	NMR 1	10/24/08 10:30 AM	11.4	-1.7	-1.2
NMR08-83	NMR 2	10/24/08 10:45 AM	10.8	-2.7	-1.1
NMR08-84	NMR 3	10/24/08 11:30 AM	16.0	3.8	-1.4
NMR08-85	NMR 1	11/7/08 10:30 AM	11.3	-0.9	-1.0
NMR08-86	NMR 2	11/7/08 11:00 AM	12.3	-1.0	-0.9
NMR08-87	NMR 3	11/7/08 11:30 AM	17.0	4.5	-1.6
NMR08-96	NMR 1	11/25/08 9:15 AM	8.8	-0.1	-0.3
NMR08-97	NMR 2	11/25/08 9:45 AM	8.7	2.9	0.7

Sample Name	***Station Name***	***Sample Date***	***$\delta^{15}N$ (‰)***	***$\delta^{18}O$ (‰)***	***$\Delta^{17}O$ (‰)***
NMR08-98	NMR 3	11/25/08 10:15 AM	10.0	11.9	3.4
NMR08-100	NMR 1	12/10/08 10:45 AM	6.7	8.2	2.5
NMR08-99	FH 1	12/10/08 11:15 AM	7.5	6.0	1.7
NMR08-101	NMR 2	12/10/08 11:45 AM	6.6	12.8	3.1
NMR08-102	NMR 3	12/10/08 12:00 PM	7.9	15.7	5.0
NMR09-01	NMR 1	1/2/09 10:45 AM	9.3	3.0	0.5
NMR09-02	NMR 2	1/2/09 11:00 AM	9.3	-0.7	-0.7
NMR09-03	NMR 3	1/2/09 11:30 AM	9.7	-0.1	-0.5
NMR09-04	NMR 1	1/16/09 8:30 AM	9.2	-0.9	-1.1
NMR09-05	NMR 1	1/30/09 8:45 AM	8.4	0.0	-0.5
NMR09-07	FH 1	1/30/09 9:15 AM	10.3	3.4	0.0
NMR09-06	NMR 2	1/30/09 9:30 AM	8.4	1.0	-0.4
NMR09-08	NMR 1	2/13/09 8:30 AM	7.9	-0.2	-0.4
NMR09-10	FH 1	2/13/09 9:15 AM	8.8	0.9	-0.6
NMR09-09	NMR 2	2/13/09 9:30 AM	8.0	-0.3	-0.6
NMR09-12	NMR 1	2/27/09 8:30 AM	8.8	5.5	1.1
NMR09-13	NMR 2	2/27/09 9:00 AM	10.0	0.5	-0.8
NMR09-14	NMR 3	2/27/09 9:30 AM	10.8	1.3	-1.0
NMR09-26	GW 1	3/4/09 4:30 PM	23.6	9.0	
NMR09-15	NMR 1	3/20/09 8:30 AM	10.3	-0.6	-0.7
NMR09-16	NMR 2	3/20/09 9:00 AM	10.7	0.2	-0.8
NMR09-17	NMR 3	3/20/09 9:30 AM	12.8	7.4	0.5
NMR09-18	NMR 1	4/6/09 8:30 AM	6.4	23.0	8.1
NMR09-21	FH 1	4/6/09 9:00 AM	10.3	2.3	-0.4
NMR09-19	NMR 2	4/6/09 9:15 AM	7.3	15.3	5.1
NMR09-20	NMR 3	4/6/09 9:45 AM	8.7	-0.3	-0.9
NMR09-28	GW 1	4/8/09 4:00 PM	28.2	6.9	
NMR09-23	NMR 1	4/21/09 8:45 AM	9.2	0.5	-0.5
NMR09-24	NMR 2	4/21/09 9:15 AM	9.1	1.6	-0.2
NMR09-25	NMR 3	4/21/09 9:45 AM	10.3	3.1	0.2
NMR10-37	Precip	7/9/10 8:30 AM	1.5	59.6	
NMR10-38	NMR 2	7/9/10 2:25 PM	14.2	1.0	-0.6
NMR10-39	NMR 2	7/9/10 2:55 PM	11.2	4.2	1.1
NMR10-40	NMR 2	7/9/10 3:25 PM	10.7	15.3	7.1
NMR10-41	NMR 2	7/9/10 3:55 PM	17.2	-16.1	
NMR10-42	NMR 2	7/9/10 4:25 PM	16.8	-12.7	0.4
NMR10-43	NMR 2	7/9/10 4:55 PM	5.1	25.7	7.5
NMR10-44	NMR 2	7/9/10 5:25 PM	4.6	21.1	6.9
NMR10-45	NMR 2	7/9/10 5:55 PM	4.7	16.9	5.4
NMR10-46	NMR 2	7/9/10 6:25 PM	4.2	12.5	3.8

Sample Name	***Station Name***	***Sample Date***	***$\delta^{15}N$ (‰)***	***$\delta^{18}O$ (‰)***	***$\Delta^{17}O$ (‰)***
NMR10-47	NMR 2	7/9/10 6:55 PM	4.1	10.5	3.4
NMR10-48	NMR 2	7/9/10 7:25 PM	6.1	12.2	4.3
NMR10-49	NMR 2	7/9/10 7:55 PM	6.2	10.7	3.6
NMR10-50	NMR 2	7/9/10 8:25 PM	6.5	9.9	3.3
NMR10-51	NMR 2	7/9/10 9:25 PM	6.9	6.5	2.1
NMR10-52	NMR 2	7/9/10 10:25 PM	7.2	7.1	2.2
NMR10-53	NMR 2	7/9/10 11:25 PM	7.5	6.8	2.6
NMR10-54	NMR 2	7/10/10 12:25 AM	7.8	6.4	2.1
NMR10-55	NMR 2	7/10/10 1:25 AM	8.0	6.0	0.5
NMR10-56	NMR 2	7/10/10 2:25 AM	8.3	5.9	2.2
NMR10-57	NMR 2	7/10/10 3:25 AM	8.5	5.9	2.0
NMR10-58	NMR 2	7/10/10 4:25 AM	8.5	5.0	1.5
NMR10-59	NMR 2	7/10/10 5:25 AM	8.6	4.6	1.2
NMR10-60	NMR 2	7/10/10 6:25 AM	9.0	4.5	0.6
NMR10-61	NMR 2	7/10/10 7:25 AM	8.9	3.3	0.9
NMR11-03	NMR 2	1/1/11 3:44 AM	11.0	-2.6	-0.3
NMR11-04	NMR 2	1/1/11 4:44 AM	11.0	-2.4	-0.1
NMR11-05	NMR 2	1/1/11 5:44 AM	11.1	-1.9	-0.2
NMR11-06	NMR 2	1/1/11 6:14 AM	11.3	-1.4	-0.5
NMR11-07	NMR 2	1/1/11 6:44 AM	11.2	-2.1	0.0
NMR11-08	NMR 2	1/1/11 7:14 AM	11.2	-2.9	-0.2
NMR11-09	NMR 2	1/1/11 8:14 AM	11.4	-1.3	-0.1
NMR11-10	NMR 2	1/1/11 9:14 AM	9.8	18.1	6.3
NMR11-11	NMR 2	1/1/11 10:14 AM	8.3	31.8	10.6
NMR11-01	Precip	1/1/11 10:45 AM	2.6	66.2	
NMR11-12	NMR 2	1/1/11 11:14 AM	6.6	22.3	9.3
NMR11-13	NMR 2	1/1/11 12:14 PM	6.6	18.6	
NMR11-14	NMR 2	1/1/11 1:14 PM	6.4	14.6	7.6
NMR11-15	NMR 2	1/1/11 2:14 PM	6.4	9.2	4.0
NMR11-16	NMR 2	1/1/11 3:14 PM	6.6	6.8	3.1
NMR11-17	NMR 2	1/1/11 4:14 PM	6.7	4.9	2.8
NMR11-02	Precip	1/1/11 5:00 PM	3.6	70.5	
NMR11-18	NMR 2	1/1/11 5:14 PM	6.9	3.8	2.0
NMR11-19	NMR 2	1/1/11 6:14 PM	3.8	63.3	
NMR11-46	Precip	3/9/11 12:00 PM	2.6	67.6	
NMR11-47	B	3/9/11 2:30 PM	4.9	5.7	2.8
NMR11-48	M	3/9/11 2:47 PM	8.0	-3.6	-1.1
NMR11-49	F	3/9/11 3:47 PM	5.0	-1.9	-0.6
NMR11-50	N	3/9/11 3:48 PM	9.5	-1.0	-0.1
NMR11-51	O	3/9/11 4:07 PM			

Sample Name	***Station Name***	***Sample Date***	***δ^{15}N (‰)***	***δ^{18}O (‰)***	***Δ^{17}O (‰)***
NMR11-53	Precip	3/10/11 8:00 AM			
NMR11-20	NMR 2	3/22/11 8:45 PM	10.2	-2.7	-0.9
NMR11-21	NMR 2	3/22/11 10:45 PM	10.1	-2.7	-1.1
NMR11-22	NMR 2	3/22/11 11:45 PM	10.3	-1.7	-0.8
NMR11-24	NMR 2	3/23/11 12:45 AM	9.8	-2.6	-1.1
NMR11-23	NMR 2	3/23/11 1:45 AM	9.8	-1.9	-0.6
NMR11-25	NMR 2	3/23/11 2:45 AM	9.2	2.5	1.1
NMR11-26	NMR 2	3/23/11 3:45 AM	8.0	10.5	3.9
NMR11-27	NMR 2	3/23/11 4:45 AM	7.0	18.9	6.7
NMR11-28	NMR 2	3/23/11 5:45 AM	7.0	19.1	6.7
NMR11-29	NMR 2	3/23/11 6:45 AM	7.6	15.7	5.9
NMR11-30	NMR 2	3/23/11 7:45 AM	7.9	15.0	5.1
NMR11-43	Precip	3/23/11 8:00 AM	2.4	77.1	27.6
NMR11-31	NMR 2	3/23/11 8:45 AM	8.0	14.5	5.0
NMR11-32	NMR 2	3/23/11 9:45 AM	9.4	7.0	2.0
NMR11-33	NMR 2	3/23/11 10:45 AM	8.3	8.2	2.8
NMR11-34	NMR 2	3/23/11 11:45 AM	7.2	19.1	6.5
NMR11-35	NMR 2	3/23/11 12:45 PM	6.4	26.8	9.1
NMR11-36	NMR 2	3/23/11 1:45 PM	5.7	28.5	10.3
NMR11-44	Precip	3/23/11 2:00 PM	1.6	73.5	26.0
NMR11-37	NMR 2	3/23/11 2:45 PM	6.1	28.9	10.6
NMR11-38	NMR 2	3/23/11 3:45 PM	6.5	26.7	9.2
NMR11-39	NMR 2	3/23/11 4:45 PM	6.7	32.5	10.7
NMR11-40	NMR 2	3/23/11 5:45 PM	5.5	31.6	10.7
NMR11-41	NMR 2	3/23/11 6:45 PM	5.2	26.5	10.4
NMR11-42	NMR 2	3/23/11 7:45 PM	5.6	13.5	6.2
NMR11-45	Precip	3/24/11 12:00 AM	4.6	71.0	
NMR12-01	A	10/17/12 4:15 PM	11.5	-7.1	-0.5
NMR12-02	D	10/17/12 4:30 PM	16.1	-2.5	-0.4
NMR12-03	F	10/17/12 4:40 PM	11.6	-7.9	-0.7
NMR12-05	H	10/17/12 5:00 PM			
NMR12-04	M	10/17/12 5:10 PM	19.7	0.4	
NMR12-27	Precip	10/18/12 2:33 PM	1.9	67.7	
NMR12-28	NMR 2	10/18/12 3:03 PM	10.9	-6.1	-0.8
NMR12-29	NMR 2	10/18/12 3:33 PM	11.3	-5.3	-0.7
NMR12-30	NMR 2	10/18/12 4:03 PM	11.6	-5.5	-0.6
NMR12-31	NMR 2	10/18/12 4:33 PM	11.6	-5.8	-0.7
NMR12-25	F	10/18/12 4:45 PM	7.7	37.7	12.4
NMR12-12	D	10/18/12 4:47 PM	8.6	33.2	11.5
NMR12-22	J	10/18/12 4:54 PM	11.7	-5.7	0.0

Sample Name	*Station Name*	*Sample Date*	*$\delta^{15}N$ (‰)*	*$\delta^{18}O$ (‰)*	*$\Delta^{17}O$ (‰)*
NMR12-07	C	10/18/12 4:56 PM	3.6	51.3	18.5
NMR12-08	Ga	10/18/12 5:00 PM	3.5	48.0	17.2
NMR12-20	M	10/18/12 5:03 PM	18.7	-0.2	
NMR12-32	NMR 2	10/18/12 5:03 PM	4.1	21.7	7.7
NMR12-11	A	10/18/12 5:05 PM	11.0	-5.2	0.4
NMR12-09	G	10/18/12 5:15 PM	3.6	59.8	21.0
NMR12-19	H	10/18/12 5:20 PM	4.8	51.0	18.2
NMR12-06	B	10/18/12 5:25 PM	5.1	51.5	
NMR12-10	I	10/18/12 5:27 PM	3.3	40.6	15.9
NMR12-33	NMR 2	10/18/12 5:33 PM	4.2	27.7	7.9
NMR12-14	A	10/18/12 5:35 PM	4.4	38.2	14.4
NMR12-18	F	10/18/12 5:35 PM	3.8	37.9	
NMR12-23	H	10/18/12 5:35 PM	4.3	36.2	
NMR12-24	D	10/18/12 5:43 PM	11.2	10.4	4.3
NMR12-16	Ga	10/18/12 5:45 PM	3.8	15.7	
NMR12-15	E	10/18/12 5:50 PM	4.6	31.1	
NMR12-21	G	10/18/12 5:50 PM	3.4	42.3	
NMR12-17	J	10/18/12 6:00 PM	4.5	15.3	6.6
NMR12-34	NMR 2	10/18/12 6:03 PM	4.4	15.1	6.5
NMR12-13	I	10/18/12 6:04 PM	5.8	12.4	5.7
NMR12-26	M	10/18/12 6:30 PM	5.7	13.7	5.3
NMR12-35	NMR 2	10/18/12 6:33 PM	11.5	-5.3	-0.1
NMR12-36	NMR 2	10/18/12 7:03 PM	11.5	-4.6	-0.3
NMR12-37	NMR 2	10/18/12 7:33 PM	6.8	19.5	8.0
NMR12-38	NMR 2	10/18/12 8:03 PM	5.0	12.2	5.5
NMR12-39	NMR 2	10/18/12 8:33 PM	4.8	20.7	8.8
NMR12-40	NMR 2	10/18/12 9:03 PM	4.4	23.0	9.4
NMR12-41	NMR 2	10/18/12 9:33 PM	11.4	-5.1	-0.3
NMR12-42	NMR 2	10/18/12 10:03 PM	11.2	-5.1	-0.7
NMR12-43	NMR 2	10/18/12 10:33 PM	5.1	12.1	5.0
NMR12-44	NMR 2	10/18/12 11:03 PM	3.3	15.5	5.4
NMR12-45	NMR 2	10/18/12 11:33 PM	10.6	-0.2	-1.1

Table A-3 Anion Concentrations

Blank spaces indicate concentrations were either 0 or below detection limits.

Sample Name	***Station Name***	***Sample Date***	Br^- mgL^{-1}	Cl^- mgL^{-1}	F^- mgL^{-1}	SO_4^- mgL^{-1}
NMR07-01	NMR 1	4/10/07 3:45 PM		336.45	0.45	175.69
NMR07-02	NMR 2	4/10/07 4:15 PM		309.07	0.69	169.82
NMR07-03	NMR 3	4/10/07 5:15 PM		290.29	0.72	183.61
NMR07-04	NMR 1	5/9/07 9:30 AM		374.36	0.64	189.94
NMR07-05	FH 1	5/9/07 10:45 AM		121.50	0.29	155.80
NMR07-06	NMR 2	5/9/07 11:15 AM		349.87	0.64	181.54
NMR07-07	NMR 3	5/9/07 12:30 PM		313.87	0.60	190.39
NMR07-08	NMR 1	5/23/07 9:30 AM	1.48	455.10	0.66	217.72
NMR07-09	NMR 2	5/23/07 10:30 AM	1.53	419.40	0.69	205.29
NMR07-10	NMR 3	5/23/07 11:30 AM	1.47	334.15	0.74	201.78
NMR07-11	NMR 1	6/7/07 8:30 AM	1.55	310.32	0.67	183.47
NMR07-12	NMR 2	6/7/07 9:15 AM	1.31	397.67	0.71	185.05
NMR07-13	NMR 3	6/7/07 9:30 AM	1.17	430.16	0.68	198.33
NMR07-14	NMR 1	6/20/07 3:15 PM	1.44	248.29	0.60	135.29
NMR07-15	NMR 2	6/20/07 4:00 PM	1.29	347.82	0.68	155.97
NMR07-16	NMR 3	6/20/07 4:30 PM	1.33	396.28	0.71	175.86
NMR07-17	NMR 1	7/6/07 7:15 AM		178.19	0.58	120.74
NMR07-18	NMR 2	7/6/07 7:45 AM	1.27	301.38	0.68	154.66
NMR07-19	NMR 3	7/6/07 8:15 AM	1.21	358.12	0.65	178.94
NMR07-20	NMR 1	7/18/07 7:30 AM	1.21	326.59	0.71	216.88
NMR07-21	NMR 2	7/18/07 8:30 AM	1.65	366.46	0.66	196.43
NMR07-22	NMR 3	7/18/07 9:00 AM	1.42	372.43	0.69	198.84
NMR07-23	NMR 1	8/2/07 8:00 AM	1.13	351.04	0.76	194.88
NMR07-24	NMR 2	8/2/07 9:00 AM	1.28	253.63	0.90	196.53
NMR07-25	NMR 3	8/2/07 10:45 AM	1.26	254.24	0.81	224.88
NMR07-26	NMR 1	8/15/07 9:30 AM	1.32	413.39	0.63	212.55
NMR07-27	NMR 2	8/15/07 10:00 AM	1.41	376.69	0.63	197.97
NMR07-28	NMR 3	8/15/07 11:30 AM	1.29	295.87	0.74	206.41
NMR07-31	NMR 3	8/30/07 7:15 AM		260.59	0.68	197.09
NMR07-32	NMR 2	8/30/07 7:45 AM	0.43	361.84	0.55	199.08
NMR07-30	FH 1	8/30/07 8:00 AM		110.18	0.32	129.53
NMR07-29	NMR 1	8/30/07 8:30 AM		382.77	0.58	209.93
NMR07-36	NMR 3	9/13/07 10:45 AM		249.47	0.55	198.79

Sample Name	Station Name	Sample Date	Br^- mgL^{-1}	Cl^- mgL^{-1}	F^- mgL^{-1}	SO_4^- mgL^{-1}
NMR07-34	NMR 2	9/13/07 11:00 AM		335.68	0.50	190.92
NMR07-33	NMR 1	9/13/07 12:00 PM		374.47	0.56	209.02
NMR07-35	FH 1	9/13/07 12:15 PM		116.77	0.24	140.39
NMR07-39	NMR 3	9/25/07 7:45 AM		274.02	0.63	254.56
NMR07-38	NMR 2	9/25/07 8:15 AM		356.52	0.55	208.69
NMR07-37	NMR 1	9/25/07 8:30 AM		362.85	0.61	210.72
NMR07-42	NMR 3	10/9/07 7:45 AM		287.03	0.63	238.31
NMR07-41	NMR 2	10/9/07 8:15 AM		329.21	0.56	194.79
NMR07-40	NMR 1	10/9/07 8:45 AM		332.67	0.57	197.53
NMR07-45	NMR 3	10/24/07 3:45 PM		106.97	0.37	77.79
NMR07-44	NMR 2	10/24/07 4:15 PM		147.80	0.40	83.54
NMR07-43	NMR 1	10/24/07 4:45 PM		250.88	0.50	130.99
NMR07-48	NMR 3	11/7/07 8:00 AM		157.16	0.47	138.86
NMR07-47	NMR 2	11/7/07 8:30 AM		298.14	0.51	161.18
NMR07-46	NMR 1	11/7/07 9:00 AM		337.79	0.59	182.78
NMR07-51	NMR 3	11/19/07 8:30 AM		294.12	0.51	198.32
NMR07-50	NMR 2	11/19/07 9:15 AM		336.48	0.60	180.37
NMR07-49	NMR 1	11/19/07 9:30 AM		349.37	0.54	187.48
NMR07-54	NMR 3	12/4/07 1:30 PM		345.48	0.82	196.48
NMR07-53	NMR 2	12/4/07 2:30 PM		486.02	0.60	197.45
NMR07-55	FH 1	12/4/07 2:45 PM		154.58	0.27	129.85
NMR07-56	FH 2	12/4/07 2:45 PM		145.79	0.28	124.94
NMR07-52	NMR 1	12/4/07 3:15 PM		488.18	0.70	203.92
NMR07-58	NMR 2	12/20/07 11:15 AM		608.40	0.78	217.56
NMR07-60	FH 1	12/20/07 11:20 AM		137.58	0.50	138.08
NMR07-57	NMR 1	12/20/07 11:45 AM		600.93	0.78	231.17
NMR07-59	NMR 3	12/20/07 1:00 PM		555.18	0.68	221.39
NMR08-01	NMR 3	1/4/08 10:30 AM	1.87	886.56	0.69	250.67
NMR08-02	NMR 2	1/4/08 11:00 AM		780.15	0.75	226.85
NMR08-03	FH 1	1/4/08 11:30 AM		182.65	0.46	179.45
NMR08-04	NMR 1	1/4/08 11:45 AM		677.71	0.77	239.76
NMR08-06	NMR 3	1/18/08 8:00 AM	1.44	929.36	0.50	124.55
NMR08-07	NMR 1	1/18/08 8:45 AM	0.60	824.68	0.50	120.98
NMR08-08	NMR 2	1/18/08 9:45 AM	0.46	683.39	0.48	97.09
NMR08-05	FH 1	1/18/08 10:15 AM		183.84	0.34	132.02
NMR08-09	NMR 3	1/29/08 9:30 AM	0.77	1187.94	0.63	0.77

Sample Name	Station Name	Sample Date	Br^- mgL^{-1}	Cl^- mgL^{-1}	F^- mgL^{-1}	SO_4^- mgL^{-1}
NMR08-11	NMR 2	1/29/08 9:30 AM		5967.77	0.67	
NMR08-12	FH 1	1/29/08 9:45 AM		366.78	0.28	
NMR08-10	NMR 1	1/29/08 10:15 AM	0.77	1187.94	0.63	0.77
NMR08-13	NMR 3	2/12/08 1:15 PM	2.30	1460.31	0.55	221.43
NMR08-15	FH 1	2/12/08 1:45 PM		124.22	0.42	136.45
NMR08-14	NMR 2	2/12/08 2:15 PM	2.52	1907.10	0.49	222.50
NMR08-16	NMR 1	2/12/08 2:45 PM	3.17	2996.70	0.58	256.89
NMR08-17	NMR 1	2/28/08 12:45 PM	2.37	1158.03	0.67	223.09
NMR08-20	FH 1	2/28/08 1:15 PM		182.22	0.27	159.79
NMR08-18	NMR 2	2/28/08 1:30 PM	1.59	1067.05	0.61	210.12
NMR08-19	NMR 3	2/28/08 2:00 PM	1.34	1119.35	0.63	220.56
NMR08-21	NMR 1	3/18/08 12:45 PM		840.94	0.66	256.25
NMR08-24	FH 1	3/18/08 1:30 PM		143.86	0.27	220.82
NMR08-22	NMR 2	3/18/08 1:45 PM		671.68	0.64	279.45
NMR08-23	NMR 3	3/18/08 2:15 PM		560.93	0.62	268.62
NMR08-26	NMR 2	4/1/08 12:45 PM		565.10	0.69	280.19
NMR08-28	FH 1	4/1/08 1:00 PM		157.63	0.26	292.73
NMR08-25	NMR 1	4/1/08 1:30 PM		655.18	0.78	290.63
NMR08-27	NMR 3	4/1/08 2:00 PM		498.43	0.75	84.35
NMR08-30	NMR 2	4/15/08 12:45 PM		560.98	0.75	281.42
NMR08-32	FH 1	4/15/08 1:15 PM		184.45	0.26	349.63
NMR08-29	NMR 1	4/15/08 1:45 PM		617.17	0.83	287.77
NMR08-31	NMR 3	4/15/08 2:15 PM		504.10	0.71	291.76
NMR08-33	GW 1	4/18/08 1:00 PM		480.54	1.35	
NMR08-34	GW 2	4/18/08 1:30 PM		15.61	1.35	320.91
NMR08-36	NMR 2	5/1/08 9:45 AM		571.27	0.59	249.67
NMR08-38	FH 1	5/1/08 10:15 AM		149.93	0.32	197.14
NMR08-35	NMR 1	5/1/08 10:45 AM	1.20	571.31	0.70	218.57
NMR08-37	NMR 3	5/1/08 11:15 AM		491.32	0.68	249.79
NMR08-39	NMR 1	5/14/08 9:30 AM		609.05	0.66	257.98
NMR08-42	FH 1	5/14/08 9:45 AM		137.97	0.33	160.94
NMR08-40	NMR 2	5/14/08 10:15 AM		553.54	0.71	241.55
NMR08-41	NMR 3	5/14/08 11:00 AM		478.40	0.68	242.10
NMR08-43	NMR 1	5/29/08 9:15 AM		610.84	0.77	291.49
NMR08-46	FH 1	5/29/08 10:00 AM		166.10	0.34	207.05
NMR08-44	NMR 2	5/29/08 10:15 AM		554.45	0.73	274.70

Sample Name	***Station Name***	***Sample Date***	***Br$^-$ mgL^{-1}***	***Cl$^-$ mgL^{-1}***	***F$^-$ mgL^{-1}***	***SO$_4^-$ mgL^{-1}***
NMR08-45	NMR 3	5/29/08 10:45 AM		449.05	0.74	279.85
NMR08-47	NMR 1	6/13/08 8:00 AM	1.83	377.51	0.95	200.25
NMR08-48	NMR 2	6/13/08 1:45 PM		66.11	0.25	32.96
NMR08-49	NMR 3	6/13/08 2:30 PM		78.00	0.46	38.91
NMR08-52	NMR 3	6/27/08 2:45 PM	1.87	278.94	0.70	157.47
NMR08-51	NMR 2	6/27/08 3:15 PM	2.09	393.34	0.63	183.28
NMR08-53	FH 1	6/27/08 3:30 PM		121.49	0.48	138.15
NMR08-50	NMR 1	6/27/08 4:00 PM	1.95	424.72	0.59	184.71
NMR08-54	NMR 1	7/9/08 5:45 PM	2.09	393.34	0.74	183.28
NMR08-57	FH 1	7/9/08 6:30 PM	1.95	474.83	0.36	208.20
NMR08-55	NMR 2	7/9/08 6:45 PM	1.87	278.94	0.56	157.47
NMR08-56	NMR 3	7/9/08 7:15 PM		121.49	0.58	138.15
NMR08-58	NMR 2	7/20/08 2:15 PM	0.89	141.44	0.64	78.56
NMR08-88	FH 1	7/20/08 2:30 PM		138.05	0.18	152.27
NMR08-59	NMR 2	7/20/08 3:00 PM		137.02	0.45	68.25
NMR08-89	FH 1	7/20/08 3:00 PM		123.82	0.21	134.67
NMR08-60	NMR 2	7/20/08 3:30 PM		60.55	0.26	34.95
NMR08-90	FH 1	7/20/08 3:30 PM		139.22	0.53	139.51
NMR08-61	NMR 2	7/20/08 3:45 PM		21.77	0.46	48.40
NMR08-62	NMR 2	7/20/08 4:00 PM		73.58	0.31	40.03
NMR08-91	FH 1	7/20/08 4:00 PM		117.85	0.22	117.61
NMR08-63	NMR 2	7/20/08 4:30 PM		75.43	0.33	42.71
NMR08-92	FH 1	7/20/08 4:30 PM		125.34	0.17	133.33
NMR08-64	NMR 2	7/20/08 5:30 PM		79.88	0.33	43.03
NMR08-93	FH 1	7/20/08 5:30 PM		128.04	0.17	139.35
NMR08-65	NMR 2	7/20/08 6:30 PM		91.16	0.32	48.30
NMR08-94	FH 1	7/20/08 6:30 PM		128.47	0.18	142.70
NMR08-66	NMR 2	7/20/08 7:30 PM		95.53	0.35	50.26
NMR08-95	FH 1	7/20/08 7:30 PM		128.52	0.17	144.17
NMR08-69	NMR 3	8/6/08 10:45 AM		111.81	0.42	80.90
NMR08-67	NMR 1	8/6/08 11:30 AM	1.10	235.71	0.46	105.14
NMR08-68	NMR 2	8/6/08 12:30 PM		103.30	0.36	55.98
NMR08-70	NMR 1	8/15/08 9:45 AM	1.74	299.12	0.57	138.20
NMR08-71	NMR 2	8/15/08 10:15 AM		167.12	0.63	73.32
NMR08-72	NMR 3	8/15/08 10:45 AM		112.68	0.49	97.73
NMR08-73	NMR 1	9/5/08 10:30 AM	1.23	290.78	0.74	146.15

Sample Name	*Station Name*	*Sample Date*	*Br^- mgL^{-1}*	*Cl^- mgL^{-1}*	*F^- mgL^{-1}*	*SO_4^- mgL^{-1}*
NMR08-74	NMR 2	9/5/08 10:45 AM	1.34	298.03	0.60	148.09
NMR08-75	NMR 3	9/5/08 11:15 AM	1.32	272.00	0.63	197.32
NMR08-78	NMR 3	9/15/08 5:00 PM	1.55	286.10	0.56	180.70
NMR08-81	NMR 3	9/29/08 4:00 PM	1.10	262.24	0.67	181.21
NMR08-79	NMR 1	9/29/08 4:45 PM	1.28	284.89	0.79	154.01
NMR08-80	NMR 2	9/29/08 5:15 PM	1.15	266.81	0.81	151.16
NMR08-82	NMR 1	10/24/08 10:30 AM	1.17	254.48	0.76	144.53
NMR08-83	NMR 2	10/24/08 10:45 AM	1.30	244.91	0.72	139.48
NMR08-84	NMR 3	10/24/08 11:30 AM	1.40	248.22	0.67	185.83
NMR08-85	NMR 1	11/7/08 10:30 AM	1.50	257.85	1.01	148.67
NMR08-86	NMR 2	11/7/08 11:00 AM	1.34	258.98	0.67	148.58
NMR08-87	NMR 3	11/7/08 11:30 AM	1.37	250.75	0.64	181.52
NMR08-96	NMR 1	11/25/08 9:15 AM	1.81	339.42	0.52	126.93
NMR08-97	NMR 2	11/25/08 9:45 AM	1.73	340.90	0.66	108.75
NMR08-98	NMR 3	11/25/08 10:15 AM	1.03	263.64	0.32	78.22
NMR08-100	NMR 1	12/10/08 10:45 AM	1.16	301.71	0.24	49.04
NMR08-99	FH 1	12/10/08 11:15 AM		148.10	0.21	71.52
NMR08-101	NMR 2	12/10/08 11:45 AM	0.65	233.72	0.19	34.29
NMR08-102	NMR 3	12/10/08 12:00 PM	0.61	225.87	0.18	33.95
NMR09-01	NMR 1	1/2/09 10:45 AM	1.74	962.84	0.47	
NMR09-02	NMR 2	1/2/09 11:00 AM	1.66	422.74	0.44	
NMR09-03	NMR 3	1/2/09 11:30 AM	1.52	459.71	0.49	
NMR09-04	NMR 1	1/16/09 8:30 AM	1.83	782.70	0.49	
NMR09-05	NMR 1	1/30/09 8:45 AM	2.42	1459.72	0.39	
NMR09-07	FH 1	1/30/09 9:15 AM		182.43	0.20	109.33
NMR09-06	NMR 2	1/30/09 9:30 AM	2.54	1412.47	0.38	
NMR09-08	NMR 1	2/13/09 8:30 AM	2.06	836.84	0.43	
NMR09-10	FH 1	2/13/09 9:15 AM		136.88	0.21	83.41
NMR09-09	NMR 2	2/13/09 9:30 AM	2.05	750.75	0.36	
NMR09-12	NMR 1	2/27/09 8:30 AM	1.79	1261.76	0.41	
NMR09-13	NMR 2	2/27/09 9:00 AM	1.79	580.00	0.40	
NMR09-14	NMR 3	2/27/09 9:30 AM	1.54	602.31	0.51	
NMR09-26	GW 1	3/4/09 4:30 PM		35.56	0.94	
NMR09-27	GW 2	3/4/09 4:40 PM	0.61	691.13	0.36	148.17
NMR09-15	NMR 1	3/20/09 8:30 AM	1.51	482.37	0.58	
NMR09-16	NMR 2	3/20/09 9:00 AM	1.43	466.90	0.41	155.44

Sample Name	*Station Name*	*Sample Date*	*Br^- mgL^{-1}*	*Cl^- mgL^{-1}*	*F^- mgL^{-1}*	*SO_4^- mgL^{-1}*
NMR09-17	NMR 3	3/20/09 9:30 AM	1.48	467.34	0.52	
NMR09-18	NMR 1	4/6/09 8:30 AM	0.87	251.52	0.29	67.99
NMR09-21	FH 1	4/6/09 9:00 AM		133.87	0.19	81.50
NMR09-19	NMR 2	4/6/09 9:15 AM	0.05	306.12	0.35	87.77
NMR09-20	NMR 3	4/6/09 9:45 AM	0.04	440.31	0.46	143.48
NMR09-28	GW 1	4/8/09 4:00 PM		20.82	1.08	
NMR09-29	GW 2	4/8/09 4:30 PM		471.43	0.90	1.89
NMR09-23	NMR 1	4/21/09 8:45 AM	0.04	558.30	0.50	
NMR09-24	NMR 2	4/21/09 9:15 AM	0.03	490.73	0.12	138.62
NMR09-25	NMR 3	4/21/09 9:45 AM	0.20	311.97	0.43	110.33
NMR10-37	Precip	7/9/10 8:30 AM	0.00	1.40	0.10	3.22
NMR10-37	Precip	7/9/10 8:30 AM	0.00	1.40	0.10	3.22
NMR10-37	Precip	7/9/10 8:30 AM	0.00	1.40	0.10	3.22
NMR10-38	NMR 2	7/9/10 2:25 PM	0.83	458.06	0.69	0.00
NMR10-39	NMR 2	7/9/10 2:55 PM	0.74	416.08	0.61	0.00
NMR10-40	NMR 2	7/9/10 3:25 PM	2.24	195.58	0.52	83.29
NMR10-41	NMR 2	7/9/10 3:55 PM	2.14	153.86	0.64	59.25
NMR10-42	NMR 2	7/9/10 4:25 PM		56.68	0.28	25.70
NMR10-43	NMR 2	7/9/10 4:55 PM	1.81	170.21	0.65	55.65
NMR10-44	NMR 2	7/9/10 5:25 PM		42.65	0.20	18.11
NMR10-45	NMR 2	7/9/10 5:55 PM		39.61	0.21	18.19
NMR10-46	NMR 2	7/9/10 6:25 PM	0.17	38.49	0.21	20.13
NMR10-47	NMR 2	7/9/10 6:55 PM		45.35	0.22	26.78
NMR10-48	NMR 2	7/9/10 7:25 PM		52.14	0.23	31.29
NMR10-49	NMR 2	7/9/10 7:55 PM		60.85	0.26	36.40
NMR10-50	NMR 2	7/9/10 8:25 PM		68.03	0.26	40.14
NMR10-51	NMR 2	7/9/10 9:25 PM		101.71	0.31	52.14
NMR10-52	NMR 2	7/9/10 10:25 PM		115.33	0.32	56.73
NMR10-53	NMR 2	7/9/10 11:25 PM		118.64	0.34	58.70
NMR10-54	NMR 2	7/10/10 12:25 AM		123.26	0.32	60.74
NMR10-55	NMR 2	7/10/10 1:25 AM		132.42	0.28	64.30
NMR10-56	NMR 2	7/10/10 2:25 AM		138.03	0.34	66.23
NMR10-57	NMR 2	7/10/10 3:25 AM		144.43	0.34	68.28
NMR10-58	NMR 2	7/10/10 4:25 AM		154.05	0.38	71.57
NMR10-59	NMR 2	7/10/10 5:25 AM		162.45	0.39	74.96
NMR10-60	NMR 2	7/10/10 6:25 AM		177.19	0.41	80.66

Sample Name	***Station Name***	***Sample Date***	***Br^- mgL^{-1}***	***Cl^- mgL^{-1}***	***F^- mgL^{-1}***	***SO_4^- mgL^{-1}***
NMR10-61	NMR 2	7/10/10 7:25 AM		196.31	0.36	88.49
NMR11-03	NMR 2	1/1/11 3:44 AM		584.81	0.39	148.42
NMR11-04	NMR 2	1/1/11 4:44 AM		563.24	0.38	142.57
NMR11-05	NMR 2	1/1/11 5:44 AM		560.82	0.40	146.08
NMR11-06	NMR 2	1/1/11 6:14 AM		557.33	0.40	146.06
NMR11-07	NMR 2	1/1/11 6:44 AM		567.87	0.42	147.61
NMR11-08	NMR 2	1/1/11 7:14 AM		557.74	0.42	145.96
NMR11-09	NMR 2	1/1/11 8:14 AM		555.04	0.40	145.28
NMR11-10	NMR 2	1/1/11 9:14 AM		925.90	0.30	77.75
NMR11-11	NMR 2	1/1/11 10:14 AM		1103.22	0.22	46.61
NMR11-01	Precip	1/1/11 10:45 AM		0.36	0.01	0.97
NMR11-12	NMR 2	1/1/11 11:14 AM		855.84	0.20	41.66
NMR11-13	NMR 2	1/1/11 12:14 PM		500.32	0.16	30.89
NMR11-14	NMR 2	1/1/11 1:14 PM		391.90	0.15	27.79
NMR11-15	NMR 2	1/1/11 2:14 PM		400.40	0.16	33.12
NMR11-16	NMR 2	1/1/11 3:14 PM		406.25	0.18	36.61
NMR11-17	NMR 2	1/1/11 4:14 PM		454.27	0.19	44.98
NMR11-02	Precip	1/1/11 5:00 PM		0.41	0.01	1.06
NMR11-18	NMR 2	1/1/11 5:14 PM		461.29	0.20	48.24
NMR11-19	NMR 2	1/1/11 6:14 PM		521.39	0.23	57.50
NMR11-46	Precip	3/9/11 12:00 PM		0.30	0.01	0.81
NMR11-47	B	3/9/11 2:30 PM		134.24	0.16	17.47
NMR11-48	M	3/9/11 2:47 PM		162.55	0.13	68.71
NMR11-49	F	3/9/11 3:47 PM		549.05	0.18	40.82
NMR11-50	N	3/9/11 3:48 PM	0.09	663.35	0.37	93.94
NMR11-51	O	3/9/11 4:07 PM		240.79	0.21	36.81
NMR11-53	Precip	3/10/11 8:00 AM		0.09	0.01	0.84
NMR11-20	NMR 2	3/22/11 8:45 PM		437.16	0.39	193.49
NMR11-21	NMR 2	3/22/11 10:45 PM		409.37	0.36	190.49
NMR11-22	NMR 2	3/22/11 11:45 PM		493.86	0.41	228.78
NMR11-24	NMR 2	3/23/11 12:45 AM		452.14	0.40	0.00
NMR11-23	NMR 2	3/23/11 1:45 AM		483.65	0.37	210.87
NMR11-25	NMR 2	3/23/11 2:45 AM		439.92	0.37	193.11
NMR11-26	NMR 2	3/23/11 3:45 AM		415.75	0.39	0.00
NMR11-27	NMR 2	3/23/11 4:45 AM		379.13	0.34	142.44
NMR11-28	NMR 2	3/23/11 5:45 AM		349.20	0.31	126.74

Sample Name	***Station Name***	***Sample Date***	***Br^- mgL^{-1}***	***Cl^- mgL^{-1}***	***F^- mgL^{-1}***	***SO_4^- mgL^{-1}***
NMR11-29	NMR 2	3/23/11 6:45 AM		331.54	0.32	2.83
NMR11-30	NMR 2	3/23/11 7:45 AM		321.47	0.32	128.13
NMR11-43	Precip	3/23/11 8:00 AM		1.04	0.03	0.00
NMR11-31	NMR 2	3/23/11 8:45 AM		313.63	0.32	128.21
NMR11-32	NMR 2	3/23/11 9:45 AM		357.97	0.41	151.41
NMR11-33	NMR 2	3/23/11 10:45 AM		360.08	0.45	153.38
NMR11-34	NMR 2	3/23/11 11:45 AM		317.30	0.39	128.73
NMR11-35	NMR 2	3/23/11 12:45 PM		276.65	0.32	107.79
NMR11-36	NMR 2	3/23/11 1:45 PM		274.98	0.31	105.86
NMR11-44	Precip	3/23/11 2:00 PM		0.81	0.03	6.21
NMR11-37	NMR 2	3/23/11 2:45 PM		240.75	0.25	90.71
NMR11-38	NMR 2	3/23/11 3:45 PM		242.33	0.24	91.79
NMR11-39	NMR 2	3/23/11 4:45 PM		121.89	0.16	48.09
NMR11-40	NMR 2	3/23/11 5:45 PM		67.13	0.11	26.40
NMR11-41	NMR 2	3/23/11 6:45 PM		66.91	0.12	24.51
NMR11-42	NMR 2	3/23/11 7:45 PM		77.22	0.29	35.63
NMR11-45	Precip	3/24/11 12:00 AM		0.13	0.01	1.70
NMR12-01	A	10/17/12 4:15 PM	0.04	302.89	0.46	227.16
NMR12-02	D	10/17/12 4:30 PM	0.07	520.01	0.31	197.86
NMR12-03	F	10/17/12 4:40 PM	0.06	529.48	0.41	150.57
NMR12-05	H	10/17/12 5:00 PM		74.02	1.03	39.70
NMR12-04	M	10/17/12 5:10 PM	0.03	206.29	0.15	154.76
NMR12-27	Precip	10/18/12 2:33 PM		0.19	0.04	1.53
NMR12-28	NMR 2	10/18/12 3:03 PM		340.85	0.33	206.17
NMR12-29	NMR 2	10/18/12 3:33 PM	0.05	337.20	0.35	206.09
NMR12-30	NMR 2	10/18/12 4:03 PM	0.04	337.12	0.36	206.67
NMR12-31	NMR 2	10/18/12 4:33 PM	0.05	336.04	0.36	205.89
NMR12-25	F	10/18/12 4:45 PM		87.16	0.46	45.04
NMR12-12	D	10/18/12 4:47 PM		150.02	0.34	73.65
NMR12-22	J	10/18/12 4:54 PM	0.05	337.13	0.43	210.63
NMR12-07	C	10/18/12 4:56 PM		45.05	0.23	22.17
NMR12-08	Ga	10/18/12 5:00 PM	0.53	40.74	0.41	33.10
NMR12-20	M	10/18/12 5:03 PM		206.14	0.12	151.43
NMR12-32	NMR 2	10/18/12 5:03 PM		38.57	0.10	19.19
NMR12-11	A	10/18/12 5:05 PM	0.05	297.00	0.42	209.15
NMR12-09	G	10/18/12 5:15 PM		18.64	0.49	16.59

Sample Name	***Station Name***	***Sample Date***	***Br^- mgL^{-1}***	***Cl^- mgL^{-1}***	***F^- mgL^{-1}***	***SO_4^- mgL^{-1}***
NMR12-19	H	10/18/12 5:20 PM	0.37	6.64	0.30	9.01
NMR12-06	B	10/18/12 5:25 PM		10.75	0.06	5.41
NMR12-10	I	10/18/12 5:27 PM		20.53	0.07	7.89
NMR12-33	NMR 2	10/18/12 5:33 PM		38.80	0.11	20.82
NMR12-14	A	10/18/12 5:35 PM		23.67	0.10	15.17
NMR12-18	F	10/18/12 5:35 PM		12.18	0.05	6.97
NMR12-23	H	10/18/12 5:35 PM	0.19	14.64	0.14	7.84
NMR12-24	D	10/18/12 5:43 PM	0.01	134.33	0.24	80.88
NMR12-16	Ga	10/18/12 5:45 PM		27.06	0.15	21.79
NMR12-15	E	10/18/12 5:50 PM		13.93	0.05	7.32
NMR12-21	G	10/18/12 5:50 PM		6.67	0.12	3.80
NMR12-17	J	10/18/12 6:00 PM		31.52	0.06	7.07
NMR12-34	NMR 2	10/18/12 6:03 PM		38.57	0.10	19.39
NMR12-13	I	10/18/12 6:04 PM		19.77	0.04	6.17
NMR12-26	M	10/18/12 6:30 PM		23.06	0.09	14.09
NMR12-35	NMR 2	10/18/12 6:33 PM	0.05	333.91	0.48	204.53
NMR12-36	NMR 2	10/18/12 7:03 PM		317.69	0.33	194.10
NMR12-37	NMR 2	10/18/12 7:33 PM		95.04	0.17	58.57
NMR12-38	NMR 2	10/18/12 8:03 PM		44.34	0.12	23.04
NMR12-39	NMR 2	10/18/12 8:33 PM		36.65	0.11	18.99
NMR12-40	NMR 2	10/18/12 9:03 PM		37.29	0.10	19.64
NMR12-41	NMR 2	10/18/12 9:33 PM	0.04	336.92	0.35	207.15
NMR12-42	NMR 2	10/18/12 10:03 PM	0.04	333.93	0.36	204.49
NMR12-43	NMR 2	10/18/12 10:33 PM		44.46	0.12	23.43
NMR12-44	NMR 2	10/18/12 11:03 PM		41.19	0.11	21.25
NMR12-45	NMR 2	10/18/12 11:33 PM	0.05	335.62	0.33	205.60

Table A-4 Water isotope data ($\delta^{18}O$, $\delta^{2}H$).

Sample Name	***Station Name***	***Sample Date***	***$\delta^{18}O$ (‰)***	***$\delta^{2}H$ (‰)***	***Storm Event Number***	***Discharge (cms)***
NMR07-08	NMR 1	5/23/07 9:30 AM	-8.84	-58.24		0.090
NMR07-09	NMR 2	5/23/07 10:30 AM	-8.05	-57.67		0.046
NMR07-10	NMR 3	5/23/07 11:30 AM	-7.42	-54.33		0.086
NMR07-11	NMR 1	6/7/07 8:30 AM	-8.14	-56.92		0.072
NMR07-12	NMR 2	6/7/07 9:15 AM	-8.10	-56.20		0.043
NMR07-13	NMR 3	6/7/07 9:30 AM	-8.33	-56.84		0.056
NMR07-14	NMR 1	6/20/07 3:15 PM	-7.85	-51.72		0.089
NMR07-15	NMR 2	6/20/07 4:00 PM	-6.79	-47.30		0.123
NMR07-16	NMR 3	6/20/07 4:30 PM	-6.58	-44.55		0.103
NMR07-17	NMR 1	7/6/07 7:15 AM	-8.06	-54.05		0.070
NMR07-18	NMR 2	7/6/07 7:45 AM	-7.04	-50.23		0.119
NMR07-19	NMR 3	7/6/07 8:15 AM	-6.43	-49.24		0.069
NMR07-20	NMR 1	7/18/07 7:30 AM	-7.39	-55.46		0.043
NMR07-21	NMR 2	7/18/07 8:30 AM	-7.03	-54.29		0.021
NMR07-22	NMR 3	7/18/07 9:00 AM	-6.61	-53.05		0.012
NMR07-23	NMR 1	8/2/07 8:00 AM	-7.97	-55.96		0.069
NMR07-24	NMR 2	8/2/07 9:00 AM	-7.08	-55.30		0.133
NMR07-25	NMR 3	8/2/07 10:45 AM	-7.39	-53.86		0.030
NMR07-26	NMR 1	8/15/07 9:30 AM	-7.40	-51.62		0.064
NMR07-27	NMR 2	8/15/07 10:00 AM	-6.86	-49.88		0.233
NMR07-28	NMR 3	8/15/07 11:30 AM	-7.21	-49.36		0.073
NMR07-31	NMR 3	8/30/07 7:15 AM	-7.13	-48.54		0.032
NMR07-32	NMR 2	8/30/07 7:45 AM	-7.08	-48.61		0.058
NMR07-30	FH 1	8/30/07 8:00 AM	-7.32	-47.12		
NMR07-29	NMR 1	8/30/07 8:30 AM	-7.60	-51.08		0.046
NMR07-36	NMR 3	9/13/07 10:45 AM	-6.11	-46.78		0.032
NMR07-34	NMR 2	9/13/07 11:00 AM	-8.06	-48.56		0.058
NMR07-33	NMR 1	9/13/07 12:00 PM	-7.23	-50.36		0.079
NMR07-39	NMR 3	9/25/07 7:45 AM	-7.54	-50.16		0.023
NMR07-38	NMR 2	9/25/07 8:15 AM	-7.54	-54.14		0.025
NMR07-42	NMR 3	10/9/07 7:45 AM	-6.36	-50.61		0.021
NMR07-41	NMR 2	10/9/07 8:15 AM	-6.21	-51.91		0.032

Sample Name	*Station Name*	*Sample Date*	*$\delta^{18}O$ (‰)*	*$\delta^{2}H$ (‰)*	*Storm Event Number*	*Discharge (cms)*
NMR07-40	NMR 1	10/9/07 8:45 AM	-8.51	-52.87		0.048
NMR07-45	NMR 3	10/24/07 3:45 PM	-11.18	-83.00		0.087
NMR07-44	NMR 2	10/24/07 4:15 PM	-10.77	-78.18		0.081
NMR07-43	NMR 1	10/24/07 4:45 PM	-8.53	-63.45		0.067
NMR07-48	NMR 3	11/7/07 8:00 AM	-5.45	-37.38		0.031
NMR07-47	NMR 2	11/7/07 8:30 AM	-7.30	-48.54		0.037
NMR07-46	NMR 1	11/7/07 9:00 AM	-8.42	-54.14		0.055
NMR07-51	NMR 3	11/19/07 8:30 AM	-7.71	-52.38		0.043
NMR07-50	NMR 2	11/19/07 9:15 AM	-7.73	-52.99		0.042
NMR07-49	NMR 1	11/19/07 9:30 AM	-8.01	-54.52		0.068
NMR07-54	NMR 3	12/4/07 1:30 PM	-7.57	-50.33		0.091
NMR07-53	NMR 2	12/4/07 2:30 PM	-7.53	-50.56		0.113
NMR07-55	FH 1	12/4/07 2:45 PM	-7.08	-48.52		0.001
NMR07-56	FH 2	12/4/07 2:45 PM	-7.17	-47.25		
NMR07-52	NMR 1	12/4/07 3:15 PM	-7.62	-51.98		0.113
NMR07-58	NMR 2	12/20/07 11:15 AM	-7.36	-51.11		0.090
NMR07-57	NMR 1	12/20/07 11:45 AM	-7.90	-52.91		0.089
NMR07-59	NMR 3	12/20/07 1:00 PM	-7.70	-51.22		0.070
NMR08-01	NMR 3	1/4/08 10:30 AM	-8.11	-55.13		0.079
NMR08-02	NMR 2	1/4/08 11:00 AM	-8.26	-55.49		0.033
NMR08-03	FH 1	1/4/08 11:30 AM	-7.73	-51.15		0.002
NMR08-04	NMR 1	1/4/08 11:45 AM	-7.67	-55.04		0.071
NMR08-06	NMR 3	1/18/08 8:00 AM	-9.44	-63.74		0.112
NMR08-07	NMR 1	1/18/08 8:45 AM	-10.23	-65.12		0.097
NMR08-08	NMR 2	1/18/08 9:45 AM	-10.28	-69.84		0.130
NMR08-05	FH 1	1/18/08 10:15 AM	-8.08	-54.51		0.000
NMR08-09	NMR 3	1/29/08 9:30 AM	-7.81	-57.43		0.134
NMR08-11	NMR 2	1/29/08 9:30 AM	-4.42	-47.38		0.745
NMR08-12	FH 1	1/29/08 9:45 AM	-7.24	-50.35		0.001
NMR08-10	NMR 1	1/29/08 10:15 AM	-6.02	-46.76		0.414
NMR08-13	NMR 3	2/12/08 1:15 PM	-8.58	-54.42		0.089
NMR08-15	FH 1	2/12/08 1:45 PM	-8.27	-52.14		
NMR08-14	NMR 2	2/12/08 2:15 PM	-7.29	-54.44		
NMR08-16	NMR 1	2/12/08 2:45 PM	-10.29	-57.05		0.095
NMR08-17	NMR 1	2/28/08 12:45 PM	-8.57	-57.73		0.101

Sample Name	*Station Name*	*Sample Date*	*δ^{18}O (‰)*	*δ^{2}H (‰)*	*Storm Event Number*	*Discharge (cms)*
NMR08-20	FH 1	2/28/08 1:15 PM	-8.13	-52.16		0.001
NMR08-18	NMR 2	2/28/08 1:30 PM	-9.06	-57.53		0.107
NMR08-19	NMR 3	2/28/08 2:00 PM	-9.37	-56.89		0.093
NMR08-21	NMR 1	3/18/08 12:45 PM	-7.66	-52.26		0.127
NMR08-24	FH 1	3/18/08 1:30 PM	-5.17	-48.75		0.000
NMR08-22	NMR 2	3/18/08 1:45 PM	-6.94	-52.46		0.154
NMR08-23	NMR 3	3/18/08 2:15 PM	-5.67	-47.04		0.184
NMR08-26	NMR 2	4/1/08 12:45 PM	-7.73	-54.69		0.077
NMR08-28	FH 1	4/1/08 1:00 PM	-8.27	-52.47		0.000
NMR08-25	NMR 1	4/1/08 1:30 PM	-8.25	-55.66		0.099
NMR08-27	NMR 3	4/1/08 2:00 PM	-6.19	-52.59		0.041
NMR08-30	NMR 2	4/15/08 12:45 PM	-8.07	-56.77		0.075
NMR08-32	FH 1	4/15/08 1:15 PM	-8.17	-52.91		0.002
NMR08-29	NMR 1	4/15/08 1:45 PM	-7.56	-55.51		0.067
NMR08-31	NMR 3	4/15/08 2:15 PM	-8.06	-54.57		0.104
NMR08-33	GW 1	4/18/08 1:00 PM	-7.92	-52.76		
NMR08-36	NMR 2	5/1/08 9:45 AM	-5.05	-50.70		0.114
NMR08-35	NMR 1	5/1/08 10:45 AM	-4.50	-35.70		0.122
NMR08-37	NMR 3	5/1/08 11:15 AM	-3.42	-52.42		0.136
NMR08-43	NMR 1	5/29/08 9:15 AM	-8.13	-54.33		0.101
NMR08-46	FH 1	5/29/08 10:00 AM	-6.74	-51.74		0.000
NMR08-44	NMR 2	5/29/08 10:15 AM	-7.41	-53.30		0.121
NMR08-45	NMR 3	5/29/08 10:45 AM	-8.34	-55.07		0.797
NMR08-47	NMR 1	6/13/08 8:00 AM	-9.78	-57.24		0.104
NMR08-48	NMR 2	6/13/08 1:45 PM	-2.75	-8.55		1.547
NMR08-49	NMR 3	6/13/08 2:30 PM	-3.18	-10.17		0.748
NMR08-52	NMR 3	6/27/08 2:45 PM	-6.26	-36.62		0.153
NMR08-51	NMR 2	6/27/08 3:15 PM	-7.25	-46.94		0.133
NMR08-53	FH 1	6/27/08 3:30 PM	-6.41	-44.74		0.001
NMR08-50	NMR 1	6/27/08 4:00 PM	-6.78	-40.32		0.175
NMR08-54	NMR 1	7/9/08 5:45 PM	-8.01	-51.25		0.059
NMR08-57	FH 1	7/9/08 6:30 PM	-8.03	-52.22		0.002
NMR08-55	NMR 2	7/9/08 6:45 PM	-7.08	-47.21		0.084
NMR08-56	NMR 3	7/9/08 7:15 PM	-7.13	-44.78		0.094
NMR08-58	NMR 2	7/20/08 2:15 PM	-6.01	-36.04	1	0.202

Sample Name	***Station Name***	***Sample Date***	***$\delta^{18}O$ (‰)***	***$\delta^{2}H$ (‰)***	***Storm Event Number***	***Discharge (cms)***
NMR08-88	FH 1	7/20/08 2:30 PM	-7.33	-47.22		
NMR08-59	NMR 2	7/20/08 3:00 PM	-3.64	-18.18	1	2.310
NMR08-89	FH 1	7/20/08 3:00 PM	-6.45	-40.04		
NMR08-60	NMR 2	7/20/08 3:30 PM	-2.83	-10.93	1	1.120
NMR08-90	FH 1	7/20/08 3:30 PM	-5.98	-37.00		
NMR08-62	NMR 2	7/20/08 4:00 PM	-2.88	-12.19	1	0.619
NMR08-91	FH 1	7/20/08 4:00 PM	-5.63	-34.34		
NMR08-63	NMR 2	7/20/08 4:30 PM	-2.14	-8.30	1	0.782
NMR08-92	FH 1	7/20/08 4:30 PM	-6.21	-39.97		
NMR08-64	NMR 2	7/20/08 5:30 PM	-1.80	-9.02	1	0.403
NMR08-93	FH 1	7/20/08 5:30 PM	-6.81	-45.21		
NMR08-65	NMR 2	7/20/08 6:30 PM	-2.48	-10.88	1	0.317
NMR08-94	FH 1	7/20/08 6:30 PM	-7.08	-47.14		
NMR08-66	NMR 2	7/20/08 7:30 PM	-1.67	-9.80	1	0.271
NMR08-95	FH 1	7/20/08 7:30 PM	-6.82	-46.52		
NMR08-69	NMR 3	8/6/08 10:45 AM	-5.24	-32.30		0.054
NMR08-67	NMR 1	8/6/08 11:30 AM	-4.24	-27.43		0.091
NMR08-68	NMR 2	8/6/08 12:30 PM	-6.17	-40.77		0.062
NMR08-70	NMR 1	8/15/08 9:45 AM	-8.25	-57.67		0.066
NMR08-71	NMR 2	8/15/08 10:15 AM	-9.71	-71.14		0.047
NMR08-72	NMR 3	8/15/08 10:45 AM	-9.59	-70.26		0.367
NMR08-73	NMR 1	9/5/08 10:30 AM	-8.51	-56.81		0.046
NMR08-74	NMR 2	9/5/08 10:45 AM	-8.10	-55.70		0.034
NMR08-75	NMR 3	9/5/08 11:15 AM	-7.02	-53.00		0.036
NMR08-78	NMR 3	9/15/08 5:00 PM	-6.65	-47.96		0.044
NMR08-81	NMR 3	9/29/08 4:00 PM	-7.40	-50.55		0.028
NMR08-79	NMR 1	9/29/08 4:45 PM	-7.75	-53.92		0.041
NMR08-80	NMR 2	9/29/08 5:15 PM	-7.97	-53.91		0.034
NMR08-82	NMR 1	10/24/08 10:30 AM	-8.35	-57.00		0.074
NMR08-83	NMR 2	10/24/08 10:45 AM	-8.50	-59.23		0.034
NMR08-84	NMR 3	10/24/08 11:30 AM	-8.26	-55.07		0.044
NMR08-85	NMR 1	11/7/08 10:30 AM	-8.41	-57.09		0.092
NMR08-86	NMR 2	11/7/08 11:00 AM	-8.17	-54.78		0.089
NMR08-87	NMR 3	11/7/08 11:30 AM	-8.37	-55.13		0.030
NMR08-96	NMR 1	11/25/08 9:15 AM	-8.05	-54.28		0.124

Sample Name	***Station Name***	***Sample Date***	***δ^{18}O (‰)***	***δ^{2}H (‰)***	***Storm Event Number***	***Discharge (cms)***
NMR08-97	NMR 2	11/25/08 9:45 AM	-8.81	-57.67		0.096
NMR08-98	NMR 3	11/25/08 10:15 AM	-9.83	-60.57		0.083
NMR08-100	NMR 1	12/10/08 10:45 AM	-12.42	-89.90		0.342
NMR08-99	FH 1	12/10/08 11:15 AM	-9.39	-64.44		0.002
NMR08-101	NMR 2	12/10/08 11:45 AM	-13.39	-96.69		0.404
NMR08-102	NMR 3	12/10/08 12:00 PM	-13.34	-96.66		
NMR09-01	NMR 1	1/2/09 10:45 AM	-9.39	-63.17		0.097
NMR09-02	NMR 2	1/2/09 11:00 AM	-8.92	-60.10		0.105
NMR09-03	NMR 3	1/2/09 11:30 AM	-8.46	-56.42		0.089
NMR09-04	NMR 1	1/16/09 8:30 AM	-7.92	-58.43		0.135
NMR09-05	NMR 1	1/30/09 8:45 AM	-9.06	-61.41		
NMR09-07	FH 1	1/30/09 9:15 AM	-7.78	-55.65		0.000
NMR09-06	NMR 2	1/30/09 9:30 AM	-8.81	-61.77		
NMR09-08	NMR 1	2/13/09 8:30 AM	-8.17	-58.96		0.146
NMR09-11	FH 2	2/13/09 9:00 AM	-8.85	-58.65		
NMR09-10	FH 1	2/13/09 9:15 AM	-8.46	-56.07		
NMR09-09	NMR 2	2/13/09 9:30 AM	-8.94	-58.32		0.117
NMR09-12	NMR 1	2/27/09 8:30 AM	-8.00	-51.25		0.202
NMR09-13	NMR 2	2/27/09 9:00 AM	-8.44	-59.07		0.127
NMR09-14	NMR 3	2/27/09 9:30 AM	-8.89	-58.09		0.110
NMR09-26	GW 1	3/4/09 4:30 PM	-8.49	-56.26		
NMR09-27	GW 2	3/4/09 4:40 PM	-8.90	-58.94		
NMR09-15	NMR 1	3/20/09 8:30 AM	-9.29	-61.58		0.080
NMR09-16	NMR 2	3/20/09 9:00 AM	-7.58	-60.18		0.069
NMR09-17	NMR 3	3/20/09 9:30 AM	-7.78	-58.16		0.062
NMR09-18	NMR 1	4/6/09 8:30 AM	-5.96	-36.94		0.327
NMR09-21	FH 1	4/6/09 9:00 AM	-0.68	-49.58		0.002
NMR09-19	NMR 2	4/6/09 9:15 AM	-6.90	-41.65		0.207
NMR09-22	FH 2	4/6/09 9:15 AM	-8.50	-55.23		
NMR09-20	NMR 3	4/6/09 9:45 AM	-9.23	-55.74		0.398
NMR09-28	GW 1	4/8/09 4:00 PM	-6.73	-52.22		
NMR09-29	GW 2	4/8/09 4:30 PM	-7.27	-58.27		
NMR09-23	NMR 1	4/21/09 8:45 AM	-8.75	-58.86		0.152
NMR09-24	NMR 2	4/21/09 9:15 AM	-8.81	-54.55		0.104
NMR09-25	NMR 3	4/21/09 9:45 AM	-6.95	-50.57		0.119

Sample Name	***Station Name***	***Sample Date***	***$\delta^{18}O$ (‰)***	***$\delta^{2}H$ (‰)***	***Storm Event Number***	***Discharge (cms)***
NMR10-37	Precip	7/9/10 8:30 AM	-7.38	-47.23		
NMR10-37	Precip	7/9/10 8:30 AM	-7.33	-45.16		
NMR10-37	Precip	7/9/10 8:30 AM	-7.36	-44.50		
NMR11-46	Precip	3/9/11 12:00 PM	-12.16	-83.51		
NMR11-53	Precip	3/10/11 8:00 AM	-7.74	-45.65		
NMR11-43	Precip	3/23/11 8:00 AM	-3.00	-8.15		
NMR11-44	Precip	3/23/11 2:00 PM	-0.70	11.35		
NMR11-45	Precip	3/24/11 12:00 AM	-5.37	-23.31		
NMR12-01	A	10/17/12 4:15 PM	-7.85	-49.07	5	
NMR12-02	D	10/17/12 4:30 PM	-7.69	-48.71	5	
NMR12-03	F	10/17/12 4:40 PM	-8.02	-51.90	5	
NMR12-05	H	10/17/12 5:00 PM	-9.91	-76.41	5	
NMR12-04	M	10/17/12 5:10 PM	-7.61	-46.65	5	
NMR12-27	Precip	10/18/12 2:33 PM	-9.00	-52.99	5	
NMR12-28	NMR 2	10/18/12 3:03 PM	-7.86	-50.03	5	0.019
NMR12-29	NMR 2	10/18/12 3:33 PM	-7.81	-50.38	5	0.019
NMR12-30	NMR 2	10/18/12 4:03 PM	-7.91	-50.24	5	0.018
NMR12-31	NMR 2	10/18/12 4:33 PM	-8.06	-50.13	5	0.020
NMR12-25	F	10/18/12 4:45 PM	-6.89	-42.85	5	
NMR12-12	D	10/18/12 4:47 PM	-6.78	-40.66	5	
NMR12-22	J	10/18/12 4:54 PM	-9.24	-53.68	5	
NMR12-07	C	10/18/12 4:56 PM	-7.09	-41.41	5	
NMR12-08	Ga	10/18/12 5:00 PM	-6.62	-38.85	5	
NMR12-20	M	10/18/12 5:03 PM	-7.78	-45.56	5	
NMR12-32	NMR 2	10/18/12 5:03 PM	-8.46	-52.83	5	0.021
NMR12-11	A	10/18/12 5:05 PM	-7.90	-49.68	5	
NMR12-09	G	10/18/12 5:15 PM	-7.52	-42.52	5	
NMR12-19	H	10/18/12 5:20 PM	-8.16	-44.36	5	
NMR12-06	B	10/18/12 5:25 PM	-9.24	-54.23	5	
NMR12-10	I	10/18/12 5:27 PM	-8.24	-45.99	5	
NMR12-33	NMR 2	10/18/12 5:33 PM	-8.89	-54.78	5	0.024
NMR12-14	A	10/18/12 5:35 PM	-8.89	-50.56	5	
NMR12-18	F	10/18/12 5:35 PM	-9.49	-53.17	5	
NMR12-23	H	10/18/12 5:35 PM	-8.81	-57.30	5	
NMR12-24	D	10/18/12 5:43 PM	-4.43	-43.32	5	

Sample Name	***Station Name***	***Sample Date***	***$\delta^{18}O$ (‰)***	***$\delta^{2}H$ (‰)***	***Storm Event Number***	***Discharge (cms)***
NMR12-16	Ga	10/18/12 5:45 PM	-9.07	-53.18	5	
NMR12-15	E	10/18/12 5:50 PM	-9.18	-54.68	5	
NMR12-21	G	10/18/12 5:50 PM	-9.29	-54.09	5	
NMR12-17	J	10/18/12 6:00 PM	-8.14	-49.62	5	
NMR12-34	NMR 2	10/18/12 6:03 PM	-8.05	-52.66	5	10.144
NMR12-13	I	10/18/12 6:04 PM	-9.11	-57.28	5	
NMR12-26	M	10/18/12 6:30 PM	-9.06	-55.33	5	
NMR12-35	NMR 2	10/18/12 6:33 PM	-7.63	-50.02	5	3.713
NMR12-36	NMR 2	10/18/12 7:03 PM	-7.64	-49.89	5	0.896
NMR12-37	NMR 2	10/18/12 7:33 PM	-8.43	-50.33	5	1.123
NMR12-38	NMR 2	10/18/12 8:03 PM	-8.18	-51.17	5	1.262
NMR12-39	NMR 2	10/18/12 8:33 PM	-8.77	-53.13	5	0.672
NMR12-40	NMR 2	10/18/12 9:03 PM	-8.92	-53.36	5	0.279
NMR12-41	NMR 2	10/18/12 9:33 PM	-7.73	-49.38	5	0.145
NMR12-42	NMR 2	10/18/12 10:03 PM	-7.58	-49.60	5	0.096
NMR12-43	NMR 2	10/18/12 10:33 PM	-8.52	-53.95	5	0.070
NMR12-44	NMR 2	10/18/12 11:03 PM	-8.29	-52.28	5	0.058
NMR12-45	NMR 2	10/18/12 11:33 PM	-8.04	-50.87	5	0.049

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