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Variation in the instream dissolved inorganic nitrogen response between and within rainstorm events in an urban watershed

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Urban streams play a significant role in the transport of dissolved inorganic nitrogen (DIN) from uplands to sensitive coastal receiving waters. In this study, we investigate the timing of DIN export through monitoring conducted during several storm events of different magnitude and with different antecedent conditions in an urban catchment. Our monitoring was conducted at a first-order stream site in a highly urban catchment in the northeastern United States during four rainstorms. Nitrate made up the dominant portion of the DIN load during all four events and the response of nitrate and ammonia were very different. Discharge, rather than concentration, was the most important factor in determining nitrate export with hot moments of nitrate export coinciding with peaks in flow. However, the highest nitrogen concentrations were observed after the streamflow peak during all of the events. During extreme rainstorms, this delayed response may constitute an important secondary hot-moment of nitrate export. These results may be significant for the development of nitrogen management plans for urban watersheds, especially since many water quality improvement BMPs (best management practices) are being designed to treat the first-flush of stormwater and would miss much of the DIN load.

Keywords: Nitrate export, dissolved inorganic nitrogen (DIN), urban watershed, first-flush, nutrients.

Introduction

Urbanization alters natural biogeochemical cycles and the function of ecosystems, often with far-reaching consequences.[1,2] An important example of this is the excessive export of nitrogen by stream from urban watersheds, which has become a major source of nitrogen to coastal estuaries.[3,4] Accelerated eutrophication, the formation of zones of hypoxia, increased frequency of harmful algal blooms, reduced biodiversity and loss of fish stocks have all been linked to increased anthropogenic nitrogen inputs to coastal waters.[5–7] Well known examples of such compromised systems include the Gulf of Mexico and Chesapeake Bay in the United States[8,9] as well as the Youngsan River Estuarine Bay and Chinhae Bay in Korea.[10]

The processes responsible for the increased export of nitrogen from urban watersheds are still actively being researched but are known to be twofold. First, urban land use activities are known to result in the production of new sources of mobile nitrogen.These include point sources, such as waste-treatment plant outfalls, along with non-point sources such as lawn-fertilizer use and the atmospheric deposition of nitrogen compounds generated by fossil fuel combustion.[11,12]

Second, the increased impervious surface and resulting modifications to hydrologic flowpaths may make naturally occurring nitrogen retention hotspots, such as riparian wetlands, less effective.[13] For example, reduced infiltration may result in lowered water tables and more oxic soils, making denitrification, which requires anoxic conditions, unfavorable. Also, in urban areas, stormwater is conveyed directly into surface waters through storm drain culverts. As a result, a significant fraction of stormwater bypasses the nitrogen retention hotspots within watersheds.[13–15]

Data from previous studies shows that, unlike streams in pristine catchments, the N-load of urban streams is comprised mostly of inorganic nitrogen (nitrate/nitrite and ammonia) and that the particulate load is relatively insignificant since nitrate is usually dominant.[15,16] Therefore, we focused on the export of the dissolved inorganic nitrogen during the rainstorm events monitored for this study. The export of DIN by streams exhibits considerable temporal

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variation at all time scales- on the scale of minutes or hours during rainstorms, days or weeks between storm events, months due to seasonal effects, and of years depending on climate patterns.

For many stormwater pollutants, including total suspended solids, total phosphorous and many heavy metals, a "first-flush" is commonly observed.[17] A 'first-flush' of a stormwater constituent occurs when a disproportionate fraction of the determinant pollutant load is conveyed during the initial period of a storm event. Within storm events, these time periods are "hot-moments"[18] of pollutant export, resulting from the mobilization of accumulated pollutants at the initiation of stormflow.[17] The developers of stormwater management plans often take advantage of this phenomenon by designing stormwater treatment infrastructure to store and treat only the first flush of stormwater. This allows for the treatment of a significant proportion of the pollutant load within space and economic constraints that are often very limiting.

Although a simple hydrograph with a predictable first-flush is observed for many stormwater pollutants, the sparse data that are available on the timing of nitrogen export during storms[16,19,20] implicate a highly variable DIN response. Even less is understood about the DIN response in catchments with predominantly urban land uses, which are likely to be more complex. In this study, we investigated the timing of DIN export through monitoring conducted during several storm events of different magnitude and with different antecedent conditions in an urban catchment. Understanding the timing of nitrogen export can provide useful information to maximize the efficiency of urban stormwater management programs. With the current projections of accelerated rates of urbanization worldwide[21] it is imperative that we improve our understanding of nitrogen export from urban watersheds and develop strategies to mitigate this problem.

Materials and methods

Site description

Harry's Brook is part of the greater Millstone-Lower Raritan Watershed, which is located in Princeton, New Jersey, in the northeastern United States. Harry's Brook watershed contains a great deal of diversity in land use within its relatively small drainage area (6.7 km^2) and has experienced high urban growth rates in the past 20 years. As a result, this watershed is considered to be at great risk for degradation in its water quality.[22]

Table 1. Land use upstream of the monitoring site.

Land use type	*% of 0.47 km^2 catchment area*
Urban	
Light residential	44.5%
Dense residential	5.6%
Commercial/services	18.2%
Other urban	12.0%
Wetlands (deciduous, wooded)	3.9%
Forest (deciduous)	15.0%

The site monitored in this study is located along a tributary of Harry's Brook (Fig. 1). The catchment upstream of our site is 0.47 km^2 in area and has been almost entirely developed for urban land uses ($\sim$ 80%) (Table 1). From Geographic Information System (GIS) analysis of the New Jersey Department of Environmental Protection's Land Use/Land Cover (NJDEP LU/LC) database (NJDEP), we estimated that 32% of the surface cover is impervious. Development in this catchment is fairly recent and several small detention ponds are present upstream of our monitoring site. Most of the catchment is drained by a storm sewer network, which empties at the outfall at the beginning of this branch of Harry's Brook. As shown in Figure 1, the monitoring site was located 300 m downstream of the storm drain outfall and the beginning of the surface stream channel. The reach between the storm drain outfall and our monitoring site is used for commercial activities including several office buildings with fertilized lawns and their parking lots.

Rainstorm events

Four storm events, which were monitored in 2005 and 2006, are used for the analyses in this paper (see Table 2 for summary).

Events 1 and 2, on October 8th and 12th of 2005, represent two back-to-back, extreme rain events, caused when the remnants of Tropical Storm Tammy and then a subtropical depression merged with incoming continental cold fronts. The combined accumulation from these two rainstorms was greater than 250 mm. Although these two events made this the wettest month in recorded history in the state of New Jersey, they were not record discharge events. The reason for this are twofold: first, in many small urban watersheds, flood peaks are produced by warm season thunderstorm systems which produce extreme rainfall rates at 1–60-minute time intervals.[23–25] While record flood peaks in Harry's Brook are associated with 1–15-minute rainfall rates that exceed 100 mm h^{-1}, the peak 1–15-minute rainfall rates for the October, 2005 storms were less than 100 mm h^{-1} and exceeded 50 mm h^{-1} only during brief periods. Second, the combined August and September 2005 rainfall was the lowest on record.[26] Therefore, the hydrologic response, especially for Event 1, the first of the two events, was strongly influenced by the anomalously low antecedent soil moisture.

In contrast, Event 3 (October 24th, 2005) was associated with only 32 mm of rain and took place late in the extremely

Table 2. Summary of storm event sample numbers and collection frequency.

Event	*Number of samples collected*	*Collection frequency*
Event 1— October 8th 10/6/05–10/11/05	135	10/7/05 19:00–10/9/05 00:00–60 min 10/9/05 00:00–10/9/05 18:30–30 min 10/9/05 18:30–10/9/05 22:15–15 min 10/9/05 22:15–10/10/05 11:00–30 min
Event 2— October 12th 10/11/05–10/16/05[a]	128	10/10/05 11:00–10/13/05 11:30–60 min 10/13/05 11:30–10/13/05 17:30–15 min 10/13/05 17:30–10/16/05 16:30–60 min
Event 3— October 24th 10/24/05–10/26/05[b]	72	Every 30 min
Event 4— April 22nd 4/21/06–4/26/06	240	Every 30 min

[a] Sampling interrupted 10/12/05 17:20–22:50.

[b] Sampling interrupted 10/26/05 18:00–23:00.

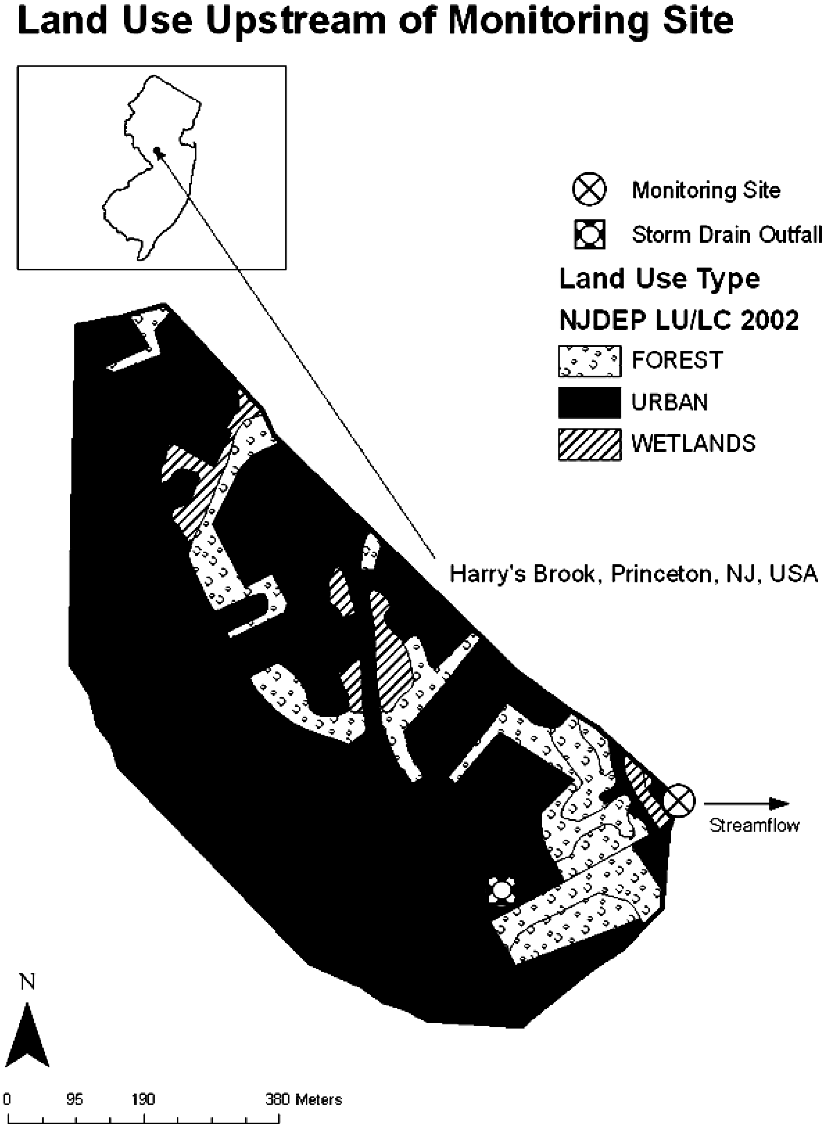

Fig. 1. Land-use data presented here were obtained from the New Jersey Department of Environmental Protection's 2002 Land Use/Land Cover (NJDEP LU/LC[39]) dataset. The watershed boundary was delineated from the NJDEP 10 m Digital Elevation Model,[40] using the TauDEM[41] extension of ArcGIS.

wet month of October, 2005. Event 4, on April 22nd, 2006, followed a record dry period, with precipitation deficits extending from February until April 22nd. The total rainfall accumulation for this event was 65 mm. The seasonal cycle of soil moisture for this region has a pronounced minimum during fall and maximum during the spring. Events 1 and 4 reflect dry antecedent conditions during the fall ("dry" season) and spring ("wet" season) respectively.

Sample collection and analytical methods

During each storm event, 200 mL of stream water was collected at pre-programmed time intervals (Table 2) using an ISCO 6712 automated water sampler (Teledyne-ISCO Inc., Lincoln, NE, USA) All samples were stored in 1 L high-density polyethylene (HDPE) bottles, which contained 0.25 mL of 2M hydrochloric acid to reduce the pH of the samples to below 2. The samples were kept cool by ice in the base of the sampler, which was changed, at least, daily.

Once transported to the laboratory, the samples were refrigerated and analyzed within 28 days. The samples were filtered; using 25 mm nylon syringe filters with a pore size of 0.23 μm, prior to analysis. Samples were analyzed for total nitrate and nitrite (NO_3+NO_2), using the cadmium reduction method and reported as nitrate, since we assumed the nitrite concentration would be negligible in the oxic stream waters. The samples were also analyzed for ammonia using the phenate method. The water quality analyses were performed using a Lachat Quik-Chem 8500 Flow Injection Analyzer (Lachat Instruments, Hach Co. Loveland, CO, USA). Nitrate was quantified using method 10-104-10-1-O, which had a laboratory-determined detection limit of 0.05 mg (NO_3+NO_2)/L. Ammonia was analyzed using method 10-106-04-1-J, with a determined detection limit of 0.1 mg (NH_3)/L.

There are short gaps in the sampling data during Events 2 and 3 due to mechanical failure of the sampler. These pauses in sampling were shorter than 5 hours in duration and are presented as a gap in the time series plots of Figures 2–5. Linear interpolation was used to calculate cumulative loading during these times.

Hydrologic and water quality data analysis

The water quality data are supported by time series of stream discharge and precipitation. Water depth in the stream was monitored continuously at one-minute intervals using a vented-cable pressure transducer. Discharge was calculated from these depth measurements using a rating curve developed from hydraulic modeling analyses. Precipitation time series were computed from radar reflectivity data from the NEXRAD WSR-88D radar at Fort Dix New Jersey (KDIX), utilizing the HydroNEXRAD algorithms.[27] Rainfall rate time series were calculated from reflectivity data using the "convective" Z-R relationship.[28] Bias correction algorithm was applied using accumulation rain gage observations from the Harry's Brook rain gage network. The rain gage network consisted of 5 stations, each with two accumulation gages. The rainfall estimation procedure provides rainfall estimates for which the total rainfall accumulation is largely determined by rain gage observations and temporal variability is specified by radar observations. Using these hydrologic data, time series of mass flux, the rate of transport of the DIN analytes by the stream, were constructed:

The precipitation and discharge data were also used to determine the runoff ratio for each storm, which was calculated as:

Runoff Ratio

$$\frac{\text{Stormwater volume}}{\text{Precipitation volume}} = \frac{\sum_{t=\text{start of rise}}^{\text{return to baseflow}} Q_t \Delta t}{\sum_{t=\text{precip. start}}^{\text{precip. end}} AR_t \Delta t}$$

Q_t = Stormflow (discharge - baseflow) measured at time t (in cubic meters per second)

A = Catchment area (in square meters)

R = Rainfall Rate measured at time t (in meters per second)

Δt = Monitoring time interval (in seconds)

where stormflow was calculated using the constant baseflow method.

In order to assess changes in DIN loading in rain events of different magnitudes, we use the event mean concentration (EMC) parameter. The EMC is defined as[29–31]:

$$\text{EMC(Mg/L)} = \frac{\text{Event analyte mass}}{\text{Event volume}} = \frac{\sum_{\text{t=start of rise}}^{\text{return to baseflow}} Q_t C_t \Delta t}{\sum_{\text{t=start of rise}}^{\text{return to baseflow}} Q_t \Delta t}$$

Q_t = Stormflow (discharge-baseflow) measuread at time t (cubic meters per second)

C_t = Instream concentration of analyte at time t (in milligrams per liter)

Δt = Monitoring time interval (seconds)

The timing of the delivery of the nitrogen load was also examined, in order to determine whether a "first-flush" of DIN was observed during these rainstorm events. There are various definitions of first-flush in the literature that specify quantitative criteria for what constitutes a "disproportionate fraction" of the determinant load and/or the "initial period" of the storm.[32] For this study, we used the non-restrictive criteria based on the total pollutant load transported by the first 25% of the runoff (FF_{25}). If this pollutant load is significantly greater than 25%, a first-flush of that pollutant was considered to have taken place during that event. Time series of cumulative stormflow and DIN loads were calculated from the stormflow and mass flux data described above and used for this analysis.

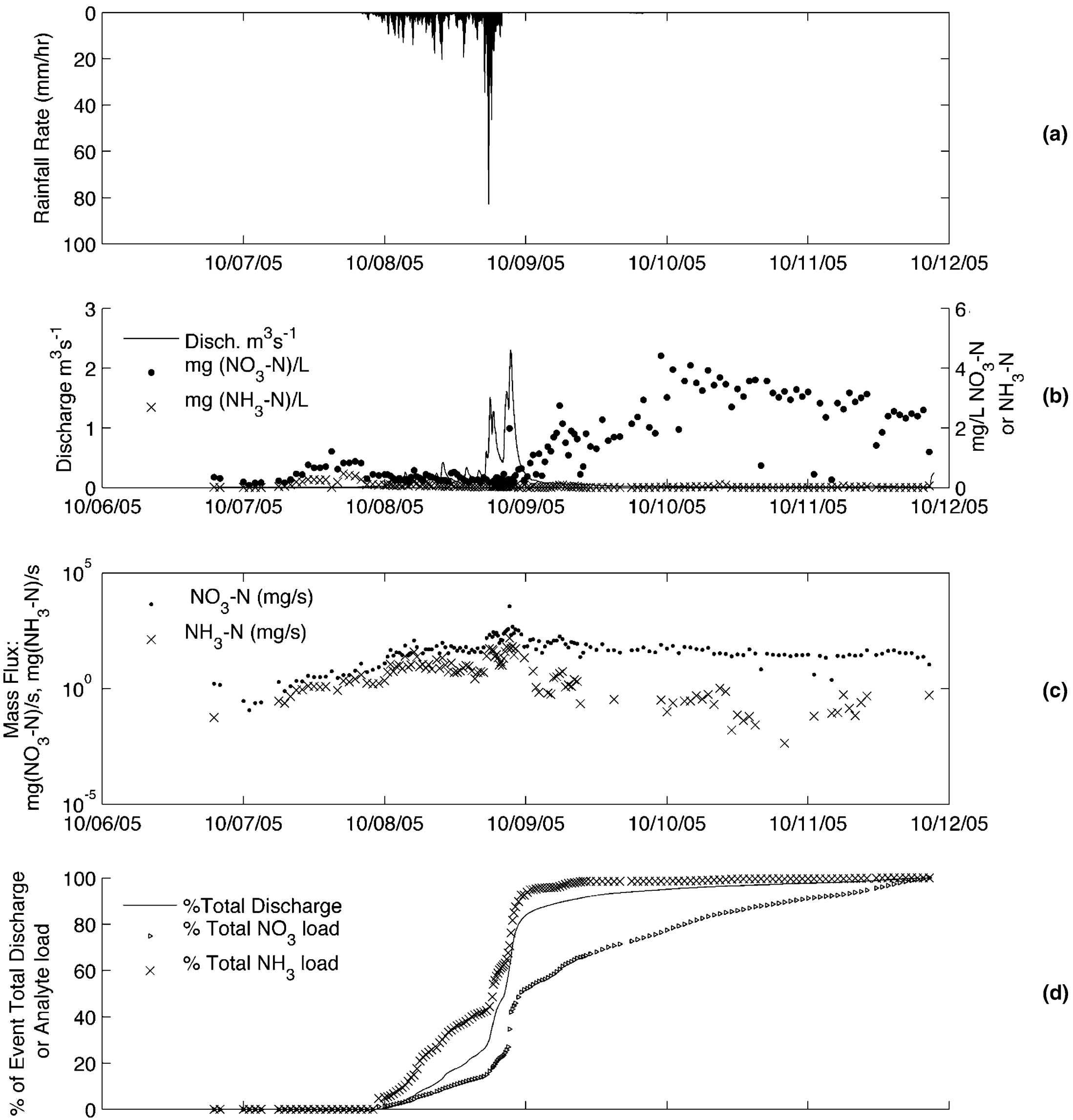

Fig. 2. Time series data from Event 1, October 6th–11th 2005. (a) rainfall rates, (b) discharge and concentration of the water quality analytes, (c) mass flux of the water quality analytes, (d) percentage of the cumulative discharge and analyte loads of the storm total. Note that the y-axis on plot (c) is in log scale.

Results and discussion

Nitrate and ammonia response

Figures 2–5 present the time series of hydrologic and water quality data obtained from monitoring during the four storm events. Each of these figures show rainfall rates (a), discharge and concentration of the water quality analytes (b), mass flux of the water quality analytes (c) and cumulative discharge and analyte loads, expressed as a percentage of the storm total (d). The availability of intensive hydrologic and water quality data allowed us to observe the timing of the instream response to variations in rainfall intensity. Multiple peaks in discharge and corresponding changes in DIN concentration can be observed during each storm event.

As shown in Figure 2, the instream nitrogen response to the extreme rainfall of Event 1 was complex. 113 mm of rain fell in Harry's Brook in only 22 hours during this rainstorm, which occurred on October 8th–11th, 2005 (Fig. 2). The highest recorded rainfall rate, 83 mm/hr was also observed during this event. While minor fluctuations in DIN concentrations (<1 mg/L of nitrate + ammonia) were observed prior to the start of precipitation, instream DIN concentrations decreased markedly at the onset of rainfall, apparently through dilution. Following the end of significant rainfall, instream nitrate concentrations increased greatly,

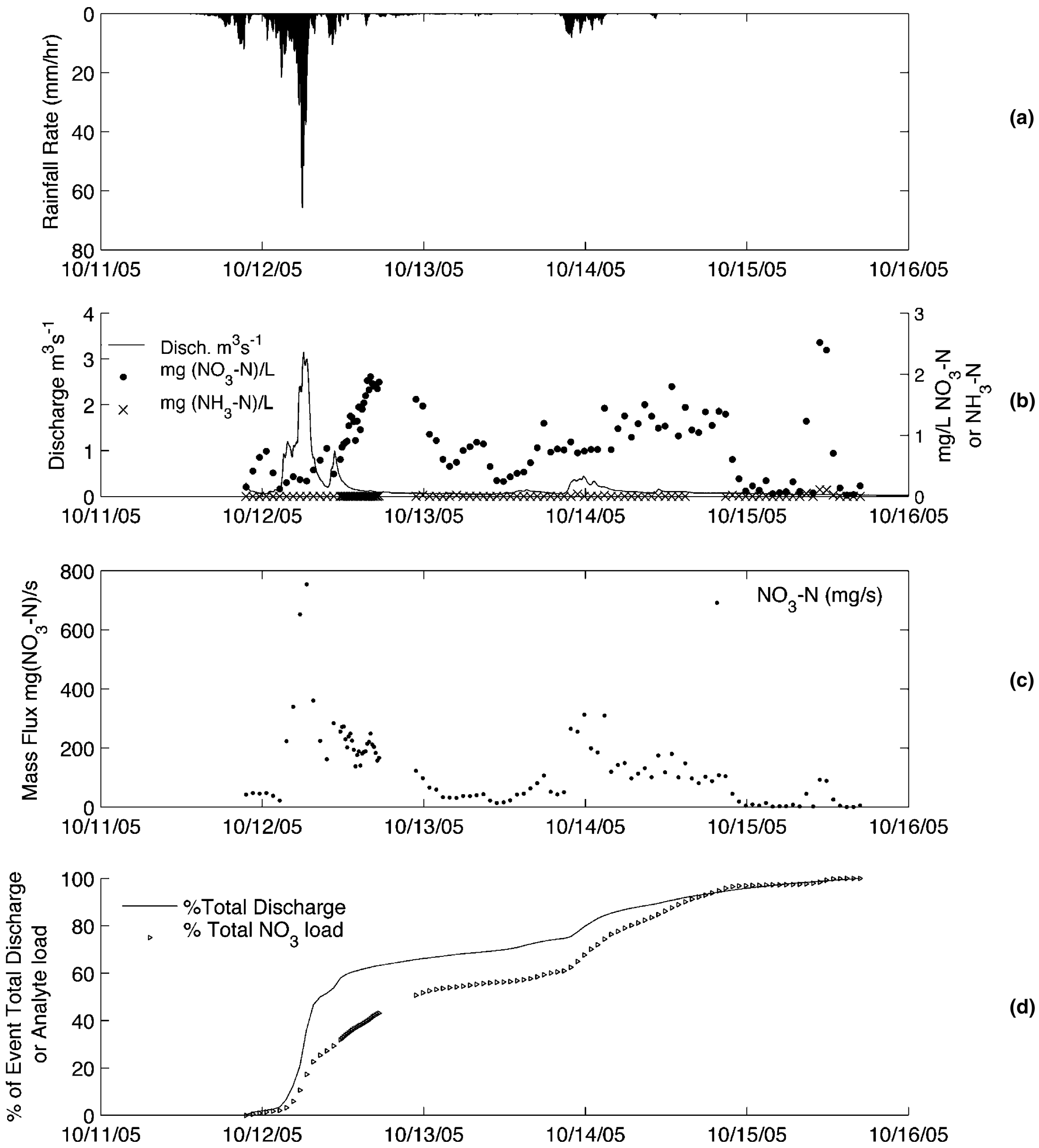

Fig. 3. Time series data from Event 2, October 11th–15th 2005. (a) rainfall rates, (b) discharge and concentration of the water quality analytes, (c) mass flux of the water quality analytes, (d) percentage of the cumulative discharge and analyte loads of the storm total.

exceeding 4 mg (NO_3-N)/L (Fig. 2b). These were the highest DIN concentrations observed during this study. Surprisingly, these elevated concentrations were observed twelve hours after the peak in discharge from this storm. They were sustained until the beginning of the equally extreme Event 2 (event October 12th, 2005), two days later (Fig. 3).

Rain Event 2 also resulted in peaks of high instream nitrate concentrations (>2 mg (NO_3-N)/L, although they were lower than those observed during Event 1. While both, the maximal concentrations and the mass flux were not as high as what was observed during Event 1, this event conveyed a greater total load of dissolved inorganic nitrogen-both as a result of a greater cumulative stormflow volume and a slightly higher EMC. Rain Event 3, which took place several weeks later was much smaller in magnitude and duration, and correspondingly lower in nitrate and ammonia levels. Rain Event 4 was similar to Event 1 in that it followed an extended dry period. Surprisingly, relatively little nitrate was transported during this event. However, ammonia loads were similar to what was transported during Event 1.

Although the high nitrate concentrations observed following Event 1 were the most extreme, a similar pattern was observed through all four events monitored (Figs. 3–5). A general decrease in nitrate concentration during times of peak discharge was observed suggesting that the baseflow

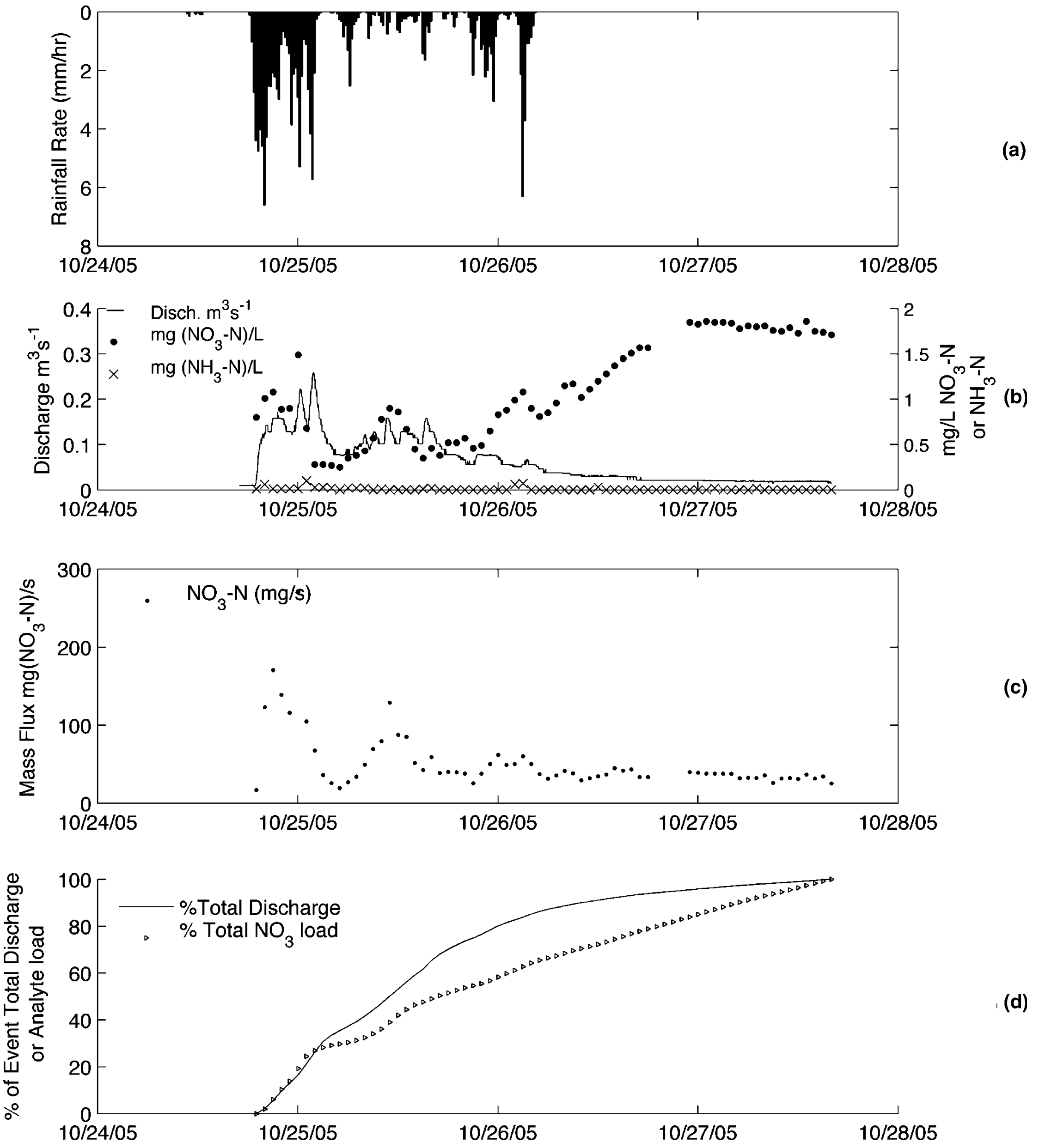

Fig. 4. Time series data from Event 3, October 24th–26th 2005. (a) rainfall rates, (b) discharge and concentration of the water quality analytes, (c) mass flux of the water quality analytes, (d) percentage of the cumulative discharge and analyte loads of the storm total.

nitrate load is diluted by the bulk of stormwater, which is conveyed rapidly into the stream by the storm drain network and through overland flow.[33] The highest sustained nitrate concentrations were always observed late in the receding limb of the stormflow peaks with multiple dilutions and rises occurring in storm events with more than one peak. Other researchers have also observed a significant export of nitrate during low-discharge periods from weekly collected water quality samples from streams in a highly urban catchment,[34] although they did not sample intensively during storm events. Our results indicate that a significant fraction of the nitrogen load may be transferred to streams by subsurface flowpaths.

Also, as was observed by previous authors,[16,19,20] ammonium concentrations and total ammonium loads were significantly lower than that of nitrate during all events monitored (Figs. 2–5, Table 3). During Event 1, peak ammonium concentrations were considerably lower than those of nitrate and ammonium made up only 6.7% of the total DIN load transported for this storm (1.62 kg NH_4^+-N). During Events 2 and 3, ammonia concentrations were below the detection limit of 0.1 mg (NH_3-N)/L. Ammonia concentrations were detectable, but also fairly low (below 1 mg (NH_3)-N/L during Event 4, in April, 2006. However, since nitrate concentrations were also much lower during this event than they had been during previous events,

Table 3. Comparison of hydrologic and water quality data during each rainstorm event.

	Event 1 *10/6/05–10/11/05*	*Event 2* *10/11/05–10/15/05*	*Event 3* *10/24/05–10/26/05*	*Event 4* *4/21/06–4/26/06*
Total precipitation (mm)	113	139	32.0	65
Duration of precipitation (hrs)	21.8	27.2	15.3	23.0
Max. precip. rate (mm/hr)	83	66	7	18
Storm total discharge[a] (mm in hrs after rise)	85.9 in 95.1 hrs	132.1 in 114 hrs	30.4 in 71 hrs	15.0 in 114 hrs
Runoff ratio	0.76	0.95	0.95	0.23
Total event nitrate load (kg NO_3-N)	22.5	37.89	12.38	2.46
Total event ammonia load (kg NH_3-N)	1.62	Below detection	Below detection	1.54
Nitrate EMC[b]	0.54	0.59	0.78	0.35
Ammonia EMC	0.04	n/a	n/a	0.22
% Nitrate load at 25% runoff delivery	13.84%	12.38%	26.22%	24.37%
% Ammonia load at 25% runoff delivery	41.60%	n/a	n/a	36.46%
% Nitrate load at 90% runoff delivery	62.78%	84.75%	70.51%	85.90%
% Ammonia load at 90% runoff delivery	97.33%	n/a	n/a	91.21%

[a] Discharge (m^3) is normalized by catchment area and expressed as a depth for convenience.
[b] Event mean concentration.

ammonia made up a much more significant percentage of the total DIN load (38.5%, 1.54 kg of (NH_3)-N).

The timing of the nitrate and ammonia responses within each event were also very different. As shown in the (d) plots of Figures 2–5, while nitrate transport lagged behind the stormflow hydrograph, the ammonia peaks tended to precede it, with the highest concentrations of ammonia observed almost immediately after the onset of a significant rainfall. Using the non-restrictive, FF_{25} definition that has been explained above, the relatively high concentrations of ammonia observed at the beginning of these events represent a first flush, with more than more than 40% of the total event ammonia load conveyed by the first 25% of the runoff during Event 1 (compared to only 14% of the total event nitrate load). Also, nearly the same amount (37%) was transported by the 25% mark during Event 4, which was the only other event monitored that followed an extended dry period and in which ammonia was above the detection level (Table 3). In contrast, no first-flush of nitrate was observed and much of the nitrate load arrived late in the hydrograph.

Temporal variation and hot moments of DIN export

The time series of DIN mass flux can be used to delineate the occurrence of hot-moments of DIN transport. As shown in Figures 2–5, hot moments of nitrate transport (periods of exceptionally high mass flux) occur during each storm event and coincide with peaks in discharge. However, although discharge is the most important determinant of nitrogen export, the high concentrations observed at low flow are, at times, significant. For example, the elevated concentrations of nitrate observed in the days following Event 1 resulted in the export of a considerable quantity of DIN and may even constitute a hot moment of nitrate export on the scale of months or years. Nearly 40% of the nitrogen exported during the event occurred after 90% of the stormflow had passed (Table 3).

The temporal variation in nitrogen concentration within storm events may provide insight on the mechanisms behind the nitrogen export from urban catchments. Previous researchers[16,35] have analyzed these types of datasets by constructing nutrient trajectories—however, while these types of analyses are useful for the brief, single-peak thunderstorms, they were not appropriate for analysis of our events, which lasted for many hours and were comprised of multiple peaks of discharge as a result of variations in rainfall intensity.

During the four storm events, nitrate concentrations generally decreased during times of peak discharge, suggesting that the instream nitrate was diluted by the bulk of the stormwater that quickly runs through the storm drain network. These results imply that nitrate is not washed off from the impervious surface, as is the case with many stormwater pollutants,[17,32] but instead is dominated by subsurface processes- this has been the conclusion of several other researches after intensive sampling during storm events.[19,36] However, these studies were of agricultural and forested watersheds, where there is little impervious cover. It is interesting that subsurface mechanisms would also be dominant in an urban catchment like Harry's Brook, where there is such a high percentage of impervious cover, where atmospheric deposition plays a significant role,[37] and where such a large percentage of the stormwater is conveyed through the stormwater network.

Temporal variation between rainstorm events

Although instream ammonia concentrations were similar for both these events, ammonia comprised only 7% of the total DIN load of Event 1, and it made up 39% of the DIN transported by Event 4 (Table 3). Among the more

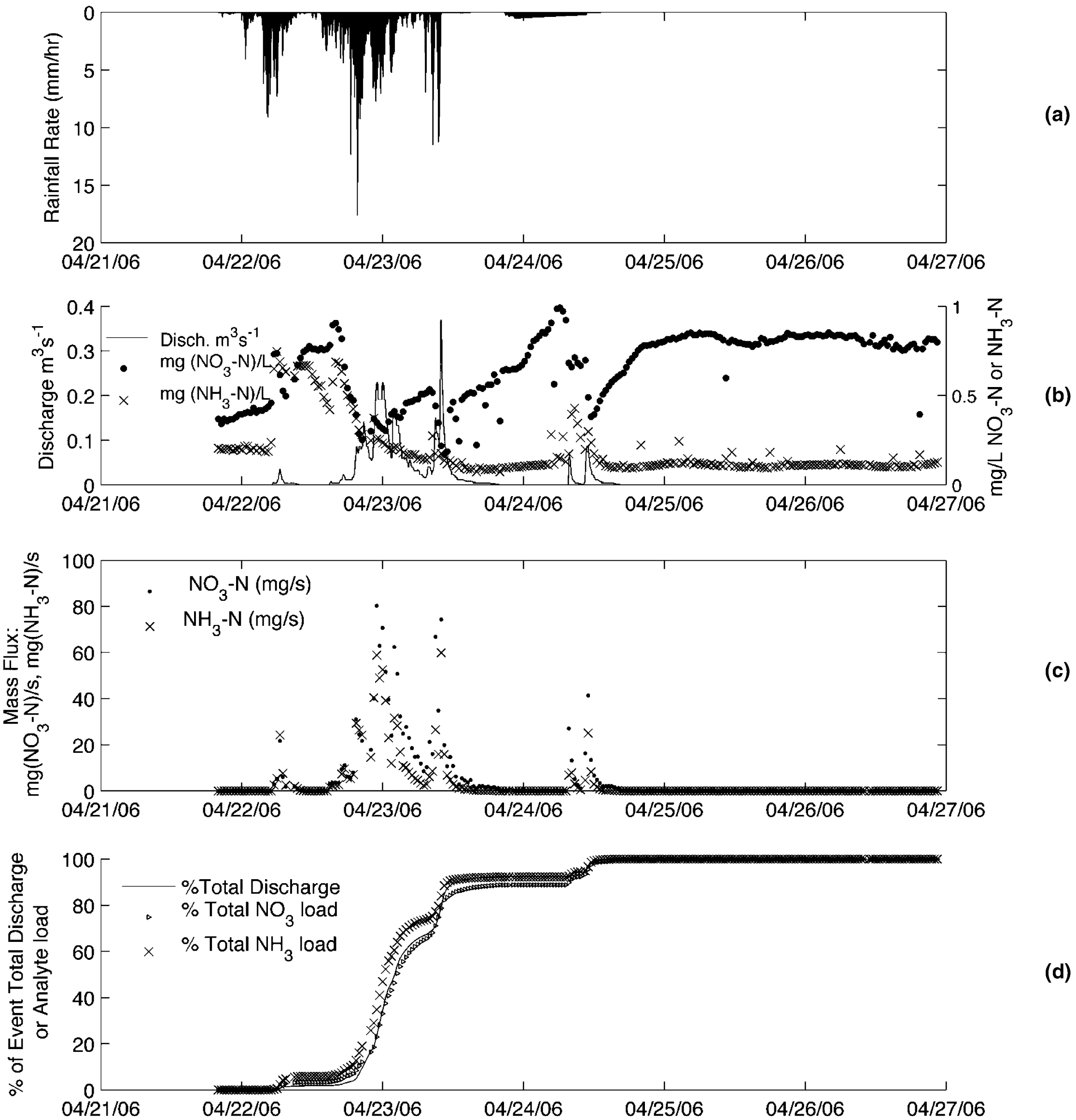

Fig. 5. Time series data from Event 4, April 21st–26th 2006. (a) rainfall rates, (b) discharge and concentration of the water quality analytes, (c) mass flux of the water quality analytes, (d) percentage of the cumulative discharge and analyte loads of the storm total.

noticeable differences in DIN between these two events was that DIN was extremely high during Event 1 and that the timing of the ammonia concentration response was somewhat different during the two events- high ammonia concentrations coincided with higher discharge during Event 4. As a result, nearly the same load of ammonia was transported by Event 4 as Event 1, even though the total cumulative discharge for this event was only 17% of that of Event 1 (Fig. 2d).

For the four rainstorm events monitored, discharge was the most important predictor of DIN exported, with a clear and positive relationship between discharge and the total loads of nitrate and ammonia (when detectable) transported for each event. As discussed above, the EMC (Event Mean Concentration) is a useful parameter for comparing nutrient loadings for events of different magnitudes. EMCs of nitrate and ammonia are presented for each event in Table 3. For rain events 1 to 3, which occurred during October, 2005, the EMC of nitrate was successively higher for each event. No relation between event magnitude and EMC was observed. Instead, the highest nitrate EMC was observed during Event 3, which was the smallest event monitored, but occurred shortly after several extreme rainstorms. This observation suggests that antecedent conditions are an important determinant of nitrate EMC. In line with this observation, the lowest nitrate EMC was that of Event 4, which took place following an extended dry period in April, 2006.

Runoff ratios calculated for each event (Table 3) may provide some insight on stormflow generating processes within the catchment. The runoff ratio was a good predictor of the event mean concentration of nitrate, in spite of the broad range of discharge magnitudes, durations, and season of occurrence for these events. In humid catchments, like Harry's Brook, there is a strong, positive relationship between runoff ratio and soil moisture conditions.[37] The extreme precipitation of October 8–12, 2005 resulted in saturated soil conditions, which are reflected in the very high runoff ratios of the storms monitored that month. These high runoff ratio storms had event mean concentrations of nitrate that were much higher than that of the low runoff-ratio April, 2006 event, in spite of the broad range of discharge magnitudes and durations of these events and the expected high levels of fertilizer use in the month of April. These results, together with the observed lag in peak nitrate concentrations during storm events, support theories of nitrate flushing from soils as the dominant mechanism of nitrogen export from urban catchments.

In contrast, EMCs for ammonia, also shown in Table 3, were nearly the same for both events during which ammonia was detectable (Events 1 and 4, October 8–12, 2005 and April 21–26, 2006). Both of these events followed record-setting extended dry periods. However, while Event 1 was an extreme precipitation event with a very high runoff ratio, Event 4 was much more typical in magnitude and most of its precipitation did not contribute to stormflow. These observations, along with the observed first-flush of ammonia during these events suggest that ammonia is washed-off of impervious surface and that flushing from soils is less important. The extended dry periods that preceded these storms may have allowed for sufficient build-up of ammonia on impervious surface to allow for its detection in stormwater. Since ammonia tends to sorb strongly to soil particles, it is less mobile in urban soils while nitrate partitions into soil porewater and can contribute to stormflow under conditions of sufficient soil moisture.[38]

Conclusions

The export characteristics of DIN (nitrate and ammonia) in urban watershed were monitored during several storm events of different magnitude and with different antecedent conditions. Nitrate made up the dominant portion of the DIN load during all four events and the response of nitrate and ammonia on rainstorm were very different. Our results clearly indicate that discharge was the most important predictive factor when considering the temporal variation of N export at both short (hourly) and long (event) time scales. However, although discharge was the most important predictor of instream DIN load, the observed temporal variation in nitrate and ammonia concentrations may also have important implications for nitrogen management.

In urban areas, many stormwater BMP (best management practice) structures are now being designed to capture the first flush of stormwater for treatment before it can enter waterways. Our research suggests that storage-type best management practices will be limited in their effectiveness for nitrogen management in urban watersheds since subsurface processes appear to dominate DIN export (mainly as nitrates) from these watersheds, non-structural BMPs, which focus on a reduction of nitrogen sources and the preservation of natural nitrogen sinks, such as riparian wetlands, are likely to be more appropriate.

Our observations also provide useful information on the monitoring of instream nitrogen. While nitrate concentrations were generally higher at lower flows, there are a few individual samples where high nitrate concentrations were observed during times of peak discharge. Although these samples were outliers, they should not be excluded from the dataset[31] and, in many instances, correspond to the observed times of maximum nitrate export. More research is required to determine the source of these short-lived, high nitrate concentrations and their significance to long-term nitrate loadings from urban catchments. Also, we can conclude that the determination of instream nitrate loading is highly sensitive to the frequency of sampling, particularly in urban catchments, where response times are rapid. Monitoring efforts where sampling intervals are greater than one-hour will not adequately represent the DIN load.

We consider the monitoring work reported here to be a useful precursor study for further work. The dataset collected for this study is one of the most comprehensive of urban instream nitrogen loads available and includes water quality data for two back-to-back, extreme rainstorm events. The results of our monitoring indicate that different transport processes are dominant for nitrate and ammonia in urban stormflows: flushing of nitrate from soil-water stores appears to be most important in the transport of DIN from uplands to streams while build-up and washoff from impervious cover appears to be most important for ammonia. Future studies, involving simultaneous measurement of moisture and nitrogen content of the soils along with instream sampling are required to better understand the mechanisms responsible for our observations.

Acknowledgments

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