Constraining Nitrogen Inputs to Urban Streams from Leaking Sewers Using Inverse Modeling: Implications for Dissolved Inorganic Nitrogen (DIN) Retention in Urban Environments

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Supporting Information

ABSTRACT: Leaking sewer infrastructure contributes nonpoint nitrogen pollution to groundwater and surface water in urban watersheds. However, these inputs are poorly quantified in watershed budgets, potentially underestimating pollutant loadings. In this study, we used inverse methods to constrain dissolved inorganic nitrogen (DIN) inputs from sewage to Nine Mile Run (NMR), an urban watershed (1570 ha) in Pittsburgh, Pennsylvania (USA) characterized by extensive impervious surface cover (38%). Water samples were collected biweekly over two years and intensive sampling was conducted during one summer storm. A nitrogen budget for the NMR watershed was constructed, ultimately inverted, and sewage DIN inputs constrained using Monte Carlo simulation. Results reveal substantial DIN contributions from sewage ranging from 6 to 14 kg ha\(^{-1}\)yr\(^{-1}\). When conservative estimates of DIN from sewage are included in input calculations, DIN retention in NMR is comparable to high rates observed in other suburban/urban nutrient budgets (84%). These results suggest a pervasive influence of leaking sewers during baseflow conditions and indicate that sewage-sourced DIN is not limited to sewer overflow events. Further, they highlight the importance of sewage inputs to DIN budgets in urban streams, particularly as sewer systems age across the U.S.

INTRODUCTION

Sewers can be important contributors to surface water 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, exacerbating existing dissolved inorganic nitrogen (DIN) loads to impaired streams. The scale of this urban problem is difficult to quantify, with over 900 000 km of sewer lines in the U.S. and many sewer systems close to 100 years old. 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. Although the U.S. EPA estimates 3 000 000 m\(^3\) of untreated sewage reach U.S. waterways annually, this nonpoint DIN source is poorly characterized in urban watershed nutrient studies. 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).

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; in watersheds dominated by septic systems, per-capita nitrate excretion rates have been coupled with estimates of retention of nitrogen compounds in septic systems; (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; (4) a combination approach utilizing water balances, water chemistry, and models of water quality has been used to predict groundwater recharge from sewage systems.

This work constrains the potential contribution of nonpoint 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). Sewage is a known source of nutrient pollution to this stream and region, 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

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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.

STUDY LOCATION AND METHODS

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 1570 ha urban watershed with 38% impervious cover. Bedrock in the area is composed of shale, limestone, siltstone, and sandstone. The upper portions of NMR are buried in storm sewers (Figure S1 (Supporting Information)). NMR emerges in Frick Park (Pittsburgh, PA) and runs for 3.5 km before it joins the Monongahela River.

The NMR watershed is served by two contrasting sewer systems (Figure 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 S1). Sanitary sewers are designed to direct waste from households and runs for 3.5 km before it joins the Monongahela River. The stream drains a 1570 ha urban watershed with 38% impervious cover. Bedrock in the area is composed of shale, limestone, siltstone, and sandstone. The upper portions of NMR are buried in storm sewers (Figure S1 (Supporting Information)). NMR emerges in Frick Park (Pittsburgh, PA) and runs for 3.5 km before it joins the Monongahela River. The stream drains a 1570 ha urban watershed with 38% impervious cover. Bedrock in the area is composed of shale, limestone, siltstone, and sandstone. The upper portions of NMR are buried in storm sewers (Figure S1 (Supporting Information)). NMR emerges in Frick Park (Pittsburgh, PA) and runs for 3.5 km before it joins the Monongahela River.

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Additionally, storm-flow samples were collected at NMR2 on July 20, 2008 following 5 mm of precipitation during 1 h ($n = 8$). Stormflow samples were collected from NMR2 before the rainfall began, at 30 min intervals for the first 3 h 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. Biweekly samples were vacuum filtered within 24 h 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.

Discharge/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). The USGS program “PART” was used for hydrograph separation of the USGS discharge record for years 2007 and 2008. Precipitation data was obtained from 3 Rivers Wet Weather, land cover data for the region was obtained from the National Land Cover Database, and watershed boundary data was obtained from the Environmental Resources Research Institute’s Small Watersheds database.

Two methods were used to calculate annual DIN export (or flux) from NMR (Figure S3). 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 to the daily average USGS discharge record (Figure S3). Discharge values below 0.065 m$^3$ s$^{-1}$ were not utilized when determining this relationship due to anomalously low NO$_3^-$-N concentrations (see Discussion and Figure S4). To calculate DIN export, NO$_3^-$-N concentrations were related to total DIN concentrations (Figure S4) 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 NMR2 were interpolated between sampling days, 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 these approaches, annual DIN export was estimated for annual periods 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.

Sewage DIN Contribution Estimations. The two flux methods described above were used to construct a NMR catchment nitrogen budget (eq 1).

\[
\text{DIN}_{\text{export}} = (\text{DIN}_{\text{ADN}} + \text{DIN}_{\text{sewage}} + \text{DIN}_{\text{fertilizer}}) \\
\times (1 - \text{Retention})
\]

Inputs to the watershed, reported in kg ha$^{-1}$ yr$^{-1}$, include DIN$_{\text{ADN}}$ (where ADN is atmospherically deposited nitrogen, consisting of total atmospheric dry and wet nitrogen species), DIN$_{\text{fertilizer}}$ (DIN contributed from lawn fertilizer), and DIN$_{\text{sewage}}$ (DIN contributed from sewage). Export from the
wastewater, DIN\textsubscript{export} is the sum of observed nitrate, nitrite, and ammonium concentrations (kg ha\textsuperscript{-1} yr\textsuperscript{-1}) in NMR streamwater (DIN = (NO\textsubscript{3}-N) + (NO\textsubscript{2}-N) + (NH\textsubscript{4}\textsuperscript{+}-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.\textsuperscript{24} Using application rates from Baltimore,\textsuperscript{24} when the age of NMR neighborhoods (53\% of housing stock built before 1939, and 76.9\% built before 1959\textsuperscript{25}) 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\textsuperscript{-1} yr\textsuperscript{-1}.

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.

\[
\text{DIN}_{\text{sewage}} = \left( \frac{\text{DIN}_{\text{export}}}{1 - \text{Retention}} \right) - \left( \text{DIN}_{\text{ADN}} + \text{DIN}_{\text{fertilizer}} \right)
\]

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\textsuperscript{26} using the “mcsm” package.\textsuperscript{27} Annual export was estimated using both methods described above, and the resulting values were used to bound a distribution of export estimates (uniform distribution, 3.4–5.6 kg ha\textsuperscript{-1} yr\textsuperscript{-1}). Southwestern Pennsylvania receives some of the highest rates of nitrate deposition nationwide (17–21 kg ha\textsuperscript{-1} yr\textsuperscript{-1}).\textsuperscript{28} 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.\textsuperscript{28–30} Thus, two scenarios utilizing deposition rates for rural areas likely represent a low estimate of ADN reaching urban surfaces.\textsuperscript{31,32}

While measurements of urban N deposition are scarce, measurements of dry ADN (NO\textsubscript{2} + HNO\textsubscript{3}) in Pittsburgh in an ongoing study are 2.3 times higher than those measured at the nearest dry deposition monitoring locations.\textsuperscript{30} Therefore, two scenarios use a “high” ADN distribution (Table 1) by assuming the same ratio of wet to dry deposition in urban and rural setting 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). Fertilizer inputs were calculated as described above and a normal distribution was 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 1\textsuperscript{5,23,33}), 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).

Table 1. Monte Carlo Simulations and Results\textsuperscript{a}

<table>
<thead>
<tr>
<th>Scenario number</th>
<th>Scenario description</th>
<th>ADN [kg ha\textsuperscript{-1} yr\textsuperscript{-1}]</th>
<th>Fertilizer [kg ha\textsuperscript{-1} yr\textsuperscript{-1}]</th>
<th>Retention [percent]</th>
<th>Estimated sewage DIN export [kg ha\textsuperscript{-1} yr\textsuperscript{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Low ADN, low retention</td>
<td>3.6 ± 0.84</td>
<td>4.2 ± 2</td>
<td>65 ± 15</td>
<td>6 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>High ADN, low retention</td>
<td>8.3 ± 1.66</td>
<td>4.2 ± 2</td>
<td>65 ± 15</td>
<td>2 ± 0.4</td>
</tr>
<tr>
<td>3</td>
<td>High ADN, high retention</td>
<td>8.3 ± 1.66</td>
<td>4.2 ± 2</td>
<td>75 ± 15</td>
<td>7 ± 2</td>
</tr>
<tr>
<td>4</td>
<td>Low ADN, high retention</td>
<td>3.6 ± 0.84</td>
<td>4.2 ± 2</td>
<td>75 ± 15</td>
<td>14 ± 4</td>
</tr>
</tbody>
</table>

\textsuperscript{a}All data distributions for ADN and retention were uniform.

Table 2. Characteristics and Retention in Urban Watershed Studies\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Study</th>
<th>Watershed</th>
<th>Landcover/landuse</th>
<th>Watershed size (ha)</th>
<th>Impervious surface %</th>
<th>Population density (per ha)</th>
<th>Inputs assumed</th>
<th>Retention %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaushal et al. 2008</td>
<td>Dead Run</td>
<td>suburban/urban</td>
<td>1414</td>
<td>41</td>
<td>12.6</td>
<td>lawn fertilizer, ADN</td>
<td>29–84</td>
</tr>
<tr>
<td>Groffman et al. 2004</td>
<td>Glyndon</td>
<td>suburban</td>
<td>81</td>
<td>22</td>
<td>9.4</td>
<td>lawn fertilizer, ADN</td>
<td>75</td>
</tr>
<tr>
<td>Groffman et al. 2004</td>
<td>Pond Branch</td>
<td>forested</td>
<td>32</td>
<td>0</td>
<td>0.0</td>
<td>ADN</td>
<td>95</td>
</tr>
<tr>
<td>Wollheim 2005</td>
<td>Sawmill Brook</td>
<td>suburban</td>
<td>810</td>
<td>25</td>
<td>9.8</td>
<td>lawn fertilizer, ADN, septic</td>
<td>78–85</td>
</tr>
<tr>
<td>This Study</td>
<td>NMR</td>
<td>urban</td>
<td>1570</td>
<td>38</td>
<td>30.0</td>
<td>lawn fertilizer, sewage, ADN</td>
<td>60–93</td>
</tr>
</tbody>
</table>

\textsuperscript{a,b}For the Kaushal et al.\textsuperscript{33} study, values were calculated assuming fertilizer application rates used in the rest of the study, 14.4 kg ha\textsuperscript{-1} yr\textsuperscript{-1}. Without assumed lawn fertilizer inputs, retention was 50\%. Values for the forested “Pond Branch” watershed (Groffman et al.) are shown for comparison between forested and urban watersheds.

RESULTS AND DISCUSSION

Precipitation and Discharge in NMR. Over the sampling period, measured discharges ranged from 0.02 to 2.31 m\textsuperscript{3} s\textsuperscript{-1}. Average rainfall in Pittsburgh is 936 mm.\textsuperscript{34} Accordingly, 2007 was a wet year (1018 mm), 2008 was an average year (963 mm), and 2009 was 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 m below stream stage over the available groundwater record (Figure S2). Contrary to “normal” stream conditions, this implies that flux is from the stream to groundwater in representative stream reaches.

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). When
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 3). 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 S1). 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$^3$ s$^{-1}$), low nitrate-N (1–1.8 mgL$^{-1}$) 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 4). While water 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 biweekly 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 0.7 to 3.8 at NMR3 (Figure 3). These observed concentrations were comparable to nitrate concentrations reported for other urban watersheds.\cite{5,33} At Fern Hollow 1 (FH1), streamwater nitrate concentrations were consistently 30–50% of those observed in NMR1, 2, and 3 (Figure 3). The highest nitrate-N concentration measured at FH1 was 1.3 mgL$^{-1}$ and the lowest was 0.4 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$^{-1}$.

Figure 2. Concentrations of nitrate-N, nitrite-N, and ammonium-N 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 3. Nitrate-N (in mgL$^{-1}$) concentrations at each sampling location over the sampling time period. “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 4. 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.

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The FH tributary drains a subwatershed that includes nonsewered parkland and a city cemetery (together comprising 43% of subwatershed). The FH subwatershed 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 corroborate the importance of leaking sewers to observed DIN concentrations.

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 (3.4−5.6 kg ha$^{-1}$ yr$^{-1}$, respectively).

Four scenarios were constructed to explore potential sewage-derived DIN to NMR using inverse modeling and Monte Carlo simulation (Table 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 5). At this level of inputs, the sewage input is essentially equivalent to export (3.4 and 3.7 kg ha$^{-1}$ yr$^{-1}$, respectively).

In Scenario 2, ADN is increased to a more realistic deposition rate based on observations in Pittsburgh30 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 5). 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 nonpoint 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 5). This load represents between 20 and 36% of the total DIN exported from NMR (Table 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 and 64% of total DIN inputs to NMR. Based on knowledge of vehicular emission rates, the fate and transport of NO$\scriptsize{x}$ emission sources, and ongoing efforts in Pittsburgh to quantify rates of urban N deposition, 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. The following section explores urban DIN retention estimates and potential mechanisms, both important to restoration and management of urban systems.

Urban DIN Retention and Potential Mechanisms. To constrain the range of DIN retention rates, Monte Carlo analysis was used to sample 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 6). 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). 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 (6–14 kg ha⁻¹ yr⁻¹) are added to other urban watershed budgets as reported (Table 2), retention rates for these sites would increase between 3.5 and 14%.

Why does DIN Retention in Urbanized Watersheds Approach That Observed in Forested Systems (Table 2)? Fundamentally, the impact of DIN on downstream systems is strongly dependent on the hydrologic connectivity between nitrogen source and surface waters. 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, suggesting similar retention of DIN from lawns 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 which promote denitrification (retention) of sewage-sourced nitrogen. 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). A network of leaking pipes may thus form a network of denitrification hotspots in urban environments throughout the watershed. 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.

Dissolved Organic Nitrogen (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. For example, Wollheim et al. observed 13% of total N exported as DON from an urban watershed. 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 preclude incorporation of DON into watershed budgets, yet make this an important area of future research.

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 per year and a watershed population density of 30 people per ha). 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. This infrastructure crisis faces a projected 180.6 billion dollar funding gap in the next 5 years alone. 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.
ASSOCIATED CONTENT

Supporting Information

Monitoring well data and stream stage reconstructions, sensitivity analysis of Monte Carlo analysis, a map of watershed sewer lines, the stream hydrograph during the sampling period, and further details about the calculation of DIN export. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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