Riverine nitrogen source and yield in urban systems

Angela H Chung[1*], Emily M Elliott[1], Daniel J Bain[1], Brian F Thomas[1,2], Mark River[1], Carl J Nim[3], and Julie A Darden[1]

Although human reshaping of the nitrogen (N) cycle is well established, contributions of individual N sources to riverine and coastal eutrophication are less certain. Urban N fluxes are potentially substantial, particularly from sewer overflows. Results from four longitudinal surveys in rivers in and around the city of Pittsburgh, Pennsylvania, were used to characterize N chemistry and isotopic composition and were compared with LOADEST-model-derived total N (TN) flux budgets from three urban areas along the Ohio River (Pittsburgh, Pennsylvania; Cincinnati, Ohio; and Louisville, Kentucky). Triple nitrate isotopes reveal that riverine nitrate in the Pittsburgh region is dominated by wastewater inputs despite high atmospheric deposition rates. Our budget estimates demonstrate that the magnitude of urban N yields is comparable to yields reported for agricultural watersheds and that these high urban N yields cannot consist of permitted, point-source discharges alone. Our results reveal that nonpoint sources in urban systems represent an important but overlooked source of TN to overall riverine budgets.

Front Ecol Environ 2023; doi:10.1002/fee.2679

Excess nitrogen (N) is a primary cause of water-quality impairment in lakes, rivers, and estuaries worldwide (eg Alexander *et al.* 2008; Robertson *et al.* 2009; Robertson and Saad 2013). Nutrient enrichment accelerates algal growth, eventually depleting dissolved oxygen in freshwater, negatively impacting other biota. A prominent example of the impacts of excess N is the hypoxic "dead zone" that has formed in the Gulf of Mexico almost every summer for the past 30 years (Rabalais *et al.* 2002). Established by the Environmental Protection Agency in 1997, the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force (also known as the Hypoxia Task Force) recommended a 20% reduction in total N (TN) load delivered to the Gulf by 2025 to begin to address the hypoxia issue (EPA 2015). While agricultural watersheds contribute substantial amounts of N to rivers (eg David *et al.* 1997), urban watersheds can also be a major N source (Lin *et al.* 2018). However, in contrast to agricultural watersheds, urban N fluxes are poorly characterized and their influence on eutrophication remains ambiguous. To effectively manage nutrient loads to freshwater and coastal ecosystems, the relative contribution of urban point and nonpoint sources to riverine N fluxes requires clarification.

Budget approaches have clarified N dynamics within focal points of urban watershed work in such cities as Baltimore, Maryland (Groffman *et al.* 2004); Phoenix, Arizona (Hale *et al.* 2014); and Minneapolis, Minnesota (Hobbie *et al.* 2017). Furthermore, urban watersheds located near estuaries have also been a focus for water-quality investigations (Oelsner and Stets 2019). However, to our knowledge, no study to date has fully accounted for a potentially large nonpoint source of N to urban rivers: namely, untreated wastewater effluent originating from leaking sanitary sewer infrastructure and contaminated groundwater systems, as well as wet-weather discharges from point-source combined sewer overflows (CSOs). (Note: In a combined sewer system, wastewater and stormwater are conveyed through a single pipe. If precipitation exceeds the collection system's capacity, the systems are designed to overflow and discharge directly to surface waters. This discharge is called a CSO and it brings untreated sewage, debris, and other pollutants into surface waters.) In a smaller urban Pittsburgh tributary, both inverse modeling and nitrate isotope analyses revealed that over 90% of streamwater nitrate during dry weather (ie periods when CSOs are not discharging) originated from untreated sewage (Divers *et al.* 2013, 2014). In cities along the Ohio River (eg Pittsburgh, Louisville, and Cincinnati), sewer systems are typical of those in other urban areas around the Laurentian Great Lakes and in the Midwest US: namely, systems are more than a century old, have exceeded their design life, and are in poor condition (eg Hopkins and Bain 2018). Leakage from failing infrastructure is exacerbated by climatic shifts that have ushered in more frequent and intense precipitation events (Lai and Dzombak 2019). Together, this increased infrastructural strain creates a critical need to evaluate the importance of untreated sewage as a source of N to streams, rivers, and downstream aquatic ecosystems.

Relative to that in other basins, N dynamics in the Ohio basin are less studied (David *et al.* 1997; Hobbie *et al.* 2017; Loken *et al.* 2018) despite the substantial contributions of water (and therefore TN) to the Ohio River (38%, the single largest contributor of water to the Mississippi River). For example, atmospheric N deposition in the Upper Ohio River basin has historically been among the highest in the US

[1]*Department of Geology and Environmental Sciences, University of Pittsburgh, Pittsburgh, PA* [*]*(ahc32@pitt.edu, angela.h.chung@nasa.gov);* [2]*School of Engineering, Newcastle University, Newcastle upon Tyne, UK;* [3]*US Army Corps of Engineers, Pittsburgh District, Pittsburgh, PA*

(1700–2100 kg N km^{-2} yr^{-1}) due to the concentration of coal-fired power plants along the Ohio River (Elliott *et al.* 2007). Furthermore, the substantial number of combined and sanitary sewer overflows along the river poses not only a critical water-quality problem but also a public health risk. Sewer overflow outfalls are notably dense in the greater Pittsburgh area, with 514 sewage overflows. Other major metropolitan areas on the Ohio River – Cincinnati and Louisville – have 206 and 137 CSO outfalls, respectively (EPA 2004). Clarification of the N contributions from Pittsburgh (and other cities) to riverine N fluxes can allow for more targeted N management in the Ohio River and beyond.

Here, we investigated urban influences on N delivery to major rivers using longitudinal sampling surveys as well as chemical and stable isotope analyses in Pittsburgh. Nitrate isotopes, including $\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$, were used to evaluate nitrate origin and the relative extent of biological processing in riverine samples. Mass-dependent nitrate isotopes, $\delta^{15}N$ and $\delta^{18}O$, distinguish waste-derived nitrate from soils and fertilizers, as well as the relative extent of denitrification (Kendall *et al.* 2007), whereas $\Delta^{17}O$ is a mass-independent tracer used to unambiguously quantify contributions of atmospheric nitrate (Kendall *et al.* 2007). Accordingly, nitrate in CSO effluent is expected to have positive $\Delta^{17}O$ values from stormwater runoff containing unprocessed atmospheric nitrate and high $\delta^{15}N$ values from untreated sewage. These isotopic investigations are placed in a larger context by estimating TN flux budgets for three large urban areas along the Ohio River: Pittsburgh, Cincinnati, and Louisville. The regression-based model LOADEST ("load estimator") was used to estimate TN yield from 2012 to 2019 for available gage data (Figure 1). Together, these approaches aim to discern urban contributions to riverine N exports.

Methods

Four longitudinal sampling trips were conducted along the Allegheny, Monongahela, and Ohio rivers (14 Aug 2016, n = 28 samples; 24 Oct 2016, n = 30 samples; 21 Aug 2017, n = 34 samples; and 21 Jun 2018, n = 38 samples). Samples were collected for chemical and isotopic analysis every ~1.5 km beginning at the location farthest upstream and proceeding downstream (WebFigure 1). Water samples were collected mid-channel at 0.5 m below the surface, filtered immediately using 0.2 µm polyethersulfone membrane filters, and frozen in high-density polyethylene bottles triple rinsed with 18 MΩ ultrapure water. Concentrations of nitrate and phosphate were measured on a Lachat QuikChem Flow Injection Analyzer.

The denitrifier method was used to convert sample NO_3^- (nitrate) into N_2O (nitrous oxide), enabling measurement of $\delta^{15}N$ and $\delta^{18}O$ of nitrate (Sigman *et al.* 2001) on an Isoprime Continuous Flow Isotope Ratio Mass Spectrometer (CF-IRMS) at the University of Pittsburgh. Measurements were corrected using international reference standards USGS-32, USGS-34, and IAEA-N3. The average standard deviations of sample duplicates were 0.20 parts per thousand (0.20‰) for $\delta^{15}N$–NO_3^- and 0.19‰ for $\delta^{18}O$–NO_3^-. To quantify $\Delta^{17}O$ values, N_2O produced with the denitrifier method was thermally decomposed at 875°C into N_2 and O_2 and analyzed with the CF-IRMS (Kaiser *et al.* 2007). USGS-34 and USGS-35 standards were used to correct $\Delta^{17}O$–NO_3^- values. $\Delta^{17}O$–NO_3^- is reported in units of parts per thousand following Equation 1:

$$\Delta^{17}O\,(‰) = 1000\ln\left(1+\delta^{17}O/1000\right) - \neg\lambda 1000\ln\left(1+\delta^{18}O/1000\right) \quad \text{(Equation 1)},$$

where λ is the slope of the mass-dependent fractionation line and equals 0.52 (Kaiser *et al.* 2007). Duplicate $\Delta^{17}O$ measurements had an average standard deviation of 0.3‰. All statistical tests were completed in R (v3.4.4).

To evaluate TN flux changes along the Ohio River, estimates of TN fluxes were developed using LOADEST (Runkel *et al.* 2004). We calculated TN fluxes for gage stations surrounding Pittsburgh, Cincinnati, and Louisville (Figure 1), including stations on tributaries that flow into the Ohio River. TN concentration and instantaneous discharge data were collected from the US Geological Survey (USGS) National Water Information System (NWIS), the Ohio River Valley Water Sanitation Commission (ORSANCO) water-quality monitoring program (ORSANCO 2021), and the STORET data repository (WebTables 2 and 3). TN flux was calculated by subtracting the sum of all upstream stations' inputs from the downstream station output flux. Pittsburgh fluxes were based on the following USGS stations: Sewickley (03086000, Ohio River), Kittanning (03036500, Allegheny River), and Elizabeth (03075070, Monongahela River). Two gage stations, one on the Youghiogheny River (a tributary of the Monongahela River, 03083500) and one on the Conemaugh River (a tributary of the Allegheny River, 03044000), were used to estimate TN fluxes into the greater Pittsburgh area (Table 1). Estimates for Cincinnati and Louisville were based on combinations of water-quality data from ORSANCO and discharge data from USGS gage stations. For Cincinnati, the following ORSANCO station/USGS station pairs were used: ORSANCO Meldahl and USGS Greenup Dam (03216600, Ohio River); ORSANCO Newtown and USGS Milford (03245500, Little Miami River); ORSANCO Covington and USGS Alexandria (03254520, Licking River); ORSANCO Elizabethtown and USGS Hamilton (03274000, Great Miami River); and ORSANCO Markland and USGS Markland Dam (03277200, Ohio River). For the Meldahl/Greenup Dam station pair, there is a substantial distance between the discharge measurement and the water-quality measurement, and therefore discharge from Greenup Dam was adjusted by a factor of 1.14 to account for the additional drainage area at the Meldahl

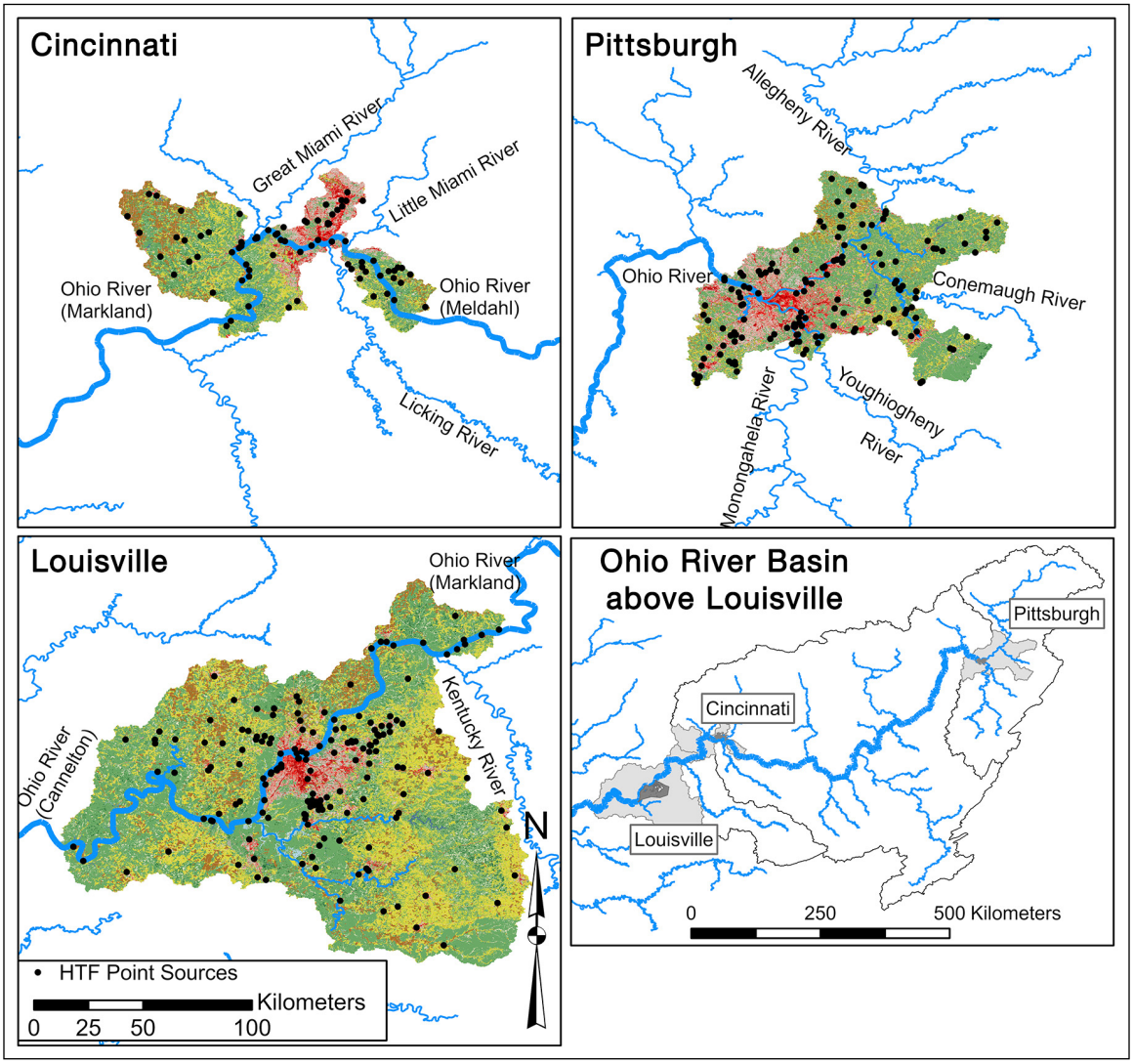

Figure 1. Map of area used in LOADEST total nitrogen flux estimates. Watershed areas were defined by gaging/monitoring stations with available data. Color indicates land-use type based on standard US Geological Survey palettes (USGS 2021). HTF = Hypoxia Task Force.

station (160,600 km^2 and 183,100 km^2 are the drainage areas upriver of the Greenup Dam and Meldahl site, respectively). For Louisville, these site pairs were used: ORSANCO Markland and USGS Markland Dam (03277200, Ohio River); ORSANCO Cannelton and USGS Cannelton Dam (03303280, Ohio River); and ORSANCO Lockport and USGS Lockport (03290500, Kentucky River).

LOADEST requires 12 or more nonzero observations for a constituent to estimate fluxes over a user-specified time interval (Runkel *et al.* 2004). Due to data availability constraints (ie 12 observations minimum), TN fluxes over 2-year intervals were estimated over the period 2012–2019, which bracketed the timeframe of our riverine sampling. For certain stations, available measurements of TN concentrations fell short of the required 12 observations for a calibrated LOADEST estimate. Stations with inadequate data were left blank. The adjusted maximum likelihood estimation (AMLE) flux estimate results from LOADEST were used (WebPanel 1). We assessed LOADEST performance on a station-by-station basis with goodness-of-fit (WebTable 1). Standard errors in mean flux estimates calculated with methods described in Gilroy *et al.* ([1990], equations 9–25 therein) represent uncertainties stemming from model calibration and are propagated through flux difference calculations. To enable comparisons across cities and the wider literature, we then calculated TN yields by dividing TN flux by drainage area (defined by the downstream and various upstream gages). The urban areas used to calculate yields were 5472 km^2, 3927 km^2, and 16,710 km^2 for Pittsburgh, Cincinnati, and Louisville, respectively. In cases where data were insufficient to constrain N flux additions to urban areas, we did not report a flux difference. For instance, except for the most recent study period, Kentucky River data were not sufficient to estimate inputs to the Louisville area.

To estimate point-source inputs of TN in the urban areas, all facilities within the respective study area (Figure 1) with reported or simulated TN discharges in the Hypoxia Task Force nutrient model (EPA 2017) were summed for each annual period (2012–2013, 2014–2015, 2016–2017, and 2018–2019). Average TN flux (kilograms per day) for each 2-year period was compared with the estimated additional TN flux downstream of each urban area.

Results and discussion

Nitrate sources and sinks

In the four longitudinal sampling trips on the Allegheny, Monongahela, and Ohio rivers, nitrate comprised an average of 55% of TN measured across all sampling dates and locations, whereas ammonium and organic N were, on average, 12% and 39% of TN concentrations, respectively (data not shown). $\delta^{15}N–NO_3^-$ values from measurements from all sampling dates ranged from +5.3‰ to +14.5‰ and fall within ranges reported for nitrate derived from human sewage or animal waste (generally 5‰ to 25‰) or from nitrification of ammonium in soils (generally 2‰ to 7‰) (Kendall *et al.* 2007). $\delta^{18}O–NO_3^-$ values ranged from –2.3‰ to +5.3‰ (Figure 2) and fall within the range of $\delta^{18}O–NO_3^-$ values reported for terrestrial nitrate sources, including sewage, manure, fertilizer, and soil nitrification, relative to those from atmospheric deposition (60‰ to 90‰; Kendall *et al.* 2007). Although there was no significant difference in mean $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ values among the sampling dates (mean ranks were the same at the 0.05 α-level using the non-parametric Kruskal-Wallis test; P = 0.463), riverine nutrient concentrations and nitrate isotopes were found to generally vary with distance downriver (Figure 2). In addition, $\delta^{15}N$ values generally increased longitudinally in each river, whereas $\delta^{18}O$ values increased toward the confluence and generally decreased with distance down the Ohio River (Figure 2). Total N and phosphate concentrations increased with distance downriver in the Monongahela River and the Ohio River (Figure 2), whereas nitrate concentrations increased downriver in the Monongahela River (not shown). Spatial patterns in the Allegheny River were less pronounced (Figure 2). Given the spatial location of 514 permitted sewer overflows in the Pittsburgh urban region, downriver flows are subject to more nutrient inputs from sewer overflows, as well as to leaking sewer infrastructure and groundwater inputs. Together, the ranges in isotopic composition, coupled with the longitudinal profiles of $\delta^{15}N$

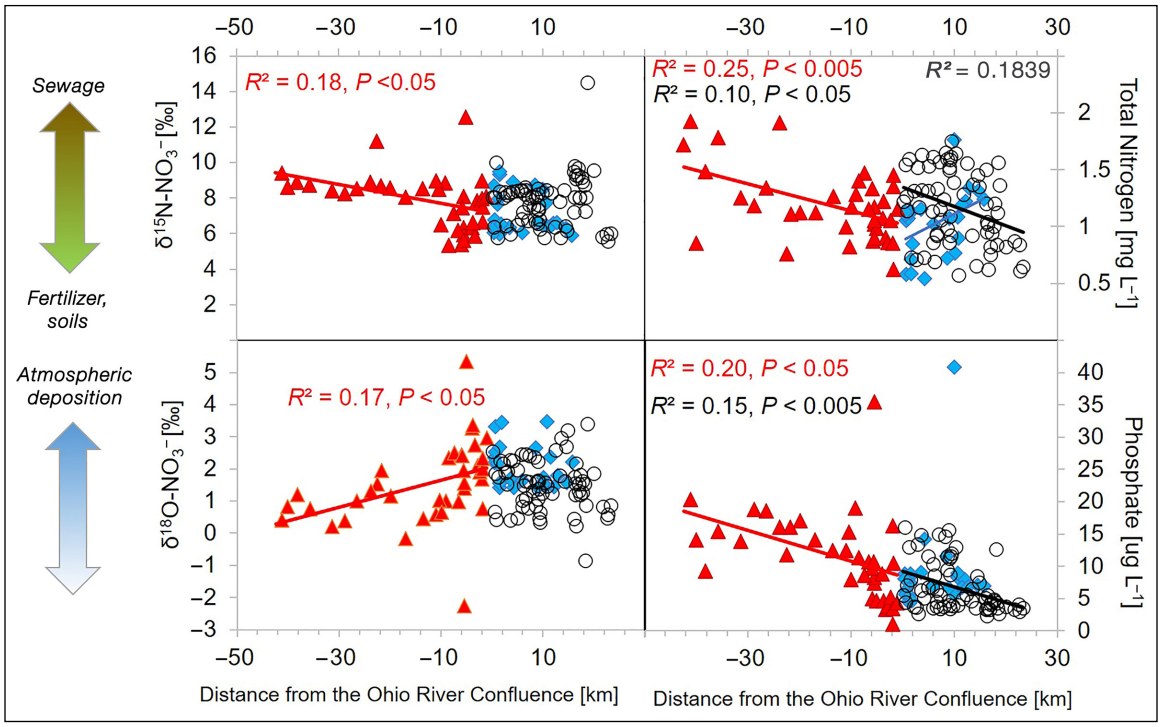

Figure 2. Longitudinal changes in riverine nitrate isotopes ($\delta^{15}N$, $\delta^{18}O$), total nitrogen, and phosphate concentrations from four sampling dates: 14 Aug 2016, 24 Oct 2016, 21 Aug 2017, and 21 Jun 2018. Longitudinal distance is shown with respect to the Ohio River confluence (0 km), where the Allegheny and Monongahela rivers join. Samples collected from each river are denoted by red triangles (Ohio River), blue diamonds (Allegheny River), and white circles (Monongahela River). The cumulative number of combined sewer overflows (CSOs) influencing riverine chemistry increases with distance downriver. For $\delta^{15}N–NO_3^-$ values (top-left panel), arrow in margin denotes direction of $\delta^{15}N$ values in nitrate originating from sewage (5‰ to 25‰) relative to other sources. For $\delta^{18}O–NO_3^-$ values (bottom-left panel), arrow in margin denotes direction of $\delta^{18}O$ values in nitrate originating from atmospheric deposition (60‰ to 90‰) relative to other sources.

Table 1. LOADEST estimates of mean daily total nitrogen (TN) fluxes for Pittsburgh, Cincinnati, and Louisville based on 2012–2019 data in 2-year increments

Year	TN flux in (kg per day)				TN flux out (kg per day)	TN added from urban area (kg per day)	Point source TN flux added within urban area (kg per day)
Pittsburgh, Pennsylvania							
	Elizabeth (Monongahela River)	Kittanning (Allegheny River)	Tunnelton (Conemaugh River)	Sutersville (Youghiogheny River)	Sewickley (Ohio River)		
2012–2013	15,839 (±905)			8694 (±798)	75,631 (±4171)		19,353
2014–2015	15,499 (±1080)		7513 (±469)	8722 (±391)	86,934 (±4225)		18,366
2016–2017	19,162 (±667)	32,045 (±3349)	7280 (±408)	9283 (±460)	85,041 (±3260)	17,271 (±4760)	18,596
2018–2019	24,873 (±1179)	3721 (±5017)	11,466 (±585)	16,254 (±1026)	121,121 (±4083)	24,807 (±6680)	18,605
Cincinnati, Ohio							
	Meldahl (Ohio River)	Newtown (Little Miami River)	Covington (Licking River)	Elizabethtown (Great Miami River)	Markland (Ohio River)		
2012–2013	244,990 (±22,794)	7731 (±864)	13,418 (±5812)	52,154 (±4841)	377,172 (±21,990)	58,879 (±32,574)	17,211
2014–2015	372,474 (±39,744)	10,965 (±794)	26,570 (±4894)	48,068 (±3365)	485,545 (±49,023)	27,468 (±63,393)	19,635
2016–2017	366,910 (±37,358)	10,601 (±1002)	10,441 (±1773)	48,725 (±7204)	459,069 (±59,044)	22,392 (±70,269)	16,723
2018–2019							20,078
Louisville, Kentucky							
	Markland (Ohio River)	Lockport (Kentucky River)			Cannelton (Ohio River)		
2012–2013	377,172 (±21,990)				441,661 (±9254)		
2014–2015	485,545 (±49,023)				621,806 (±48,099)		7498
2016–2017	459,069 (±59,044)				550,121 (± 56,418)		7374
2018–2019		33,808 (±2497)			720,481 (±25,056)		8345

Notes: Each column reports LOADEST results from stations with available TN concentration data, with LOADEST generated standard errors reported in parentheses. Stations with insufficient data were left blank. The "TN added" column was calculated by subtracting the sum of all flux inputs from outputs. In years where certain stations had inadequate data for calculating flux estimates, "TN added" was also left blank.

values, TN, and phosphate concentrations, document the cumulative influence of sewage-derived nitrate increases in the urban area. In the Ohio River, higher $\delta^{18}O$ values near the confluence suggest decreasing atmospheric nitrate contributions from stormwater runoff as the river flows downstream from Pittsburgh. This presumption is affirmed by measured $\Delta^{17}O$–NO_3^- values, a conservative tracer of atmospheric nitrate. Although ranges of $\Delta^{17}O$ values were generally low (–1.9‰ to +0.5‰) relative to atmospheric nitrate values (20‰ to 30‰), they are similar to values reported for other major rivers, such as China's Yellow River (0‰ to 1.6‰) (Liu *et al.* 2013; Dejwakh *et al.* 2012). In the baseflow conditions sampled for this study, a maximum of 2% of riverine nitrate was derived from unprocessed atmospheric nitrate (assuming precipitation $\Delta^{17}O$–NO_3^- = 24‰). Given high rates of atmospheric deposition in the region and the magnitude of urban stormwater runoff, the results indicate that most atmospheric nitrate is quickly cycled prior to or upon entering the rivers, thus diminishing the detectable atmospheric nitrate isotopic signal during baseflow conditions. However, the results also reflect the fact that atmospheric nitrate deposition is a small portion (<0.03%) of the total daily N exported from urban Pittsburgh.

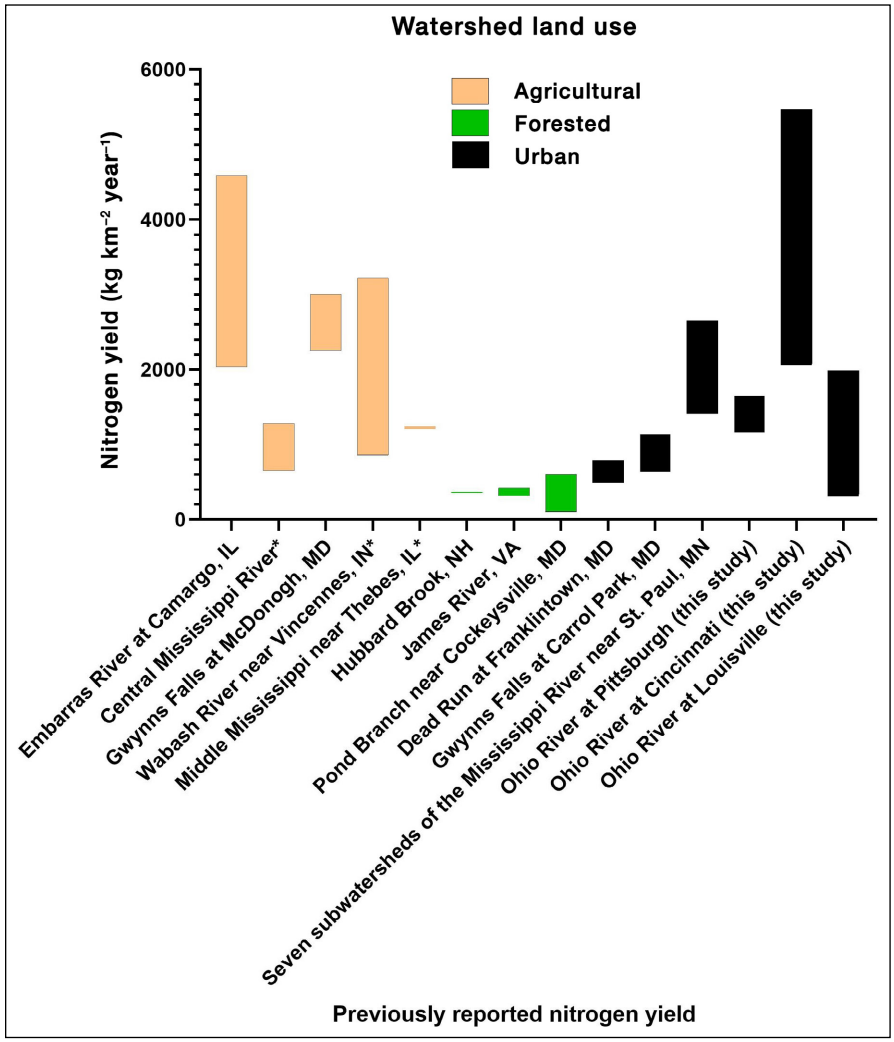

Figure 3. Nitrogen yields for watersheds under different dominant land uses reported in previous studies – Hubbard Brook, New Hampshire (Likens and Bormann 1995); Embarras River, Illinois (David *et al.* 1997); James River, Virginia (Boyer *et al.* 2002); Dead Run at Franklintown, Maryland, and Gwynns Falls at Carrol Park, Maryland (Groffman *et al.* 2004); Central Mississippi River (Alexander *et al.* 2008); Gwynns Falls tributary at McDonogh, Maryland, and Pond Branch near Cockeysville, Maryland (Shields *et al.* 2008); Wabash River, Indiana (Robertson *et al.* 2009); Middle Mississippi River near Thebes, Illinois (Robertson and Saad 2013); and seven subwatersheds of the Mississippi River near St Paul, Minnesota (Hobbie *et al.* 2017) – were compared to yields estimated in this study. Land uses for watersheds were designated according to the land use reported by each respective study. Watersheds marked with an asterisk (*) were selected from studies reporting yields using the statistical/mechanistic watershed model SPARROW (Spatially Reference Regression On Watershed attributes).

Denitrification, the microbially mediated reduction of nitrate to gaseous N_2O or N_2, can be a major sink for riverine N. Although denitrification measurements were beyond the scope of this study, several lines of evidence support that water-column denitrification was not a major sink for urban TN. First, $\delta^{15}N$–NO_3^- values are not correlated with nitrate concentrations for any river (not shown, $R^2 < 0.05$). Second, the slope of $\delta^{15}N$–NO_3^- and $\delta^{18}O$–NO_3^- values ranged from –0.9 to 0.32, which is generally outside the expected slope of 1 that typically occurs during denitrification (WebFigure 3; Kendall *et al.* 2007; Granger and Wankel 2016). Third, high dissolved oxygen concentrations (7.5–11.5 mg L^{-1}) were observed during sampling and would limit denitrification reactions. Moreover, previous studies have reported minimal denitrification in impounded reaches of the Mississippi River, where nitrate retention is relatively low (12.5%; Loken *et al.* 2018). Therefore, although we cannot definitively quantify the influence of denitrification on N retention and export, our results suggest that N loads, once in the Ohio River, undergo minimal denitrification, and thus likely contribute to Mississippi River N flux and ultimately N delivery to the Gulf of Mexico.

Urban river N flux, point sources, and yields

Our TN export budget calculated using LOADEST indicated increased TN flux in the Ohio River below the Pittsburgh, Cincinnati, and Louisville urban areas relative to TN fluxes from upstream river sources (Figure 1). The TN added within urban study areas (Figure 1) varied considerably both across stations and years. In contrast, average point source flux sums were consistent in

all three cities across the time periods of interest (Table 1). The urban additions to TN flux inferred at downstream monitoring stations were generally larger than summed TN fluxes from point sources. Regardless, point sources of N cannot account for observed TN fluxes added to the rivers by urban centers.

To enable comparison across cities and land-use types, we calculated TN yields by dividing TN flux by drainage area (defined by the downstream and various upstream gages) (Figure 1). For Louisville yield approximations, the 2018–2019 Kentucky River flux was included as an input in all study periods. Estimated yields from the urban areas were substantial as compared to yields reported in the literature (Figure 3). TN yields from urban areas varied widely (Pittsburgh [1152–1654 kg km^{-2} yr^{-1}], Cincinnati [2081–5472 kg km^{-2} yr^{-1}], and Louisville [670–2237 kg km^{-2} yr^{-1}]), were similar to or larger than TN yields reported for areas dominated by agriculture (David *et al*. 1997; Alexander *et al*. 2008; Robertson *et al*. 2009; Robertson and Saad 2013), and were generally higher than urban yields in Baltimore (863 kg km^{-2} yr^{-1}) (Figure 3; Groffman *et al*. 2004).

The large yield estimates for Cincinnati are noteworthy. They are both higher than what is typically found in intensely fertilized agricultural systems (David *et al*. 1997) and higher than similar estimates for Pittsburgh and Louisville. The Cincinnati yield estimates are also generally higher than estimates from separated sewer systems (eg Baltimore; Shields *et al*. 2008) and comparable to previous estimates of combined systems (eg Minneapolis; Hobbie *et al*. 2017). This outcome may be due in part to the larger urban areas used to calculate yield in Pittsburgh and Louisville relative to that in Cincinnati. The larger Cincinnati yields also highlight the potential for large magnitude urban inputs. Although some of the Cincinnati yield magnitude may result from data limitations that required the use of Greenup Dam discharge data for the Meldahl site, this approach was conservative and thus would have led to underestimations of Cincinnati yields. These high yields underscore the importance of clarifying urban contributions in comprehensive basin nutrient analyses.

All three Ohio River urban systems were found to contribute substantial N flux to the river, and this flux is generally in excess of known point-source inputs. The consistently high $\delta^{15}N–NO_3$ values observed for Pittsburgh indicate that sewage is most likely the dominant nitrate source, whereas the $\Delta^{17}O–NO_3^-$ values confirm that there is minimal unprocessed atmospheric nitrate deposition contributing to the TN flux. In addition, TN export estimates coupled with insights into N transformations from dual nitrate isotopes suggest that minimal N is being removed from the river channel. Together, these findings indicate that urban systems can be important sources of TN to downstream receiving waters. Such urban nutrient inputs are potential foci for nutrient reduction measures in efforts to reduce TN export to coastal systems.

Acknowledgements

This research was supported by US National Science Foundation grants #1253000 and #1939977 to EME. Additional funding was provided by an Andrew Mellon Predoctoral Fellowship, a Geological Society of America Graduate Student Research Grant, and the Heinz Endowments to the Pittsburgh Collaboratory for Water Research, Education, and Outreach. Much gratitude is owed to G Brkovich of the US Army Corps of Engineers for his assistance in the field. Additional fieldwork was made possible by D Sanchez. We thank R Dabundo, B Forgrave, Z Yu, and K Maurer for helpful discussions and sample analysis, and R Sabo for constructive and insightful comments.

Data Availability Statement

Data were previously published and are publicly available, with sources properly cited in the text and in the Supporting Information. For a list of relevant public databases and query details, see WebPanel 2.

References

Alexander RB, Smith RA, Schwarz GE, *et al*. 2008. Differences in phosphorus and nitrogen delivery to the Gulf of Mexico from the Mississippi River Basin. *Environ Sci Technol* **42**: 822–30.

Boyer EW, Goodale CL, Jaworski NA, and Howarth RW. 2002. Anthropogenic N sources and relationships to riverine N export in the northeastern USA. *Biogeochemistry* **57**: 137–69.

David MB, Gentry LE, Kovacic DA, and Smith KM. 1997. N balance in and export from an agricultural watershed. *J Environ Qual* **26**: 1038–48.

Dejwakh NR, Meixner T, Michalski G, and McIntosh J. 2012. Using ^{17}O to investigate nitrate sources and sinks in a semi-arid groundwater system. *Environ Sci Technol* **46**: 745–51.

Divers MT, Elliott EM, and Bain DJ. 2013. Constraining nitrogen inputs to urban streams from leaking sewers using inverse modeling: implications for dissolved inorganic nitrogen (DIN) retention in urban environments. *Environ Sci Technol* **47**: 1816–23.

Divers MT, Elliott EM, and Bain DJ. 2014. Quantification of nitrate sources to an urban stream using dual nitrate isotopes. *Environ Sci Technol* **48**: 10580–87.

Elliott EM, Kendall C, Wankel SD, *et al*. 2007. N isotopes as indicators of NO_x source contributions to atmospheric nitrate deposition across the midwestern and northeastern United States. *Environ Sci Technol* **41**: 7661–67.

EPA (US Environmental Protection Agency). 2004. Report to Congress on impacts and control of combined sewer overflows and sanitary sewer overflows. Washington, DC: EPA.

EPA (US Environmental Protection Agency). 2015. Mississippi River/Gulf of Mexico Watershed Nutrient Task Force report to Congress. Washington, DC: EPA.

EPA (US Environmental Protection Agency). 2017. Hypoxia Task Force nutrient model. Washington, DC: EPA.

Gilroy EJ, Hirsch RM, and Cohn TA. 1990. Mean square error of regression-based constituent transport estimates. *Water Resour Res* **26**: 2069–77.

Granger J and Wankel SD. 2016. Isotopic overprinting of nitrification on denitrification as a ubiquitous and unifying feature of environmental nitrogen cycling. *P Natl Acad Sci USA* **113**: E6391–400.

Groffman PM, Law NL, Belt KT, *et al*. 2004. N fluxes and retention in urban watershed ecosystems. *Ecosystems* **7**: 393–403.

Hale RL, Turnbull L, Earl S, *et al*. 2014. Sources and transport of nitrogen in arid urban watersheds. *Environ Sci Technol* **48**: 6211–19.

Hobbie SE, Finlay JC, Janke BD, *et al*. 2017. Contrasting nitrogen and phosphorus budgets in urban watersheds and implications for managing urban water pollution. *P Natl Acad Sci USA* **114**: 4177–82.

Hopkins KG and Bain DJ. 2018. Research note: mapping spatial patterns in sewer age, material, and proximity to surface waterways to infer sewer leakage hotspots. *Landscape Urban Plan* **170**: 320–24.

Kaiser J, Hastings MG, Houlton BZ, *et al*. 2007. Triple oxygen isotope analysis of nitrate using the denitrifier method and thermal decomposition of N_2O. *Anal Chem* **79**: 599–607.

Kendall C, Elliott EM, and Wankel SD. 2007. Tracing anthropogenic inputs of N to ecosystems. In: Michener RH and Lajtha K (Eds). Stable isotopes in ecology and environmental science. Oxford, UK: Blackwell Publishing.

Lai Y and Dzombak DA. 2019. Use of historical data to assess regional climate change. *J Climate* **32**: 4299–320.

Likens GE and Bormann FH. 1995. Biogeochemistry of a forested ecosystem. New York, NY: Springer Verlag.

Lin J, Böhlke JK, Huang S, *et al*. 2018. Seasonality of nitrate sources and isotopic composition in the Upper Illinois River. *J Hydrol* **568**: 849–61.

Liu T, Wang F, Michalski G, *et al*. 2013. Using ^{15}N, ^{17}O, and ^{18}O to determine nitrate sources in the Yellow River, China. *Environ Sci Technol* **47**: 13412–21.

Loken LC, Crawford JT, Dornblaser MM, *et al*. 2018. Limited nitrate retention capacity in the Upper Mississippi River. *Environ Res Lett* **13**: 074030.

Oelsner GP and Stets EG. 2019. Recent trends in nutrient and sediment loading to coastal areas of the conterminous US: insights and global context. *Sci Total Environ* **654**: 1225–40.

ORSANCO (Ohio River Valley Water Sanitation Commission). 2021. Bimonthly water quality sampling program. Cincinnati, OH: ORSANCO.

Rabalais NN, Turner RE, and Wiseman Jr WJ. 2002. Gulf of Mexico hypoxia, aka "the dead zone". *Annu Rev Ecol Syst* **33**: 235–63.

Robertson DM and Saad DA. 2013. SPARROW models used to understand nutrient sources in the Mississippi/Atchafalaya River Basin. *J Environ Qual* **42**: 1422–40.

Robertson DM, Schwarz GE, Saad DA, and Alexander RB. 2009. Incorporating uncertainty into the ranking of SPARROW model nutrient yields from Mississippi/Atchafalaya River Basin watersheds. *J Am Water Resour As* **45**: 534–49.

Runkel RL, Crawford CG, and Cohn TA. 2004. Load estimator (LOADEST): a FORTRAN program for estimating constituent loads in streams and rivers. Reston, VA: US Geological Survey.

Shields CA, Band LE, Law N, *et al*. 2008. Streamflow distribution of non-point source nitrogen export from urban–rural catchments in the Chesapeake Bay watershed. *Water Resour Res* **44**: W09416.

Sigman DM, Casciotti KL, Andreani M, *et al*. 2001. A bacterial method for the N isotopic analysis of nitrate in seawater and freshwater. *Anal Chem* **73**: 4145–53.

USGS (US Geological Survey). 2021. National Land Cover Database. Reston, VA: USGS.

Supporting Information

Additional, web-only material may be found in the online version of this article at http://onlinelibrary.wiley.com/doi/10.1002/fee.2679/suppinfo