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Water and sediment as sources of phosphate in aquatic ecosystems: The Detroit River and its role in the Laurentian Great Lakes

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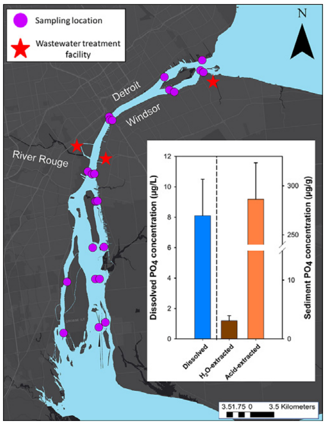
HIGHLIGHTS

- Chemical tracers can identify point and non-point sources of nutrients, including phosphorous.
- Water quality parameters in Detroit River derive from urban runoff and/or fertilizer.
- Legacy mineralized P stored in sediments may impact future water quality.

GRAPHICAL ABSTRACT



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ABSTRACT

Eutrophication of freshwater ecosystems and harmful algal blooms (HABs) are an ongoing concern affecting water quality in the Great Lakes watershed of North America. Despite binational management efforts, Lake Erie has been at the center of dissolved reactive phosphate driven eutrophication research due to its repeated cycles of algae blooms. We investigated the Detroit River, the largest source of water entering Lake Erie, with the objectives to (1) characterize Detroit River phosphate levels within water and sediment, and (2) use multiple chemical and isotopic tracers to identify nutrient sources in the Detroit River. Riverine water and sediment samples were collected at 23 locations across 8 transects of the Detroit River. The bulk δ^{15}N values from sediments were enriched compared the δ^{15}N values of nitrate from water samples, consistent with biogeochemical cycling in the sediment. Principle component analysis of multiple chemical tracers from water samples found spatial variation consistent with multiple sources including synthetic and manure-derived fertilizers and wastewater effluent. The concentrations of phosphate dissolved in water were within regulatory guidelines; however, sediments had elevated concentrations of both water- and acid-extractable phosphate. Sediment-sequestered legacy phosphorus historically deposited in the Detroit River may be transported into Lake Erie and, if mobilized into the

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water column, be an unrecognized internal-load that contributes to algal bloom events. Globally, freshwater ecosystems are impacted by numerous non-point source phosphorus inputs contributing to eutrophication and the use of multiple tracer approaches will increase our ability to effectively manage aquatic ecosystems.

1. Introduction

Freshwater and marine ecosystems are experiencing numerous anthropogenic stressors that threaten ecosystem stability. A pressing concern is the eutrophication of lakes, rivers, and streams from nutrient inputs. Phosphorus and nitrogen from point and non-point sources related to agricultural practices, industrial pollution, and densely populated urban centers are a concern (Cao et al., 2016; Smith, 2003; Smith et al., 2006). Elevated nutrient inputs cause imbalances at the base of food webs that impair ecosystem function (Grman et al., 2010) and community structure (Sayer et al., 2010; Valley et al., 2010). The widespread occurrence of eutrophication and the scale of its impact on aquatic ecosystems is a significant water quality concern for the 21st century (Schindler et al., 2012; Zamparas and Zacharias, 2014).

The Laurentian Great Lakes stand out for the degree of anthropogenic nutrient inputs (Beeton, 1965; Scavia et al., 2014) and the binational efforts between Canada and the United States to develop and implement the Great Lakes Water Quality Agreement (GLWQA, 2012) (see Botts and Muldoon, 2005). Within the Great Lakes basin, Lake Erie has been deemed the most impacted of all the Great Lakes with respect to eutrophication. The intensity of agricultural activity within its watershed as well as the high population density translates into substantial wastewater inputs and industrial runoff (Conroy et al., 2005; Maguire et al., 2018; Paytan et al., 2017). Lake Erie was known as the “Dead Sea of America” by the mid-20th century (Ludsin et al., 2001; Sweeney, 1993), but successful implementation of the GLWQA reduced total phosphorus loadings from 25,000 metric tons per year (Mg/year) to an average of 9491 Mg/year (1981 through 2011) (Dolan and Chapra, 2012; Baker et al., 2014). Despite success in achieving reduced phosphorus loading targets from point sources, algal blooms began to reappear periodically in the western basin of Lake Erie during the mid-1990's (see Watson et al., 2016). Subsequently, non-point sources of phosphorus continue to enter the system (Matisoff et al., 2016) and, more recently, internal phosphorus loading of the water column from lake sediments (Elsbury et al., 2009; Paytan et al., 2017) have become a concern in managing harmful algal blooms. Regulatory changes in the United States and Canada have increased the impairment classification of Lake Erie and led to an on-going update to the GLWQA that is intended to further decrease phosphorus loading by an additional 40% from currently accepted levels. As a result of these recent shifts in policy, it is necessary to re-evaluate all potential sources of phosphorus entering Lake Erie.

The objectives of this research were to evaluate the largest source of water entering Lake Erie via the Detroit River by (i) measuring the concentrations of phosphate in water and sediment; and (ii) applying multiple chemical tracer techniques to identify potential nutrient sources, including phosphorous, along the river. Extensive urban development and agricultural activities surrounding the Detroit River and its tributaries, and the high flow rates of the Detroit River, all contribute to sediment-bound phosphate being carried into Lake Erie (Carter and Hites, 1992; Drouillard et al., 2006). Given the complexity of point and non-point sources to the system, we developed a multiple tracer approach capable of identifying potential mixed sources and sinks of nutrients that will contribute to the expanding efforts to monitor the Detroit River for its role in Lake Erie eutrophication (e.g. Maccoux et al., 2016; Burniston et al., 2018).

2. Methods

2.1. Location information

The Detroit River is a connecting channel forming the lower portion of the Huron-Erie corridor at the border between Michigan (USA) and Ontario (Canada). As an international waterbody shared between the U.S.A. and Canada it has been designated both as an International Heritage River and Great Lakes Area of Concern. At 51 km in length, the river drops 0.9 m along its run and sustains an average annual flow of 5300 m^3/s (range 3200–7100 m^3/s) with a typical water renewal time of <1 day (Manny et al., 1988). In addition to the standard flow patterns from the Detroit River into Lake Erie, storms and periodic flow reversals due to seiche events have the capacity to increase the transfer of consolidated sediments and associated pollutants and nutrients from the Lower Detroit river downstream (Drouillard et al., 2006). More than 98% of the Detroit River's flow derives from Lake St. Clair and the remaining from 4 smaller tributaries and 3 creeks with a combined drainage of 161,000 ha (UGLCCS, 1988). The river is divided by two islands at its head after which it narrows into a single channel through its central reach before widening in its downstream reach where it becomes broken up into multiple manmade channels separated by a number of islands. The average depth is 10.7 m in the navigation channels, which carries the bulk of flow, ranging from 9 to 15 m and non-channelized areas generally between 2 and 4 m deep (UGLCCS, 1988). The two major cities along its shoreline include the City of Detroit, Michigan (Detroit metropolitan population 3,734,090) and the City of Windsor, Ontario (population 217,188) both having rich pasts of industrialization and urban populations contributing to wastewater inputs from three wastewater treatment facilities. The Detroit Wastewater Treatment Plant is one of the largest facilities in North America, treating between 0.5 and 1 billion m^3 of wastewater per year and discharging about 6.75% of the annual total phosphorus load to Lake Erie from the River Rouge (Maccoux et al., 2016; UGLCCS, 1988). The City of Windsor supports two smaller wastewater treatment facilities discharging effluents into the Detroit River, one from Little River (near Lake St. Clair) and a second near the midpoint of the river (Fig. 1). Detroit River sediment chemistry surveys indicate limited cross channel mixing between U.S.A. and Canadian nearshore areas and marked gradients in metal and organic sediment contamination between adjacent shorelines and between the upstream to downstream river reach along the U.S.A. shoreline (Drouillard et al., 2006; Szalinska et al., 2006). Owing to its high flow, contributing 80% of Lake Erie's total inflow (UGLCCS, 1988), the Detroit River is a major nutrient loading source, albeit diluted in concentration relative to other Lake Erie tributaries (Maccoux et al., 2016).

2.2. Sample collection

Sampling occurred at multiple sites across 8 transects along the length of the Detroit River for a total of 23 sampling locations (Fig. 1). Samples were collected on 14, 17, or 22 November 2016, the mean discharge of the river was 533, 516, and 513 × 10^6 $m^3 \cdot day^{-1}$, respectively (U.S. Geological Survey Flow Gauge, 04165710). At each sampling location, water was collected using a Kemmerer Water Sampler (volume = 1.5 L) suspended 1–2 m above the sediment. Water samples were stored in 1 L BPA-free Nalgene bottles on ice until being refrigerated at

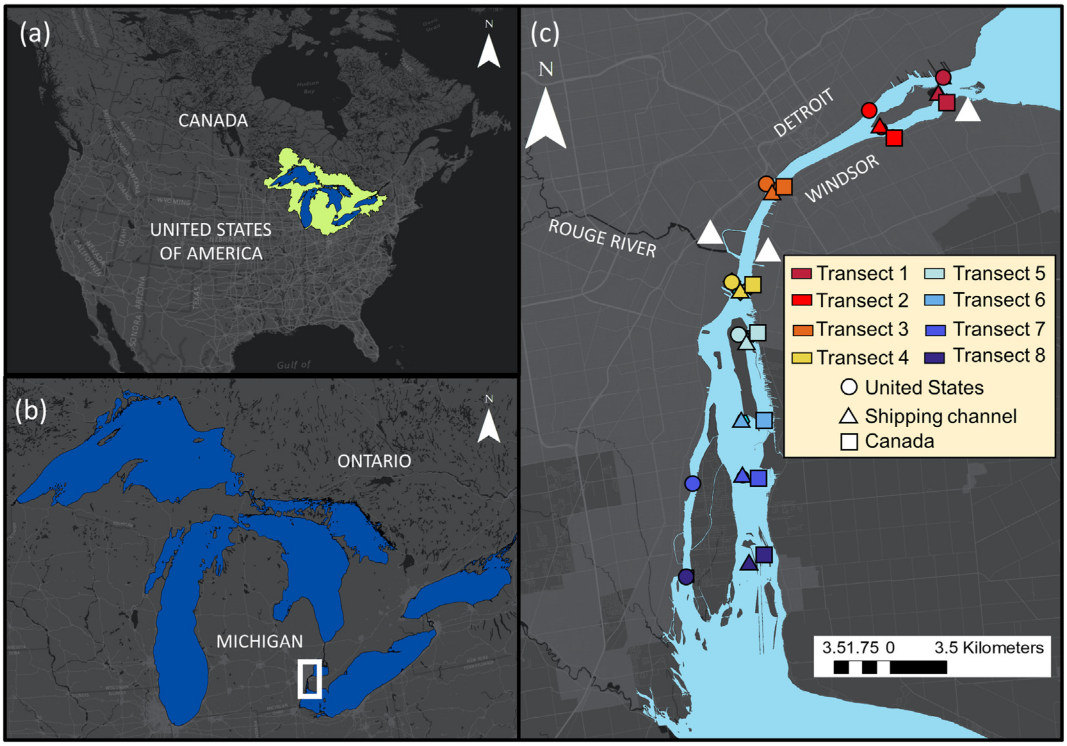


Fig. 1. Location of the Detroit River study system within (a) North America, and (b) the Laurentian Great Lakes. Also indicated are the eight transects with 2–3 sampling sites along the Detroit River (total n = 23 sampling locations). White triangles (Δ) indicate the position of three wastewater treatment facilities.

the Great Lakes Institute for Environmental Research (GLIER, University of Windsor, Windsor ON) for analysis.

Over 40.5 km^2 of river bottom have been covered by dumped dredge spoils over the period of shipping channel creation and maintenance (Bennion and Manny, 2011), potentially effecting longer term examination of sediment history in much of the Detroit River. While it is likely that sampling locations vary in dredge spoil dumping history, the sediment samples collected were from the upper most layer and represent the most recently deposited sediments across all transects. Sediment samples were collected using Ponar Grabs and sediment from the uppermost 3–5 cm were manually removed and stored in 200 mL plastic Nalgene bottles with up to four jars being collected from each site. When possible, each sediment vial was filled from a single grab of the Ponar unit, but when necessary multiple grabs were pooled together. All sediment samples were placed on ice at the time of collection in the field and subsequently frozen (−20 °C) at GLIER within four hours for processing.

2.3. Geochemical analysis

The refrigerated water samples and freeze-dried sediment samples were transported to the Applied Geochemistry Group (University of Calgary, Department of Geoscience) for chemical and isotopic analyses. As part of a multi-tracer approach, concentrations of nitrate (NO_3), phosphate (PO_4), calcium (Ca), chloride (Cl), potassium (K), magnesium (Mg), sodium (Na), silica (Si), and strontium (Sr) dissolved in the water were determined after filtering samples through 0.45 μm nitrocellulose filters (Millipore Corporation). Analysis of anion concentrations involved transferring filtered water samples into 2.0 mL glass vials and then into a Dionex ICS 2000 ion chromatograph (Dionex Corporation). A 25 mL aliquot of each sample was injected onto an Ion Pac AS18 anion column (Dionex Corporation) and anions were separated by isocratic elution using 35.0 mM potassium hydroxide, a flow rate of 1.1 mL/min, and column temperature of 30 °C. Water samples for cation concentration analysis were placed in 15 mL Falcon tubes and analyzed using a Varian 725-ES Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES). The spectrophotometer was calibrated via serial dilution of certified standards (BDH Ltd.). Analytical precision and accuracy for anion and cation analyses was typically ± 5.0%. Through both processes the concentration of various tracers dissolved in water were determined.

Frozen sediment samples were also sent to the Applied Geochemistry Group in the Department of Geoscience at the University of Calgary for geochemical analyses. Parameters assessed for each sediment sample were the concentrations of chloride (Cl; μg/g), sulfate (SO_4; μg/g), nitrate (NO_3; μg/g) and phosphate (PO_4; μg/g) in sequential pore water and acidified extractions. Water-extractable phosphate and compounds in sediment samples were those released by re-suspending the frozen samples in type 1 deionized water (18.2 MΩ, 30 m, at room temperature, sediment to water ratio 1:5) and analyzing the resulting supernatant. It is assumed that the water extraction method would represent pore water phosphorus fractions, where a component of this phosphate would be bioavailable. However, it does not reflect total bioavailable phosphate as it is possible for other fractions to remain bound to the sediment during the water-extraction process. Concentrations were measured using a Dionex ICS 2000 ion chromatograph, injected onto an Ion Pac AS18 anion column, and then separated by isocratic elution using 35.0 mM potassium hydroxide, a flow rate of 1.1 mL/min, and column temperature of 30 °C. Following water extractions of sediment samples, acidified extractions using hydrochloric acid (1 N HCl, 24 h, at room temperature, sediment to acid ratio 1:5; Tamburini et al., 2010) were completed to release mineralized compounds with stronger interactions with the sediment, which would reflect the total inorganic phosphate fraction including Ca-bound phosphate and apatite minerals (see Reedy et al., 1998). Following acid treatment, the concentrations of acid-soluble compounds (chloride (Cl; μg/g), sulfate (SO_4; μg/g), nitrate (NO_3; μg/g) and phosphate (PO_4; μg/g)) were analyzed using a Gallery Automated Photometric Analyzer.

2.4. Stable isotope analysis

The $^{15}N/^{14}N$ and $^{16}O/^{18}O$ ratios of dissolved nitrate in the water samples were determined using bacterial (*Pseudomonas aureofaciens*) reduction of nitrate to nitrous oxide (N_2O) with a bacterium lacking nitrous oxide reductase (Casciotti et al., 2002). The bacteria were placed in vials and flushed with inert N_2 gas. The water samples were injected into the vial and left for a 16-h period, followed by injection of 0.1–0.2 mL of 10 N NaOH to lyse the bacteria. The vials were then placed in a 24-vial auto sampler interfaced to a HP Agilent 6890 Gas Chromatograph with a PreCon® device interfaced to a Finnigan Mat DELTAplus XL mass spectrometer for automated determination of $\delta^{15}N$ and $\delta^{18}O$ values of dissolved nitrate with a measurement uncertainty of ±0.5‰.

Sediment samples were analyzed for bulk $\delta^{15}N$ values at the University of Windsor (Chemical Tracers Laboratory, GLIER) by freeze drying at −48 °C for a minimum of 48 h or until the sample was completely dried. Dried sediment samples were ground into a homogenous powder by hand using a mortar and pestle. The samples were then weighed into tin capsules (12–13 mg) and thermally decomposed in an elemental analyzer (Costech Analytical Technologies Inc., Valencia, CA USA) coupled to a continuous-flow isotope ratio mass spectrometer (ThermoFinnigan, San Jose, CA USA) to produce N_2 gas for nitrogen isotope ratio analysis ($\delta^{15}N_{total}$) with a measurement uncertainty of ±0.15‰.

Stable isotope values from both methods above are reported in per mil (‰) in the internationally accepted delta notation:

$$\delta^{15}N \text{ or } \delta^{18}O\ [‰] = \left[(R_{sample}/R_{standard})-1\right]$$

where R is the ratio of $^{15}N/^{14}N$ or $^{18}O/^{16}O$ in the sample and standard, respectively. Nitrogen isotope ratios are measured with respect to air and oxygen isotope ratios with respect to Standard Mean Ocean Water (SMOW) (Coplen, 2011). The measured nitrogen and oxygen isotope ratios of nitrate were normalized using international reference materials with the following isotope values: USGS32 ($\delta^{15}N = +180‰$; $\delta^{18}O = +25.7‰$), USGS34 ($\delta^{15}N = -1.8‰$; $\delta^{18}O = -27.9‰$), and IAEA-NO3 ($\delta^{15}N = +4.7‰$; $\delta^{18}O = +25.6‰$).

2.5. Principal component analysis of water samples

Principal component analysis (PCA) has been used to summarize the multivariate relationships among environmental tracers to characterize source types and spatial distribution of anthropogenic inputs into aquatic ecosystems (Parinet et al., 2004; Simeonov et al., 2003). The development of standardized PCA approaches specific to water nutrient analysis studies is opening this analytical tool for accurate evaluation of complicated nutrient relationships without depending on the use of many pairwise correlations (e.g. Olsen et al., 2012). Following the procedures outlined by Olsen et al. (2012), tracers of interest were identified based on their potential relationships to different source types (PO_4, NO_3, Cl, Na, Ca, Mg, K, Sr, and Si) and all concentration measures were standardized using the *z*-transformation. The number of meaningful principal component (PC) axes was determined by eigenvalues ≥1. Individual tracers were considered to be significant to a given PC axis when the absolute value of the loading scores were ≥0.75 and moderately significant between 0.50 and 0.75.

3. Results and discussion

3.1. Dissolved nutrients

In 2012, the Great Lakes Water Quality Agreement established an open water target of 15 μg phosphorus/L (spring total phosphorus concentration) within the western basin of Lake Erie and maintained a lake-wide maximum total phosphorus annual loading of 11,000 metric tons (GLWQA, 2012) with further reductions announced in spring 2018 (EPA, 2018). The mean concentration of dissolved phosphate from water samples collected in the Detroit River was 8.1 ± 2.4 μg/L, but values ranged between 4.8 μg/L and 15.5 μg/L (Fig. 2a). The highest concentrations of dissolved phosphate were observed upstream near Lake St. Clair on the Canadian shoreline and downstream from the River Rouge outflow into the Trenton Channel of the Detroit River, near the outflow into Lake Erie (Fig. 2a). Furthermore, the samples were taken during the autumn, outside the generally assumed peak loading period of May – July when runoff from agricultural activities is expected to reach peak annual levels (Michalak et al., 2013; Nürnberg and LaZerte, 2016; Stumpf et al., 2016).

The broad-scale level identification of potential nutrient sources was approached using multiple tracers. In particular, Cl is a conservative tracer, assuming there are relatively low naturally occurring background Cl concentrations (Vandenberg et al., 2005). Across sampling sites in the Detroit River, Cl had a mean (±S.D) concentration of 9.5 (±2.2) mg/L and ranged from 7.4 to 15.2 mg/L. The highest Cl concentrations were found on the Canadian side of the upper Detroit River and near the River Rouge outflow into the Trenton Channel (Fig. 3a, b). Dissolved PO_4 and Cl were positively correlated (Spearman's $\rho = 0.48$, $P < 0.001$; Fig. 3a), indicating that areas of peak dissolved PO_4 concentrations were associated with increased Cl concentrations. Previously recognized sources of Cl are urban groundwater and WWTP effluent (Chapra et al., 2009; Howard and Maier, 2007; Williams et al., 2000). Chloride and sodium (Na) also had a positive relationship (Spearman's $\rho = 0.92$, $P < 0.001$; Fig. 3b), consistent with salts being a primary source in this system. The lowest Cl concentrations were found within the shipping channel in the middle of the Detroit River, the area of highest flow. As a conservative tracer, Cl suggested the presence of additional salt sources to the Detroit River that were also associated with phosphate; however, the current dataset was not sufficient to delineate sources (for example, groundwater flow through underlying salt deposits, versus anthropogenic sources associated with urban activity) (Table 1).

Multiple pairwise correlations among the tracers within the water samples indicated a significant relationship between many of the tracers (Table 2); however, these correlations did not provide an indication of how groups of tracers may be related to each other. Multivariate analysis of tracers in water samples using PCA identified two axes with eigenvalues ≥1 representing a combined 75% of the total variation (PC1: eigenvalue = 5.31, % = 58.96; PC2: eigenvalue = 1.40, % = 15.51). The PC1 and PC2 loadings and the spatial distribution of their PC scores can be used to identify nutrient sources. PC1 loads were highlighted by significant variables NO_3, Cl, Na, Ca, Mg, and K, all with loading values ≥0.87 (Table 1; Fig. 4a). The spatial distribution of the PC1 scores indicated high positive values east of Belle Isle, coincident with in-flows of the Thames River. The Thames River discharges into Lake St Clair (42.31° N, 82.45° W); however, the riverine waters do not thoroughly mix with Lake St Clair. The Thames River water mass travels along the southern shore of Lake St Clair and enters the Detroit River (Leach, 1980). The land-use of the Thames River watershed is dominated by agriculture (Stone and Saunderson, 1992), and thus PC1 loadings and the spatial pattern of PC1 scores indicated that the source of NO_3, Cl, Na, Ca, Mg, and K in the Detroit River was agricultural land-use in the Thames River watershed.

Si and Sr loaded as moderately important variables on PC2 with values of −0.71 and +0.71, respectively (Fig. 4a). The spatial pattern of Si concentrations were highest at the northern extent of the Detroit River without distinction between flows to either side of Belle Isle (Fig. 5a). The separation of Si from the other nutrients in PC1 indicated that while agricultural inputs from the Thames River flowing into the Detroit River may contain Si, Lake St. Clair was the Si source. Up gradient of Lake St Clair, Lake Huron may be acting as the ultimate supply of silica as the establishment of dreissenids in the upper lakes has altered spring diatom blooms and facilitated export of dissolved Si to the lower lakes (Makarewicz et al., 2000). Concentrations of Sr are highest at the southern end of the Detroit River (Fig. 5b) and may represent an indicator of industrial activity, urban runoff, or wastewater effluent, constituents of which may release a variety of compounds that accelerate cation release from the environment and increase Sr downriver from activity centers (Nakano et al., 2005).

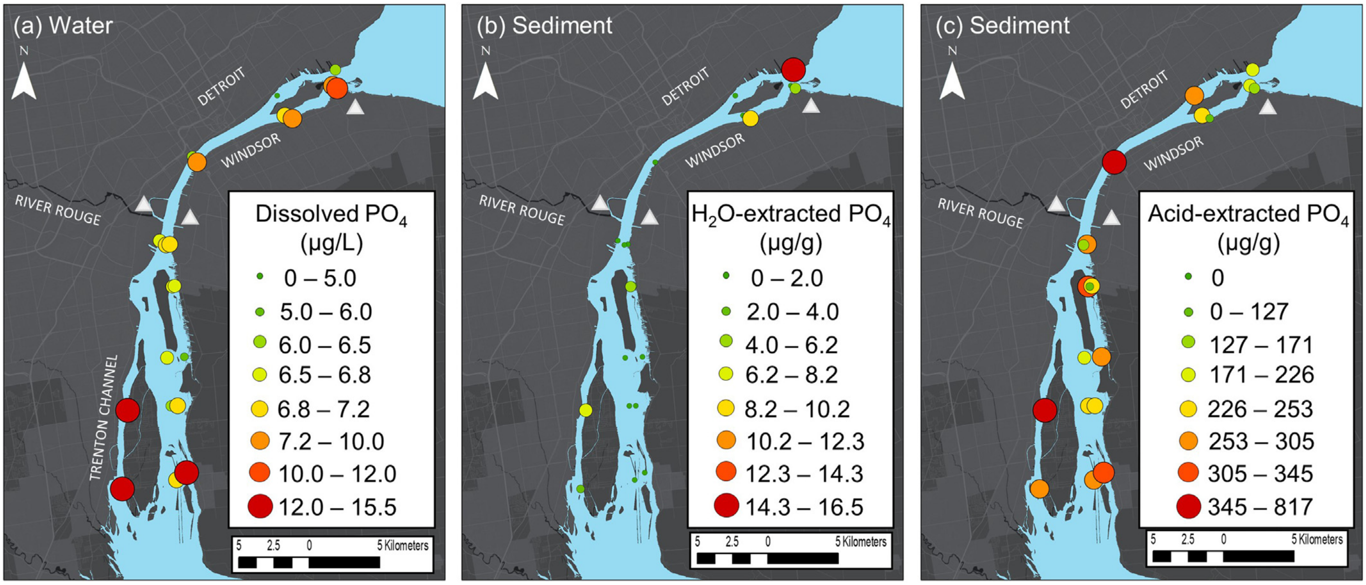


Fig. 2. Geographical plot displaying the distribution of phosphate (PO_4) (a) dissolved in water, (b) water-extracted from sediment samples, and (c) acid-extracted from sediment in the Detroit River. Each point represents PO_4 concentrations at a single location measured in either µg/L (water samples) or µg/g (sediment samples) for a single time point collected between 14 and 17 of November, 2016. Three wastewater treatment facilities are indicated by white triangles (Δ).

Using the PC loadings and spatial pattern of PC scores and nutrient concentrations three distinct sources contributing nutrients to the Detroit River were identified: Lake St Clair, the Thames River, and urban runoff and wastewater effluent (Fig. 4a). The position of PO_4 PC1 and PC2 loads between the signals of urban sources and the agricultural Thames River were consistent with mixed sources (Fig. 4a). Despite the dominance of agricultural land-use delivering nutrients throughout the Laurentian Great Lakes (Scavia et al., 2014) and the regulatory focus on agricultural P (GLWQA, 2012), our results suggest that urban runoff and wastewater are also important sources of PO_4 in the Detroit River. High PO_4 concentrations at both ends of the Detroit River (Fig. 2a) were coincident to the flows from the Thames River, wastewater treatment facilities, and the two urban centres (Detroit, MI and Windsor, ON) (Fig. 5a).

In addition to conservative tracers, the application of stable isotope ratios provides indicators of the types of effluent entering aquatic ecosystems (Kaushal et al., 2011; Kendall et al., 2007). In particular, oxygen and nitrogen isotope ratios of nitrate ($\delta^{18}O_{nitrate}$ and $\delta^{15}N_{nitrate}$, respectively) may identify multiple nitrate sources including wastewater treatment plants (WWTPs), agricultural fertilizer runoff, natural processes in soils, and the potential role of N_2 fixation from the atmosphere relevant to eutrophic water bodies (Kendall et al., 2007; Mayer and Wassenaar, 2012). We found variable $\delta^{15}N_{nitrate}$ values among sampling locations ranging between +0.9 and +6.2‰ (mean = 2.3‰). Detroit River water at the upper Canadian shoreline had the highest $\delta^{15}N_{nitrate}$ values, which consistently decreased at sample points downriver. Water samples from the American shoreline and shipping channel did not exhibit clear patterns of $\delta^{15}N_{nitrate}$ variation along the length of the river. Nitrate concentrations were positively correlated with $\delta^{15}N_{nitrate}$ (Spearman's $\rho = 0.60$, $P < 0.01$; Fig. 3e) and may have been related to high values of both NO_3^- and $\delta^{15}N_{nitrate}$ at the three upper Canadian shoreline sample sites. The correlation between NO_3^- and $\delta^{15}N_{nitrate}$ is consistent with wastewater inputs as one source of nitrogen to the Detroit River, with isotope values that were impacted by mixing with agricultural and soil N (Kendall et al., 2007). The relationship between $\delta^{15}N_{nitrate}$ and phosphate concentrations demonstrate variable sources of nutrients being released into the Detroit River, where one group has a $\delta^{15}N_{nitrate}$ values and phosphate concentrations consistent with ammonium-based fertilizers and the second has $\delta^{15}N_{nitrate}$ values consistent with a mixture of wastewater effluent and fertilizers (Fig. 3c, f). Although N_2 fixation from the atmosphere could have similarly low $\delta^{15}N_{nitrate}$ values, the correlation between $\delta^{15}N_{nitrate}$ values and chloride concentrations support a potential link to WWTPs and/or groundwater inputs impacted by salt mines in the area. Combined water chemistry and isotope indicators demonstrate that distinct sources can be characterized by differences in the source of nitrate based on the isotope values (Fig. 3d). Combining nutrient source identification using stable isotopes with concentrations of the chemical species that are typically released with these nitrates are consistent with wastewater being a major source of N along the length of the Detroit River.

3.2. Distribution and sources of nutrients in sediment

Despite successful efforts in many regions to reduce the current phosphorus inputs to aquatic ecosystems, restoration efforts may be limited by the long-term release of phosphorus bound within sediments through internal loading of nutrients into the water column (e.g. Powers et al., 2016; Roy et al., 2012; Søndergaard et al., 2003) drawing from legacy phosphorus sinks historically deposited over extended periods of time (e.g. Jarvie et al., 2013; Reddy et al., 2011). Sediment transport into Lake Erie is the highest of all the Great Lakes and includes an estimated 1.4×10^6 metric tons per year from the Detroit River (Kemp et al., 1976). Sediment phosphate concentrations varied in both water-extractable phosphate (mean = 3.1 µg/g; range 0.3–16.4 µg/g; Fig. 2b) and acid-extractable phosphate concentrations (mean = 286.3 µg/g; range 122.7–817.5 µg/g; Fig. 2c) along the course of the Detroit River. The highest water-extractable phosphate concentrations that reflect a component of more readily bioavailable phosphate were at the uppermost sampling site on the American side of the river near Lake St. Clair. In comparison, the highest acid-extractable phosphate concentrations reflecting mineralized deposition were found near Zug Island, midway along the course of the river, and within the Trenton Channel, two-sites of long-term large-scale industrial activity. Despite the variation in phosphate concentrations among the two sediment extraction methods, the measured values of sediment phosphate, i.e. bioavailable (water-extracted) and mineralized (acid-extracted), were not correlated with each other (Spearman's $\rho = -0.32$, $P = 0.16$) or with dissolved phosphate (water samples) for either bioavailable (Spearman's $\rho = 0.33$, $P = 0.14$) or mineralized phosphate (Spearman's $\rho = 0.03$, $P = 0.89$). Therefore, sediments within the Detroit River

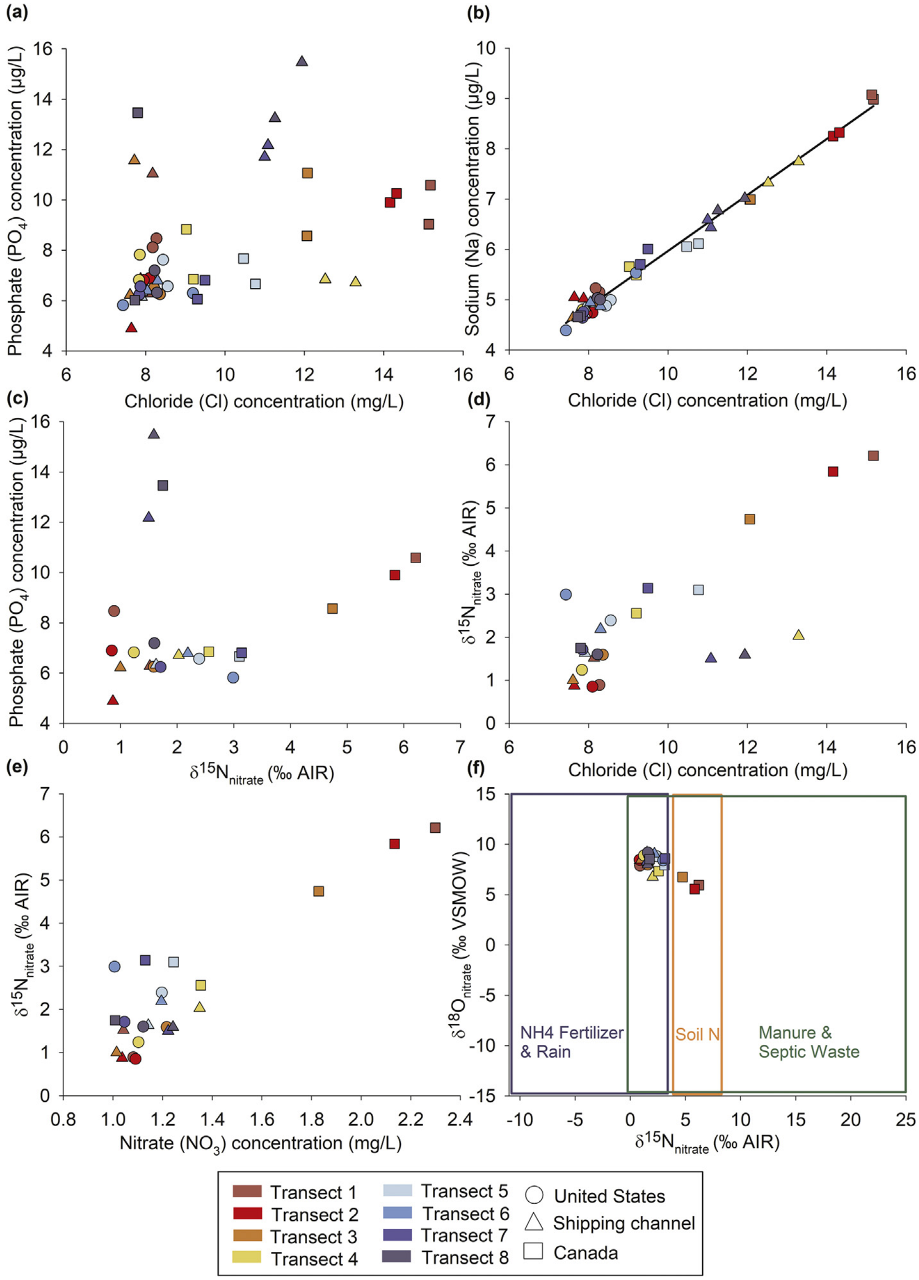


Fig. 3. Detroit river water sample crossplots of (a) chloride concentration (mg/L) versus phosphate concentration (μg/L), (b) chloride concentration (mg/L) versus sodium concentration (mg/L), (c) $\delta^{15}N_{nitrate}$ values (‰ AIR) versus phosphate concentration (μg/L), (d) $\delta^{15}N_{nitrate}$ values (‰ AIR) versus chloride concentration (mg/L), (e) nitrate concentration (mg/L) versus $\delta^{15}N_{nitrate}$ values (‰ AIR), and (f) $\delta^{15}N_{nitrate}$ values (‰ AIR) versus $\delta^{18}O_{nitrate}$ values (‰ Vienna Standard Mean Ocean Water), with the typical range in isotope values of major sources outlined in boxes (based on Kendall et al., 2007).

Table 1

Descriptive statistics of multiple tracers dissolved in water samples collected from 23 sampling locations along the Detroit River. Also shown are the principal component (PC) loadings of each chemical tracer for the first two PC axes (PC1, PC2), significant PC loadings (≥0.75) are in bold and moderately significant values (0.50–0.75) are in italics.

Tracer	Minimum	Maximum	Mean	S.D.	PC1 loading	PC2 loading
PO_4 (μg/L)	4.88	15.47	8.06	2.42	0.45	*0.51*
NO_3 (mg/L)	0.90	2.30	1.26	0.34	**0.91**	0.05
Ca (μg/L)	18.23	33.69	28.14	2.25	**0.87**	0.05
Cl (mg/L)	7.43	15.17	9.51	2.23	**0.91**	0.14
K (μg/L)	0.86	1.79	1.17	0.23	**0.92**	−0.29
Mg (μg/L)	6.63	9.57	8.35	0.43	**0.90**	0.07
Na (μg/L)	4.39	9.08	5.70	1.25	**0.92**	0.12
Si (μg/L)	0.68	2.79	1.35	0.51	0.41	**−0.71**
Sr (μg/L)	0.08	0.62	0.14	0.10	0.03	**0.71**

Table 2

Pairwise correlation matrix of multiple chemical tracers dissolved in water samples from the Detroit River. Spearman's rank correlation coefficients (ρ) are presented with statistically significant correlations (P-value ≤ 0.05) in bold text.

	PO_4	NO_3	Ca	Cl	K	Mg	Na	Si	Sr
PO_4	–	–	–	–	–	–	–	–	–
NO_3	**0.36**	–	–	–	–	–	–	–	–
Ca	**0.35**	**0.48**	–	–	–	–	–	–	–
Cl	**0.48**	**0.90**	**0.62**	–	–	–	–	–	–
K	**0.43**	**0.59**	**0.72**	**0.65**	–	–	–	–	–
Mg	**0.41**	**0.37**	**0.88**	**0.49**	**0.75**	–	–	–	–
Na	**0.50**	**0.81**	**0.69**	**0.92**	**0.72**	**0.66**	–	–	–
Si	0.18	0.21	**0.30**	0.12	**0.70**	**0.39**	0.17	–	–
Sr	**0.36**	**0.56**	**0.77**	**0.60**	**0.52**	**0.75**	**0.61**	0.10	–

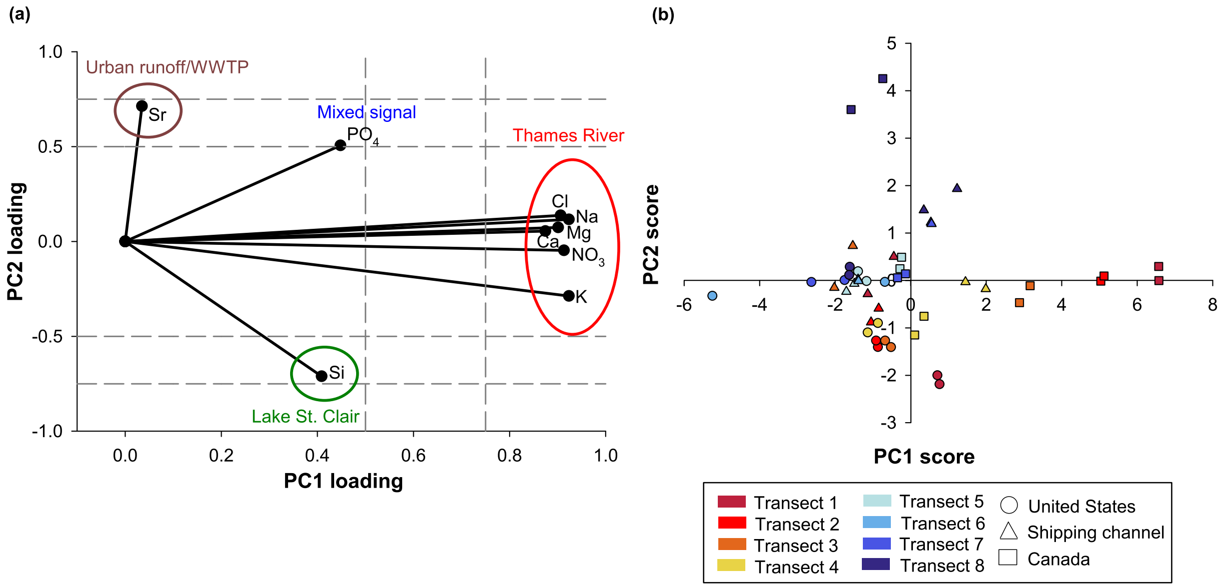


Fig. 4. Principal component analysis (PCA) of multiple chemical tracers dissolved in water samples from the Detroit River. Shown are (a) the PC1 and PC2 loading of each tracer (PO_4, NO_3, Ca, Cl, K, Mg, Na, Si, Sr), and (b) the overall PC1 and PC2 scores for each sampling site within the Detroit River. Dashed lines in panel (a) represent the 0.5 and 0.75 thresholds for moderately significant and significant loadings, respectively (see methods for details).

which are a significant sink of phosphate and concentrations of mineralized and bioavailable phosphate are not correlated with current water conditions over a limited sampling period.

Sediment chloride concentrations were not correlated with bioavailable (water-extracted) sediment phosphate (Spearman's $\rho = -0.32$, $P = 0.16$; Fig. 6a), but there was a positive relationship between chloride and mineralized (acid-extracted) PO_4 concentrations (Spearman's $\rho = 0.45$, $P = 0.04$; Fig. 6b). Stable isotope compositions of $\delta^{15}N_{nitrate}$ (water samples) and $\delta^{15}N_{bulk\ sediment}$ values were correlated (Spearman's $\rho = 0.54$, $P = 0.01$; Fig. 6c), but on average the $\delta^{15}N_{bulk\ sediment}$ values were elevated +2.0‰ above those of water $\delta^{15}N_{nitrate}$. Isotopic enrichment of nitrates can occur due to biogeochemical processes in sediments, including microbial denitrification from the preferential metabolism of ^{14}N by microorganisms in the sediment resulting in elevated $\delta^{15}N$ values of sediment (Mayer and Wassenaar, 2012), indicating the potential for biogeochemical processes between bulk sediment and nitrate in the water column (Weisener et al., 2017). Despite the presence of high phosphate concentrations within the sediment it was not possible to identify specific sources or types of input, consistent both with high flow rates moving and sediment mixing along the course of the river (e.g. Carter and Hites, 1992) and the gradual accumulation of legacy phosphorus within the system (Jarvie et al., 2013; Reddy et al., 2011). While it was not possible with our study design to identify particular sources or forms of phosphate in sediment, the broad scale approach shows evidence of variable sources and significant concentrations of phosphate in Detroit River sediment, representing a source of legacy phosphate.

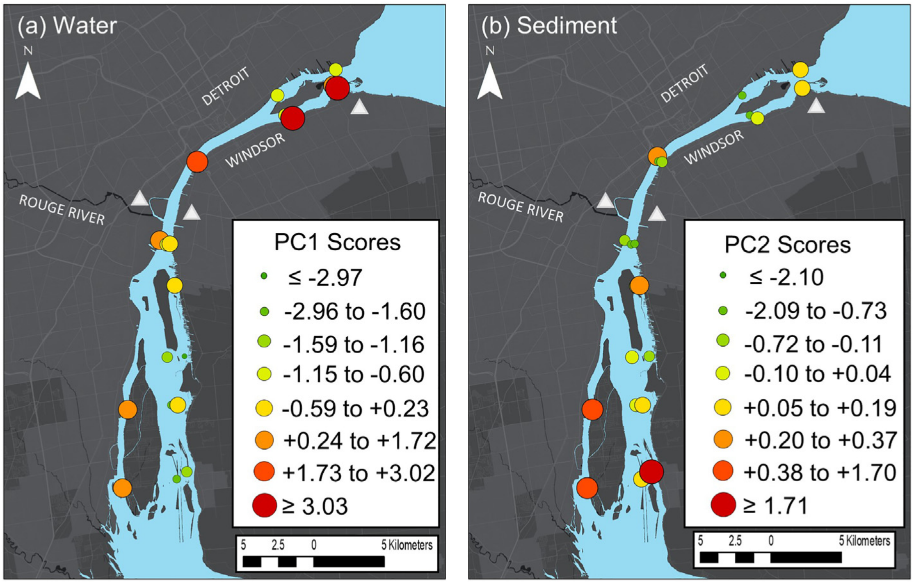
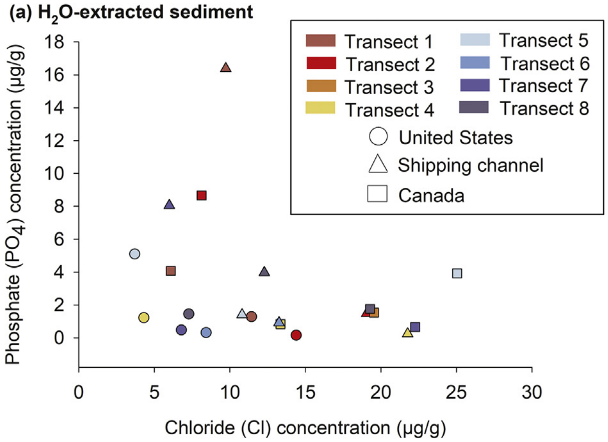
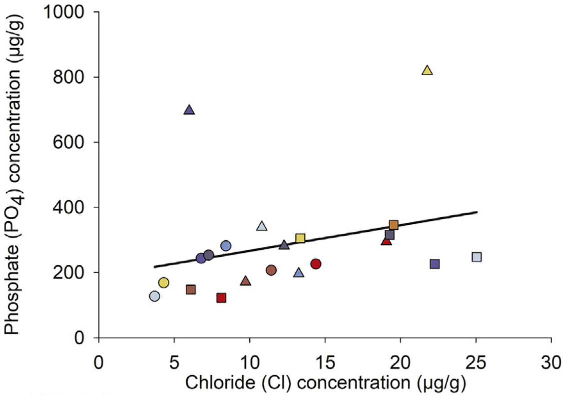


Fig. 5. Geographical plots displaying the distribution of principal component analysis (PCA) scores for (a) PC1 and (b) PC2 along the Detroit River. Each point represents the mean PC axis score of two water samples for each site. Three wastewater treatment facilities are indicated by triangles (Δ).

(a) H_2O-extracted sediment



(b) Acid-extracted sediment



(c) Stable isotopes

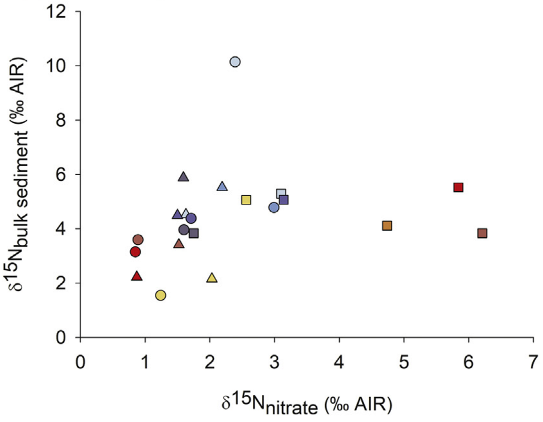


Fig. 6. Detroit River sediment sample crossplots of (a) bioavailable (water-extracted) sediment chloride concentration (μg/g) versus phosphate concentration (μg/g), (b) mineralized (acid-extracted) sediment chloride concentration (μg/g) versus phosphate concentration (μg/g), and (c) $\delta^{15}N_{nitrate}$ values (‰ AIR) from dissolved water samples versus $\delta^{15}N_{bulk}$ values (‰ AIR) of sediment.

3.3. Sources and sinks of legacy nutrients

Research on Lake Erie eutrophication and the GLWQA has concentrated primarily on the contributions of Maumee River runoff as a point-source to the western basin (Baker et al., 2014; Paytan et al., 2017), with less concern directed towards the Detroit River (Scavia et al., 2016; Verhamme et al., 2016). At the time, this was a logical approach because the Maumee River flows through agricultural areas and seasonally carries significant dissolved phosphorus runoff at elevated concentrations into Lake Erie (Kane et al., 2014; Matisoff et al., 2016). Spring loading levels from the Maumee River have repeatedly been the primary predictor in multiple models of algal bloom timing and strength (e.g. Obenour et al., 2014; Stumpf et al., 2012). Initial efforts focused on reducing the annual loading appeared to have a positive overall effect on Lake Erie for several years. Despite representing only 4% of all water entering the western basin, 48% of the TP entering the western basin comes from the Maumee River (Baker et al., 2014; EPA, 2015). However, given the 2018 target loading revisions to further reduce Lake Erie loading by 40% and the emergence of both non-point sources and internal loading of phosphorus from legacy sediment as contributors to eutrophication (Jarvie et al., 2013; Reddy et al., 2011), it is necessary to question and re-examine the current approach to nutrient loading assessments, which includes considering sources that may contribute to algal blooms after they are initially triggered by primary inputs. Even though the Detroit River may not be the primary source of dissolved phosphorus in the region, it contributes large annual quantities of sediment, e.g. 1.4 × 10^6 Mg/year, to the western basin of Lake Erie (Kemp et al., 1976), spreading material as far south as the Toledo, Ohio shoreline (Kovacik, 1972). The western basin retains up to 73% of all sediment carried into it via the Detroit River (Carter and Hites, 1992), allowing the long-term accumulation of sediment-bound phosphate within this specific region of Lake Erie. Although the acid-extraction approach (hydrochloric acid) used in this study may have extracted multiple forms of phosphorus, including bound complexes that may be biologically unavailable, (e.g. mineralize apatite) there is recent evidence using comparable methods that demonstrated sediments in the central basin of Lake Erie contain bioavailable Ca-bound phosphorus, not in the form of apatite minerals (Paytan et al., 2017). Accumulated sediment represents a phosphorus pool that may fuel algal blooms through conditions that increase internal mobilization of multiple forms, including activity of cyanobacteria (Cao et al., 2016) and increased water pH during bloom events (Paerl et al., 2011).

As indicated by the PCA loadings of phosphate on both axes, the Detroit River does not have a single point source of phosphate entering Lake Erie. The identification of non-point sources of nutrients is improved by using a multi-tracer approach that integrates multiple chemical and isotopic tracers with spatial and/or temporal sampling designs. In this study, based on phosphate concentrations alone we would not have been able to identify candidate PO_4 sources to the Detroit River, but multiple tracers and PCA identified groups of tracers consistent with mixing of urban and industrial inputs that varied spatially along the river. Additionally, these same approaches could be applied to water and sediment entering from other parts of the Huron-Erie Corridor to distinguish inputs from other waterbodies, e.g. Lake Huron or the Thames River, and those directly related to activity on or near the Detroit River and its tributaries. If we can identify various sources and sinks of anthropogenic phosphorus we can improve management approaches for aquatic ecosystems. Regional, national, and international efforts to reduce anthropogenic nutrient loading and control eutrophication have frequently targeted point sources for effluent reduction, e.g. outflow pipes from WWTPs and industrial sources (Cullen and Forsberg, 1988; Jarvie et al., 2006); however, these efforts are likely to be insufficient if non-point sources are not addressed, e.g. agricultural runoff (Paytan and McLaughlin, 2012; Young et al., 2009). Spatially diverse dissolved riverine nutrients (Fig. 2) underlies the complexity of anthropogenic sources entering waterways and as this paradigm becomes appreciated it must be matched with sophisticated multi-factor analyses to optimize resources allocated to remediation efforts.

The role of legacy deposits in sediments for phosphorus loading extends beyond the Laurentian Great Lakes. The gross inputs of phosphorus to the Thames River (United Kingdom) has declined from peak values of nearly 15 kt annually in the 1950s to approximately 5 kt in the early 2000s, similar to the Maumee River and western basin of Lake Erie (Powers et al., 2016). In both regions, the reduction in loadings to rivers has been primarily associated with significant decreases in fertilizer sources, but corresponding decreases in output from rivers have not been observed and were linked to internal loading of legacy phosphorus that had a compensatory effect as annual external loading was reduced (Powers et al., 2016). The mineralized phosphate deposits, likely to represent the bulk of sediment bound phosphorus in Detroit River sediment, reached as high as 818 μg/g and this river annually contributes 1.4×10^6 metric tons of sediment to the western basin of Lake Erie (Kemp et al., 1976). Efforts to reduce sediment loading have been suggested, including the dredging and removal of sediment layers likely to include legacy phosphate. However, an experimental assessment of dredging sediments near river outflows into Lake Chaohu (China), a heavily urbanized lake with three major rivers draining into it, found that dredging amplified the problem and was not a viable solution (Liu et al., 2016). There may not be a simple solution to address phosphorus bound into sediments, but it should be considered as a component of any efforts to monitor, assess, or remediate aquatic ecosystems facing eutrophication.

The general consensus that phosphorus suspended in water from the Detroit River is unlikely to be the primary trigger of algal blooms is likely correct, as our results suggest bioavailable phosphorus concentrations in sediments are lowest adjacent to Lake Erie (Fig. 2b), but the combination of non-point source effluents and legacy sediment effects from the large-scale deposition of mineralized phosphate-rich sediments throughout the western basin warrant revisiting the role of the Detroit River's internal loading on Lake Erie eutrophication. Even though sediment-bound phosphate alone is unlikely to trigger algal blooms (Matisoff et al., 2016) changing environmental conditions during bloom events, e.g. local pH (Cao et al., 2016), may cause mobilization of multiple phosphorous forms and result in positive feedback cycles enhancing the severity and longevity of bloom events. Phosphate may be bound in multiple forms and the use of sequential extraction techniques will allow for further differentiation of phosphorus types and bioavailability at a finer scale (see Reedy et al., 1998; White et al., 2004; Adhikari et al., 2015). The role of non-point source effluent and sediment-bound phosphate should be addressed in management efforts in Lake Erie and other waterbodies facing eutrophication.

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Conflict of interest

To the best of our knowledge, none of the authors listed on this paper have competing or conflicting interests related to financial, personal or other relationships with people or organizations that would have influenced, directed, or otherwise impacted the findings presented here.

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