Internal loading of phosphate in Lake Erie Central Basin

Adina Paytan [a,*], Kathryn Roberts [a], Sue Watson [b], Sara Peek [c], Pei-Chuan Chuang [a],
Delphine Defforey [d], Carol Kendall [c]

[a] Institute of Marine Sciences, University of California, Santa Cruz, 1156 High St., Santa Cruz, CA 95064, USA
[b] Water Science and Technology, Environment and Climate Change Canada, 867 Lakeshore Rd, Burlington, Ontario L7S 1A1, Canada
[c] United States Geological Survey, 345 Middlefield Rd, Menlo Park, California 94025-0434, USA
[d] Department of Earth and Planetary Sciences, University of California, Santa Cruz, 1156 High St., Santa Cruz, CA 95064, USA

HIGHLIGHTS

- Eutrophication and hypoxia in Lake Erie are fueled by phosphorus (P); yet P loads are unconstrained.
- We use pore-water profiles, core incubations and isotopes to estimate P loading from sediments.
- Sediment P loading amounts to as much as 20% of external loading.
- P loading from sediments is in the form of biologically available phosphate.

GRAPHICAL ABSTRACT
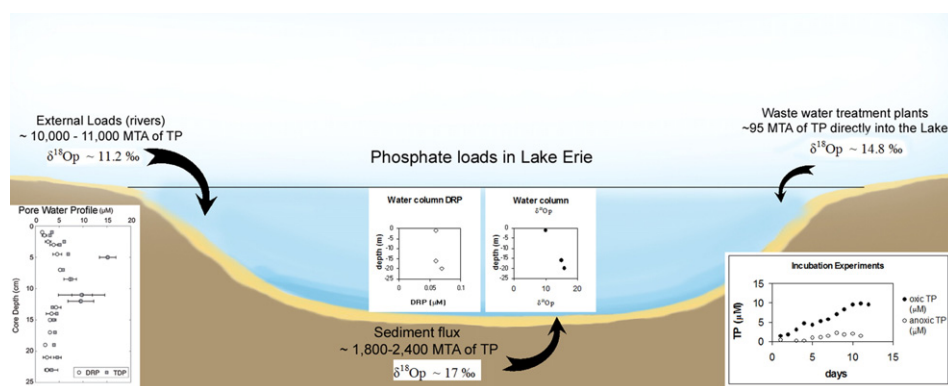
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ABSTRACT

After significant reductions in external phosphorus (P) loads, and subsequent water quality improvements in the early 1980s, the water quality of Lake Erie has declined considerably over the past decade. The frequency and magnitude of harmful algal blooms (primarily in the western basin) and the extent of hypoxic bottom waters in the central basin have increased. The decline in ecosystem health, despite meeting goals for external P loads, has sparked a renewed effort to understand P cycling in the lake. We use pore-water P concentration profiles and sediment cores incubation experiments to quantify the P flux from Lake Erie central basin sediments. In addition, the oxygen isotopes of phosphate were investigated to assess the isotopic signature of sedimentary phosphate inputs relative to the isotopic signature of phosphate in lake water. Extrapolating the total P sediment flux based on the pore-water profiles to the whole area of the central basin ranged from 300 to 1250 metric tons per year and using the flux based on core incubation experiments an annual flux of roughly 2400 metric tons of P is calculated. These estimates amount to 8–20% of the total external input of P to Lake Erie. The isotopic signature of phosphate in the extractable fraction of the sediments (~18‰) can explain the non-equilibrium isotope values of dissolved phosphate in the deep water of the central basin of Lake Erie, and this is consistent with sediments as an important internal source of P in the Lake.

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* Corresponding author.
  E-mail address: apaytan@ucsc.edu (A. Paytan).

1. Introduction

Lake Erie, the shallowest of the Great Lakes, is arguably the most anthropogenically impacted of these water bodies (Burns et al., 2005; Michalak et al., 2013; Stumpf et al., 2012). In the 1970s, in response to large algal blooms and anoxic events leading to fish kills, international agreements and regulations lead to a significant reduction of total phosphorus (TP – defined as all forms of P including dissolved and particulate inorganic and organic P) and other nutrients and pollutant inputs in the Great Lakes (Dove and Chapra, 2015). As the target loads were met, significant improvements in water quality were observed in Lake Erie that lasted for almost a decade. However, in the mid to late 1990s, harmful algal blooms began to return to this lake, particularly in the western basin, where they now occur with varying severity on an annual basis (Bridgeman et al., 2012; Michalak et al., 2013; Stumpf et al., 2012). In the mid-2000s, the extent of the oxygen depleted zone in the central basin also began to increase (Burns et al., 2005; Hawley and Eadie, 2006; Rucinski et al., 2010; Scavia et al., 2014; Zhou et al., 2013). As in many other lakes, P has been identified as the limiting nutrient in Lake Erie (Bertram, 1993; Makarewicz and Bertram, 1991); hence identifying sources of P to the lake has been a focus of research (Depinto et al., 1986; Scavia et al., 2014). Specifically, it has been suggested that the fraction of dissolved reactive P (DRP – defined as the 0.45 μm filtered fraction that complexes with molybdenum, also referred to as soluble reactive P (SRP); primarily orthophosphate (Matisoff et al., 2016)) of the TP load from external sources has increased (Baker et al., 2014; Depinto et al., 1981; Richards et al., 2010) and/or that internal loading of bioavailable P from the sediment is playing an important role (Conroy et al., 2005). Recent work in the western basin of Lake Erie has documented a wide range of P diffusive fluxes from the sediments to the water column under both oxic and anoxic conditions (Matisoff et al., 2016). Release from sediments is considered an internal load of P (annual, gross and areal load of TP from the sediments; (Nürnberg, 2009)). The change in internal loading of P from sediments might in part be due to the introduction of invasive species, particularly dreissenid mussels, which may influence nutrient cycling dramatically when introduced to lakes (Dove and Chapra, 2015; Holland et al., 1995). Using the oxygen isotopes of phosphate ($\delta^{18}O_P$) and depth distribution of dissolved phosphate (PO_4), Elsbury et al. (2009) also suggested internal loading from sediments may be a potentially important P source. In particular, these authors observed $\delta^{18}O_P$ values that were higher than expected equilibrium values in deep waters of the central basin during the summer and early fall, and hypothesized that the release of P from lake sediments may be responsible for the deep water PO_4 with $\delta^{18}O_P$ values of ~17‰.

In this study we aimed to provide a quantitative estimate of internal P loading from lake sediments with a focus on the central basin of Lake Erie where seasonal stratification and anoxic zones occur annually in summer to early fall (Charlton, 1980; Watson et al., 2016). We use DRP and total dissolved P (TDP – defined as all forms of P that remain after 0.45 μm filtering, this includes polyphosphates, and dissolved organic phosphates (Matisoff et al., 2016)) concentration profiles in pore-water as well as whole core incubations to estimate the TDP flux from sediments under oxic and anoxic conditions. We also report the $\delta^{18}O_P$ of PO_4 extracted from different sediment reservoirs and in sewage effluent discharged into Lake Erie to evaluate these as possible sources of the observed above-equilibrium values reported previously for lake water samples particularly from the central basin (Elsbury et al., 2009).

2. Materials and methods

2.1. Study site

Lake Erie is comprised of a shallow western basin, which receives the bulk of the external nutrient loading, a large central basin, and a deep eastern basin (National Geophysical Data Center). Both the central and eastern basins thermally stratify during the summer. In the central basin, the settling organic material from a disproportionately large volume of epilimnetic water to a smaller hypolimnetic volume often leads to bottom water hypoxia in the summer months, generally starting in late summer and extending until fall mixing in October (Beletsky et al., 2013). Samples for the current study were collected by Environment and Climate Change Canada (ECCC) at station 880 in the central basin during research and monitoring cruises in the spring and summer of 2010 and 2012 (2 cores were collected in July 2010 (used for the isotope work), 1 in May 2012 (used for pore water profiles), and 2 in July 2012 (used for incubations), (several additional cores were collected in August of 2012 but arrived damaged and were unusable). The site is located in the area that develops annual bottom hypoxia, near the center of the central basin, (41°56′09″N, 81°39′16″W) in approximately 24 m water depth (Fig. 1). The water column and sediment characteristics at this site are typical to vast off shore areas in the central basin (Herdendorf, 1984; Kemp et al., 1976).

The largest source of external P to Lake Erie is delivered by the large rivers (collective input from the Detroit, Maumee, Sandusky, and Cuyahoga rivers) draining agricultural, urban and forested land around the western end of the lake. The majority of the water volume (80–90%; with a constant discharge of 5324–5800 $m^3 \, s^{-1}$ (Carter and Hites, 1992)) input into Lake Erie arrives via the Detroit River into the western basin contributing 3550–4320 million metric tons annually (MTA) (32–39%) of TP to the Lake (Burniston, 2014). The Maumee River whose water volume discharge averages 150 $m^3 \, s^{-1}$, contributes roughly 2500 MTA of P, (2003–2012 the Maumee averaged a load of 2437 MTA into Lake Erie, 23% of which was DRP; Baker et al., 2014) also enters the lake in the western basin. Overall 60% of the TP, and 70% of the DRP annual loads enter the west basin of Lake Erie (Baker et al., 2014; Leon et al., 2005; Scavia et al., 2014). Other significant inputs of P to lake Erie include the Sandusky and Cuyahoga Rivers, which enter into the Sandusky basin (western edge of central basin) and the central basin respectively (Baker et al., 2014). The water moves from the western basin through the central basin and exits the eastern basin via the Niagara River. In most years 10,000–11,000 MTA of P enter Lake Erie from these rivers (Baker et al., 2014). The residence time for water in Lake Erie is 2.7 years (Quinn, 1992).

Lake Erie also receives direct and indirect (i.e. initial discharge is into rivers) sewage effluent from several major wastewater treatment plants. Most proximal to the central basin is the Northeast Ohio Regional Sewer District Easterly treatment facility, located in Cleveland, OH on the shoreline south of the long-term ECCC central monitoring station 880 (Fig. 1). The facility processes residential, business, and stormwater, discharging to the lake about 48 MTA of TP (based on permit limits). The current permit limit under the discharge agreement for P for the facility is 132 kg/day monthly load average (Permit Number 3PF00001*KD). Waste water treatment samples were collected by hand (2 L grab samples) post treatment, prior to discharge into the lake, on a monthly basis. Magnesium chloride and sodium hydroxide were added to precipitate brucite, and samples were shipped to the University of California, Santa Cruz (UCSC) for isotope analysis.

2.2. Sediment and pore-water extractions

Sediment cores (internal diameter 70 mm) were collected to a depth of 30 cm using a gravity corer, sectioned in a cold room immediately after collection at 1 cm intervals down to 10 cm and then sectioned at 2 cm intervals for the remainder of the core length. Sectioned sediments were centrifuged to extract pore-water, which was then filtered through 0.45 μm membrane filters (Sartorius Cellulose Acetate (CA) Membrane Filter 11104-47-N), collected into 50 mL Falcon tubes, frozen at −20 °C and shipped to UCSC. While core sectioning was not done in a glove box under anoxic conditions we note that the specific cores used were all collected in May when the bottom water at the site of collection was oxic. Moreover, if any iron from the pore fluids got oxidized and
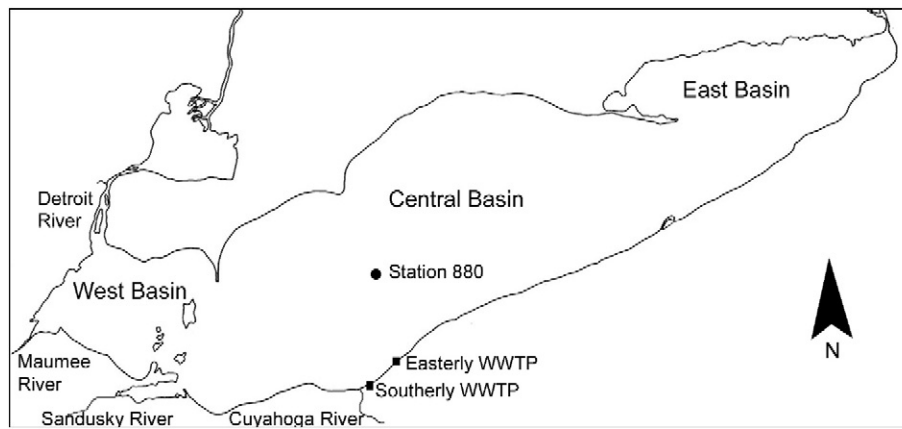
Fig. 1. Map of Lake Erie showing the location of station 880 in the central basin.

precipitated during processing potentially removing some of the P, such precipitate would have been dissolved prior to analysis because of the low pH of reagents added for P concentration analyses (see below). Regardless, if any P was lost during processing this will render fluxes calculated here as minimum values. Additional sediment cores were sectioned at 1 cm intervals down to 10 cm then 5 cm down to 30 cm and used for sequential PO_4 extraction, following a modification of the Hedley (Hedley et al., 1982) method as described in Tiessen and Moir (Tiessen and Moir, 1993). This modified procedure enables simultaneous processing for P concentrations and oxygen isotope analyses of PO_4 (Zohar et al., 2010). In brief, 3.3 g of dried sediment was shaken (~180–200 rpm) overnight (16 h) with 200 mL of successive extraction solutions. Solutions used were Milli-Q water, 0.5 M $NaHCO_3$ at pH 8.5, 0.1 M NaOH, and 1 M HCl. The water extraction is defined as labile, readily available PO_4, the $NaHCO_3$ and NaOH both target the Fe and Al associated PO_4, which is considered available on intermediate timescales, with the $NaHCO_3$ accessing the more labile, and the NaOH the less labile portions of this pool, and finally the HCl targets the Ca-associated PO_4 which is considered less labile than the other 3 fractions (Tiessen and Moir, 1993). The following day, samples were centrifuged at 3500 rpm for 15 min and the supernatants filtered through 0.45 μm filters. Aliquots of the resultant filtrate were taken for determination of DRP and TDP concentrations. The remainder of the extraction solution was used for measuring $\delta^{18}O_p$ of the different sediment fractions. Additional cores (20 cm length) were used whole for benthic flux incubations.

2.3. Dissolved reactive phosphate (DRP)

Solutions (pore-water and sediment extracts) were analyzed for DRP via the molybdenum blue method which is done at low pH conditions (Murphy and Riley, 1962). Samples were processed on a QuikChem FIA+ 8000 Series autoanalyzer by Lachat Instruments using method 31-115-01-3-A. Water extracts were run at full strength, while the $NaHCO_3$, NaOH, and HCl extracts were run at 1:5, 1:10, and 1:20 dilutions respectively, to ensure concentrations within the range of the calibration curve, and to minimize the impact of sample matrices. Standards were made fresh daily in the matrix analyzed. Sample reproducibility was 0.5%, with a detection limit of 0.15 μM.

2.4. Total dissolved phosphorus (TDP) and additional key elements

Solutions (pore-water and sediment extracts) were analyzed for TDP, along with calcium (Ca), iron (Fe), and manganese (Mn) on an inductively coupled plasma optical emission spectrometer [ICP-OES, Perkin-Elmer Optima 4300 DV] operated by the UCSC Marine Analytical Laboratory. Water extracts were run without dilution, while the $NaHCO_3$, NaOH, and HCl extracts were run at 1:5 dilutions to ensure concentrations within the calibration range, and to minimize the impact

of the matrices on the plasma in the OES. The detection limit on this instrument for P is 0.12 μM, the calibration ranged between 12.5 and 50 μM corresponding to the range of concentrations in the samples and reproducibility of duplicate analyses was 10% or better. Detection limits for other elements are as follows: Ca 0.5 μM, Fe 0.1 μM, and Mn 0.1 μM. Measured blanks were always <1% of signal.

2.5. Oxygen isotopes of phosphate ($\delta^{18}O_P$)

Silver phosphate (Ag_3PO_4) was precipitated for $\delta^{18}O_p$ analyses of sediment extracts and waste water treatment plant (WWTP) water as described in Zohar et al. (2010). In brief, $MgCl_2$ was added to the solution (e.g. sediment extracts or WWTP water) and the pH increased to ~10 by adding NaOH to precipitate brucite ($MgOH_2$), which co-precipitates the dissolved PO_4 (Karl and Tien, 1992; McLaughlin et al., 2004). Brucite is then dissolved in 5 mL acetic acid, and a minimum amount of 10 M HNO_3. Solutions were brought up to pH 5.0 and shaken with DAX 8 resin to remove organic matter. Sample pH was adjusted to pH 5.5 and cerium nitrate added to precipitate $CePO_4$. Samples were settled for 24 h then centrifuged and the supernatant discarded. The cerium PO_4 precipitate was dissolved in 1 M HNO_3, diluted to 0.2 M HNO_3 and shaken overnight with 4–12 mL of cation resin (Biorad AG50x8). The cation resin was removed and $AgNO_3$ and buffering reagents added to the solution to precipitate Ag_3PO_4. The Ag_3PO_4 was cleaned (treated with H_2O_2), dried, and $\delta^{18}O_p$ was analyzed at the US Geological Survey Stable Isotope Laboratory in Menlo Park, CA using a Eurovector elemental analyzer connected to a Micromass Isoprime mass spectrometer. Internal standards (calibrated using fluorination) with values of 11.3 ± 0.15‰ and 20.0 ± 0.25‰ were used for mass and drift corrections, sample standard deviation averaged ±0.3‰. Details about the equipment and standards are described in McLaughlin et al. (2004). Select samples were processed spiked and un-spiked with ^{18}O enriched reagents to ensure no artifacts are impacting the data (McLaughlin et al., 2004; Zohar et al., 2010).

2.6. Phosphorus flux calculations

The DRP and TDP sediment flux was calculated using two independent methods; i) the commonly used pore-water diffusive flux calculated using Fick's first law (Lavery et al., 2001), and ii) fluxes assessed from sediment core incubations under oxic and anoxic conditions.

The diffusive flux (J) was calculated from the observed pore-water to bottom water DRP and TDP gradient using Fick's First Law (Berner, 1980):

$$J = \Phi \bullet D_s \bullet (\partial C / \partial x) \tag{1}$$

$$D_s = D_0 \cdot \Phi^2 \qquad\qquad (2)$$

where D_s is the whole-sediment molecular diffusion coefficient of PO$_4$ (cm^2/s), Φ is the porosity (0.86) (Steely, 2015), C is the concentration of DRP or TDP (µM) and x is the depth (cm). Ds can be calculated from Eq. (2) (Ullman and Aller, 1982) where D_0 is the molecular diffusion coefficient of PO$_4$ (3.907×10^{-6} cm^2 s^{-1}) in water at in situ temperature, salinity, and pressure (7 °C, 3.53 bar, and salinity = 0) (Schertzer et al., 1987; Small et al., 2014) calculated according to Boudreau (Boudreau, 1997).

2.7. Core incubations

For the incubation experiments, two 20 cm sediment cores were incubated in the dark at 7 °C (average annual temperature in the bottom water of Lake Erie central basin and also the temperature at the time of core collection) (Schertzer et al., 1987) under oxic and anoxic conditions (one each as replicate cores were damaged during transport). For both incubations the overlaying water was removed, much of the P removed by co-precipitation with brucite and pH adjusted to natural conditions. One liter of this lake water which had DRP concentrations similar to ambient lake water was gently returned to the core tube. We used this treated lake water for the incubation because the overlaying water had very high concentrations of DRP and TDP prior to the start of the experiment due to accumulation for almost 2 months during storage in the cold room between time of collection and the start of incubation (see below). The overlaying water in the oxic core was gently bubbled with ambient air, maintaining approximately 12 mg L^{-1} dissolved oxygen (DO), while the anoxic core had N$_2$ gas bubbled gently through the overlying water, maintaining a DO concentration of <1 mg L^{-1}, monitored with a hand held DO probe. Subsamples of 10 mL from the overlying water were taken daily for concentration analysis of DRP, TDP, as well as Ca, Mn, and Fe. The duration of incubations was 12 (oxic) and 11 days (anoxic). Fluxes were calculated from the difference in TDP concentration over the linear portion (day 1 to day 10 oxic core, and day 3 to day 8 anoxic core) of the incubation time per surface area of the core, corrected for change in water volume (via conversion to mass, and flux calculated from the slope of mass over time). The fluxes calculated this way are most likely an underestimate of the actual in-situ flux, as the cores did not include bioturbation by epifauna, and also because the concentration of the overlying water increases over time, reducing the concentration gradient and hence the flux.

3. Results

Here we present estimates for the DRP and TDP fluxes from the sediments of the central basin of Lake Erie to quantify this contribution in comparison to the overall P loading to the lake. We also present $\delta^{18}O_P$ data from four operationally-defined sedimentary PO$_4$ pools, as well as $\delta^{18}O_P$ data of dissolved PO$_4$ from a WWTP that discharges treated effluent into the central basin in order to characterize the $\delta^{18}O_P$ of these PO$_4$ sources and compare them to the values previously reported for Lake Erie water.

3.1. Pore-water DRP and TDP concentrations and diffusive flux calculations

Pore-water concentrations of DRP and TDP ranged from 0.4 to 4.7 µM, with DRP generally comprising the largest fraction of TDP (dissolved organic P calculated by difference between TDP and DRP ranged from 0.4 to 59%, with an average of 18% of TDP) (Fig. 2, Supplemental Table S1). Depth profiles of both DRP and TDP showed an increase with depth from low concentrations at the surface and a maximum at about 5 cm, decreasing below that depth, suggesting a flux from the upper 5 cm of the sediments to the overlying water column (Fig. 2). The peak at 5 cm was sharp and based on one data point; however,
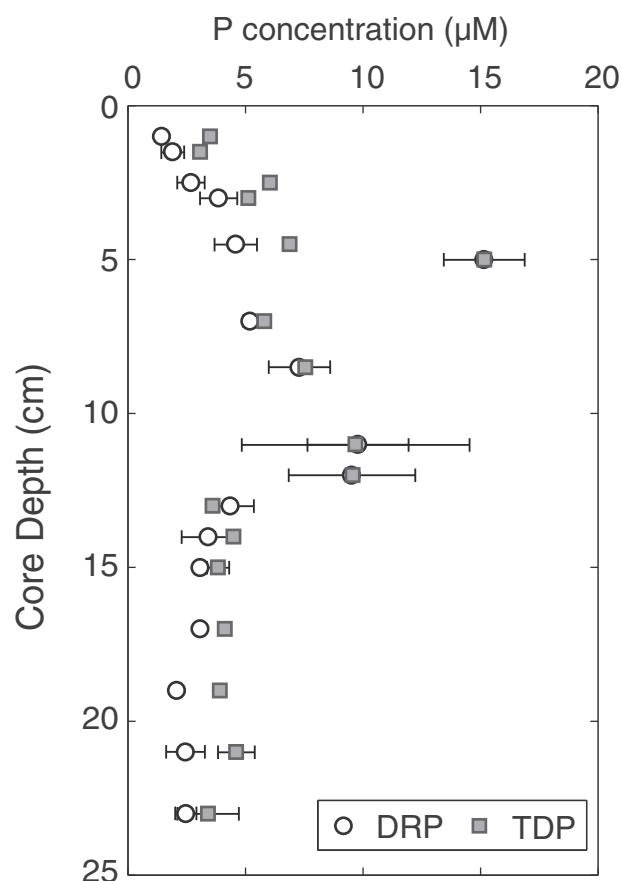

Fig. 2. DRP and TDP concentrations in the pore-water. Error bars are based on analytical replicates of samples processed repeatedly for specific depths intervals.

samples were measured multiple times on two instruments, so analytically the pore-water concentration at 5 cm is accurate. Since the maximum concentration gradient was based on this one point, we calculated the flux twice as a precaution, once using the 5 cm value and a second time with it removed (e.g. using the maximum value at ~12 cm).

The calculated P flux (J) using Fick's First Law (Berner, 1980) for the observed TDP pore-water gradient at average annual temperatures and in-situ porosity, including the value at 5 cm depth, was 0.21 mg P m^{-2} d^{-1} (76.65 mg P m^{-2} yr^{-1}). Calculating the diffusive flux from the sediment using the more conservative gradient (removing the maximum concentration at 5 cm depth) the flux obtained was 0.05 mg P m^{-2} d^{-1} (18.25 mg P m^{-2} yr^{-1}).

3.2. Core incubation flux

Fluxes calculated via oxic and anoxic sediment core incubations using the increase in DRP over time (Fig. 3) were 0.58 and 0.32 mg P m^{-2} d^{-1}, respectively; on par with the Fick's law calculated flux based on the maximum value at 5 cm. As mentioned above, we removed much of the DRP from the Lake water prior to incubation due to its accumulation in the overlying water during the ~2 months of storage between sampling and the incubation experiment. The initial (post storage) DRP in the overlying water was 2.3 and 3.1 µM in the two cores. An approximate calculation of flux from the sediment to the overlying water over the 2 months using these concentrations provides values of 0.33 and 0.45 mg P m^{-2} d^{-1} (118 and 164 mg P m^{-2} yr^{-1}, respectively), similar to those from the incubation experiment. The TDP concentrations measured in both incubations were higher than the DRP and if the flux is calculated using TDP, values of 0.65 mg P m^{-2} d^{-1} in the oxic incubation, and 0.36 mg P m^{-2} d^{-1} in the anoxic incubation
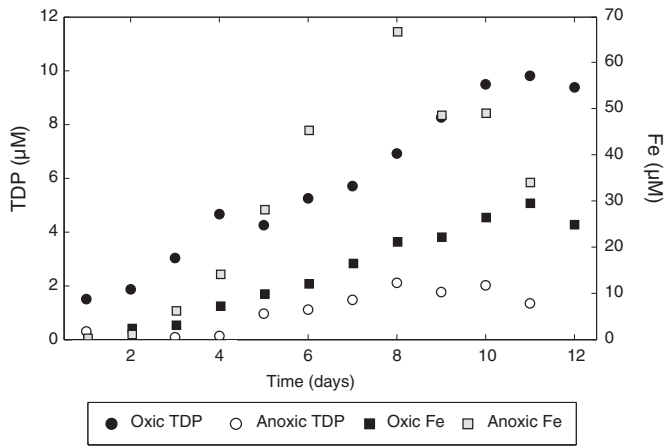
Fig. 3. Concentrations of TDP and Fe over time in the overlying water obtained from core incubations under oxic conditions (filled symbols), and anoxic conditions (unfilled symbols).

are obtained. Nitrate concentrations in the lake water used for the incubations were 2.0 and 2.3 μM. Total Fe, Ca and Mn also increased over time. Ca (up to 300 μM in both incubations) had the highest concentrations, followed by Mn (up to 40 μM and 100 μM in the oxic and anoxic incubations, respectively) and then Fe (22 μM and 66 μM in the oxic and anoxic incubations respectively). The concentrations of Ca, Mn and Fe in the overlying water can shed light on potential mineral association of the P released. The concentrations of all of these elements were much higher than those of DRP (Table S2, Supplemental data).

3.3. Sediment composition, DRP and TDP concentrations

To assess P concentrations associated with different sediment fractions we analyzed DRP and TDP in the four sediment extracts at different depths (Fig. 4). Measured DRP in the sediment water extract reached a maximum concentration of 39 μg P g^{-1} sediment at 6 cm. The maximum concentrations were 378 μg P g^{-1} sediment for NaHCO$_3$, 228 μg P g^{-1} sediment for NaOH, and 814 μg P g^{-1} sediment for HCl sediment extractions. These maxima for these latter extracts were all deeper, at 10–15 cm. For all extracts except NaOH, P was
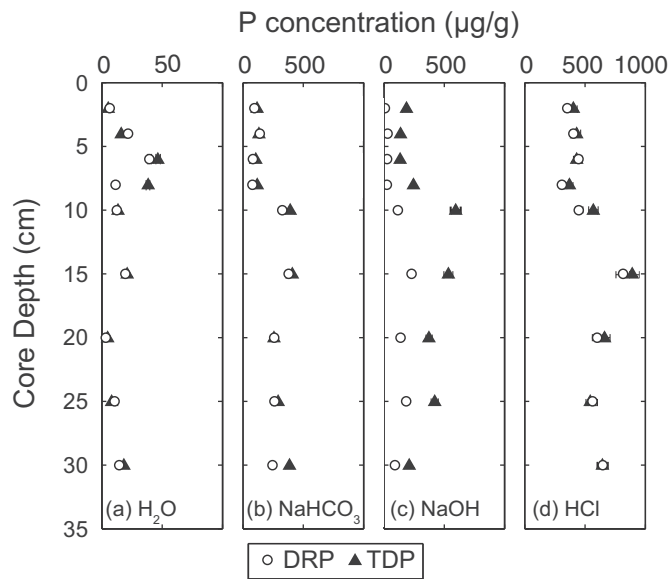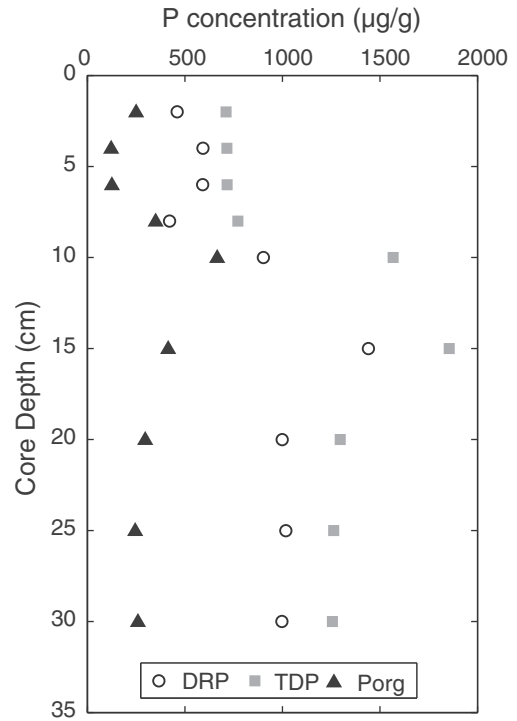

Fig. 5. Total solid-phase DRP, TDP and organic P extractable concentrations (sum of concentration in all 4 leaching steps averaged from multiple cores), in μg g^{-1} dry sediment plotted along the depth in the cores. Organic P is determined by the difference between the combined fractions TDP and DRP values.

primarily in the form of DRP (e.g. DRP and TDP similar in concentration in the extraction solutions). The NaOH extract also contained organic P (calculated by difference). The DRP, organic P and TDP distribution combined for all fractions extracted from the sediment is shown in Fig. 5, and Table S3, Supplemental data.

Other elements (Ca, Mn and Fe) that may be associated with P were also analyzed in the extracted solutions (Fig. 6). Overall the H$_2$O, NaHCO$_3$ and NaOH extraction solutions had similar concentrations for all the elements measured (<1.5 mg g^{-1} soil). The HCl extract had considerably higher concentration for all of the measured elements. For most of these elements no coherent trends with depth were observed.

Fig. 4. DRP and TDP concentrations in μg g^{-1} dry sediment, in sediment fraction extracts: (a) water, (b) sodium bicarbonate, (c) sodium hydroxide and (d) hydrochloric acid. Error bars represent standard deviation between samples from multiple cores.
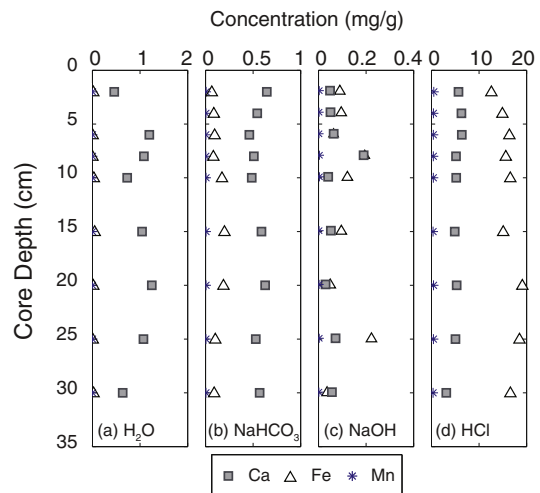

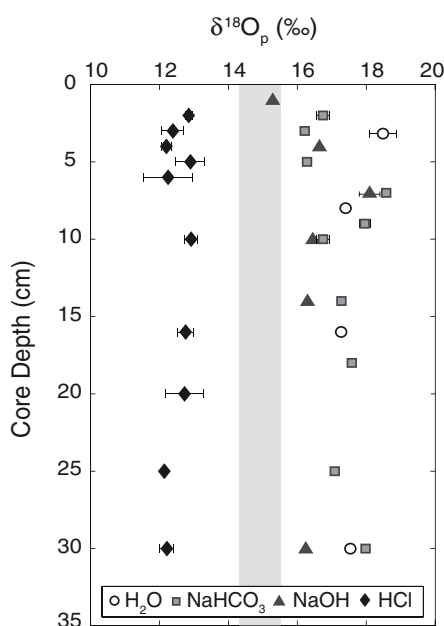Fig. 6. Concentrations of Ca, Fe and Mn in the Hedley extraction pools, in mg g^{-1} dry sediment.

Fig. 7. $\delta^{18}O_P$ for each of the soil fractions extracted. Error bars on individual samples represent analytic standard deviation for the samples that were analyzed in duplicate. The gray bar represents the range of values of WWTP $\delta^{18}O_P$.

3.4. $\delta^{18}O_P$ of sediment extracts and WWTP effluent

The $\delta^{18}O_P$ values for each of the sediment fractions extracted are shown in Fig. 7. The average $\delta^{18}O_P$ for the 1 M HCl extract was 12.8‰ ± 0.4 and was fairly constant with depth. This value likely represents the isotopic signature of particulate mineral-bound P in the watershed. Indeed the average isotope value of the mineral bound P in the surrounding watersheds is 12.5‰ (range between 11.7‰ and 13.6‰ for different basins) (Elsbury personal communication). For the other three more labile fractions, $\delta^{18}O_P$ was higher and a slight trend with depth was observed, with maximum values around 5 cm depth decreasing below and above this depth. The average $\delta^{18}O_P$ for the H$_2$O extract is 16.9‰ reaching a maximum of 18.5‰ at 5 cm depth. The average $\delta^{18}O_P$ for the 0.5 M bicarbonate extracts is 17.4‰ (± 0.98) and for the 0.1 M NaOH it is 16.78‰ (± 1.07), with maximum values of 18.6 and 18.1‰ respectively.

The $\delta^{18}O_P$ from the WWTP water showed seasonal variability; however, the isotopic signatures of effluent phosphate were consistently in or very close to equilibrium with water temperatures and the $\delta^{18}O_W$ (see Supplemental data Table S6). The annual average $\delta^{18}O_P$ of the WWTP effluent was 14.8‰, with winter and summer averages of 15.5‰, and 14.3‰ respectively.

4. Discussion

4.1. Benthic flux estimates

Calculated P diffusive fluxes from the sediment using the pore water gradient (gradient calculated using DRP and the gradient between 5 cm and the sediment surface) reached up to 76 mg PO$_4$—P m^{-2} yr^{-1}, and the core incubations, assuming 3 months of anoxic conditions (and using the lower flux for these 3 months), provide an estimate of 190 mg P m^{-2} yr^{-1}. These fluxes are relatively similar to each other despite the distinct methods used to obtain them and the use of several cores collected during different years, providing some confidence that the values are representative. Matisoff et al. (2016) using cores from the western basin of Lake Erie for incubations found no significant difference between years; however they observed a very large range of P

fluxes from the sediment. They report fluxes spanning 2 orders of magnitude, ranging between 0.16 and 2.91 mg P m^{-2} day^{-1} for aerobic incubations, and between 0.58 and 27.26 mg P m^{-2} day^{-1} for anaerobic incubations and calculate annual fluxes between 378 and 808 MTA in the western basin (Matisoff et al., 2016). It is worth noting that the western basin incubations were done at 20 °C, while the central basin cores in this study were incubated at 7 °C (the average annual bottom water temperature in the central basin). Work by Holdren and Armstrong (Holdren and Armstrong, 1980) demonstrated the effects of temperature on P release, and showed that rates are significantly lower, sometimes non-detectable as temperatures approach 7 °C. While we did not have replications (due to loss of duplicate cores) the fact that our values are within the range of the measured values in the western basin, lends confidence that P release from the sediments of the central basin is indeed occurring. Our fluxes are on the lower end of the estimates from the western basin as expected from the lower temperature of incubation as well as lower current and historical P input in the central basin compared to the western basin. Contrary to the general assumption of sediment P release mechanisms the P flux in our anoxic incubation was similar or slightly lower than in our oxic treatment. However when considering the observed variability in the core incubation results from the western basin (oxic 0.16–2.9 mg P m^{-2} day^{-1} and 0.58–27.26 mg P m^{-2} day^{-1} for the anoxic incubations) (Matisoff et al., 2016) when individual cores are compared it is evident that measured anoxic fluxes can be lower than oxic fluxes and only when multiple cores are used on average the anoxic flux is higher. Similar results (e.g. overlap in ranges of flux observed between oxic and anoxic conditions, and low anoxic fluxes at low temperatures) were also reported in other studies (Holdren and Armstrong, 1980).

Extrapolating our sediment fluxes (using the TDP flux from the incubation experiment assuming 3 months of anoxic conditions with the lower anoxic flux and 9 months of oxic conditions with the oxic flux level) to the entire central basin area (16,425 km^2) (Mortimer, 1987) we obtain a flux of 190 mg P m^{-2} yr^{-1} which results in 2400 MTA of P. However temperatures in the deeper part of the central basin generally are below 4 °C in the winter months, which would reduce the P flux from the sediments during those months. During May through July temperatures rise to between 5 and 10 °C, and by September temperatures could reach up to around 12 °C; in October, before the fall mixing, temperatures of up to 14 or 15 °C are seen (Beletsky et al., 2013). If we assume 4.5 winter months with negligible flux (e.g. extrapolating our incubation fluxes only for 7.5 months), then our adjusted annual flux from the central basin becomes 111 mg P m^{-2} yr^{-1}, with a corresponding 1400 MTA. However this does not take into account the potential for higher fluxes during the late summer when temperatures are much higher than 7 °C. We note that fluxes in the same range (e.g. 118–164 mg P m^{-2} yr^{-1}) are obtained when we use the DRP concentration we measured in the overlaying water prior to incubation (2.0–2.3 μM) and the time between core collection and setting of the experiment (8 weeks). Importantly these estimates account only for the diffusive flux and hence are likely lower than the actual fluxes as they exclude bioturbation and related advective fluxes which could be an order of magnitude higher than diffusive fluxes alone (Eleftheriou, 2013).

These data, assuming they are representative of fluxes throughout the open waters of the central basin, suggest a significant benthic flux of P. In particular, as previously mentioned our estimates accounted only for diffusive fluxes and did not include bioturbation by macro-benthic fauna such as mussels (no mussels were observed in the cores). Chaffin (Chaffin and Kane, 2010) reported potential contributions of 1.03 mg P m^{-2} d^{-1} due to burrowing mayflies in the western basin (of Lake Erie), which is indeed higher than the diffusive flux we calculated. Interestingly, Matisoff et al. (1985) observed no effect of oligochaetes and chironomids on P flux in central basin sediments (Matisoff et al., 1985); however, that study was conducted in the mid-1980s, prior to the introduction of dreissenid mussels, which have dramatically changed the benthic community and nutrient cycling in Lake

Erie (Burlakova et al., 2014). Dreissenids mussels comprise the majority of the benthic biomass in Lake Erie, from 88% in the west basin to 99.8% of benthic biomass in the central basins of Lake Erie (Burlakova et al., 2014). Despite comprising 99.8% of the biomass there are large swaths of the central basin without dreissenids, possibly in part due to their inability to tolerate hypoxic conditions (Burlakova et al., 2014) which occur on an annual basis in parts of the central basin. Thus, based on published data from Lake Erie (Chaffin and Kane, 2010) and observations in many other lakes (Caliman et al., 2007; Gallepp, 1979) we expect that the benthic flux of P in much of the central part of Lake Erie where bioturbation occurs to be higher than our diffusive flux estimates from the pore water profile and the core incubation estimates. However, because we did not measure the total net benthic flux (e.g. diffusive, advective and bioturbation effects, as well as possible uptake by benthic organisms) in the lake we use the diffusive flux to estimate the internal loading of P in the central lake. Our estimates of 1800 to 2400 MTA (depending on the range of fluxes we measured and the details used for the extrapolation) of TDP is equivalent to approximately 16–24% of the total reported external P loading to the lake (TP of ~10,000–11,000 MTA) (Baker et al., 2014). Recent work by Matisoff and Carson (who used ^{7}Be and ^{210}Pb to calculate nutrient flux from sediments), suggested that the internal flux of TP from Lake Erie sediments is of an equal magnitude to that of external loads from rivers; however they conclude that much of this P is particle bound and hence not readily bioavailable (Matisoff and Carson, 2014). Our data is based on bioavailable TDP and suggests that bioavailable fluxes from the sediment could actually be quite high and equivalent to at least 16% of the total external load which is dominated by the input from rivers (and likely more as we only consider diffusive processes).

The similar fluxes obtained from the oxic and anoxic core incubations is interesting, because as we mentioned above it has been suggested that benthic fluxes of P are higher under reducing conditions due to the release of P that is bound to Fe-oxides (Hupfer and Lewandowski, 2008; Mortimer, 1942). Based on the high concentrations and rapid increase in Ca in our incubations (Supplemental Table S2) it appears that P associated with Ca is likely the dominant source of the P released in both incubations. In the anoxic incubation, Mn and Fe concentrations were about 3 fold higher than the in the oxic incubation, but still considerably lower than those of Ca and the changes in P concentration did not correspond to those of Fe and Mn. Calcium was extracted from the sediment readily in all four fractions of the Hedley sequential extraction, perhaps indicating that under certain conditions in these sediments calcium bound P acts as a readily available source of P (e.g. likely not in the form of mineral apatite). Indeed, Hupfer and Lewandowski (2008) present data showing that in many lakes, redox cycling is not the major mechanism for P release (Hupfer and Lewandowski, 2008). Many processes can contribute to the release of P from sediments, including; desorption, ligand exchange mechanisms, dissolution of precipitates, mineralization processes, release from living cells, and autolysis of cells (Holdren and Armstrong, 1980; McCulloch et al., 2013; North et al., 2015; Orihel et al., 2015). Factors that affect these processes include; pH, temperature, redox potential, concentrations of nitrate and sulfate, bioturbation, and other biological processes (McCulloch et al., 2013; North et al., 2015). The core incubation fluxes we observed indicate that in the central basin of Lake Erie, release of P from the sediment occurs both at oxic and anoxic conditions and the fluxes are within the same order of magnitude, indicating that benthic fluxes from the sediment are the net result of multiple aerobic and anaerobic processes, and more work is required to both identify these processes and their controls in this and other lakes.

We note that our calculated fluxes are based on data from one site in the deepest part of the central basin of Lake Erie and may not be representative of fluxes throughout the central basin. However because the water column and sediment characteristics are our site are similar to much of the off shore area of the central basin we expect that at least in terms of order of magnitude the flux is representative. Accordingly,

our calculations likely provide an order of magnitude for the diffusive flux, and total fluxes may be higher in areas with more extensive bioturbation. Our values are on the low end of reported P fluxes from lake sediments (see Table 1); however given the lower temperature of our incubation conditions, the lower fluxes we obtained seem reasonable. We also note that, as observed by Matisoff (Matisoff et al., 2016), the western basin is likely to have higher benthic P fluxes due to higher historic P loading and the shallower depth and hence higher temperatures and more sediment resuspension into the water column (Hawley and Eadie, 2006; Lick et al., 1994; Matisoff et al., 2016). In a setting somewhat similar to the western basin of Lake Erie, Lake Winnipeg, a large, shallow (12 m), eutrophic polymictic lake, Nürnberg and LaZerte (2016) calculated internal P loading of 0.5–5.5 mg P m^{-2} d^{-1} (Nürnberg and LaZerte, 2016). However, in-situ estimates from Lake Erie by Burns and Ross (Burns and Ross, 1972) at 11 °C report fluxes of 0.68 mg P m^{-2} d^{-1}, and work by Holdren and Armstrong (Holdren and Armstrong, 1980) show overlapping ranges for oxic and anoxic cores in all for lakes studied, with the low end of their flux rates ranging from −1.9 to 0.95 mg P m^{-2} d^{-1} (Holdren and Armstrong, 1980), which is of similar magnitude to our estimates. Lake Simcoe, a large, mesotrophic lake in southern Ontario, which shares many characteristics with Lake Erie (in particular seasonal hypoxia) was shown by Nürnberg et al. (2013), to have anoxic diffusive fluxes of 7.7–12.8 mg P m^{-2} d^{-1} at 21–24 °C. One core incubated at 10 °C had a flux of 4.3 mg P m^{-2} d^{-1}, demonstrating again the effect of temperature. The calculated internal fluxes were about 45–89% of the external loads to that lake (Nürnberg et al., 2013). Similarly, in Lake Diefenbaker, a large reservoir in southern Saskatchewan, Doig et al., 2016 reported flux rates ranging from 1.49 ± 1.8 (oxic average) to 16.28 (±3.48) mg P m^{-2} d^{-1} from incubations at 15 °C (Doig et al., 2016). Clearly, a wide range of sediment P fluxes to lakes have been reported (Table 1) and overall it is clear that this internal source of P cannot be ignored. At the very least, our results demonstrate a need for more systematic monitoring of sediment internal loading throughout the lake in all basins and at different times of the year to quantify this important flux. Ideally in addition to traditional sediment core methods such as those used here in-situ approaches such as the deployment of benthic chambers and modeling methods such as those developed by Nürnberg et al. (2012), or as modified by Steinman and Ogdahl (2015), could be used simultaneously.

4.2. Oxygen isotopes in phosphate ($\delta^{18}O_P$)

The $\delta^{18}O_P$ values (up to 18.8‰; average of 17‰) observed in the more labile fractions extracted from the sediment pools may in part account for the higher-than-equilibrium water column values reported by Elsbury et al. (2009) (up to 17‰), and supports our conclusions that sedimentary P fluxes are important. These higher isotope ratios may be derived from historical use of chemical fertilizers, detergents (Young et al., 2009), or vegetative organic matter (Pfahler et al., 2013), all of which have isotopic signatures above 15‰ and ranging up to 25‰ (Young et al., 2009) and higher (Pfahler et al., 2013). The weighted average isotopic signature of the external riverine DRP is 11‰ (and average mineral bound P $\delta^{18}O_P$ in the surrounding watersheds is 12.5‰, Elsbury personal communication) while the expected $\delta^{18}O_P$ at equilibrium with lake water at spring and summer lake temperatures is ~14‰. This not only suggests that sediment derived DRP which has elevated $\delta^{18}O_P$ values relative to both lake water equilibrium, and the other input signatures, is a highly possible source of the observed above-equilibrium values, but also that this flux is not negligible (see below).

WWTP effluent is another source of DRP for which the $\delta^{18}O_P$ has not been previously reported. Although the total P flux from WWTPs to the lake (48 MTA) is small compared to the ~10,000 MTA riverine fluxes, if its isotopic signature is very high it may also contribute to the higher than equilibrium values observed in the lake. We analyzed the $\delta^{18}O_P$

Table 1
A summary of measured P diffusive flux from core incubations from similar settings.

Location	Incubation temperature (C)	Incubation duration (days)	Depth cores sampled from (m)	Oxic P release rate (mg P/m^{-2}/d^{-1})	Anoxic P release rate (mg P/m^{-2}/d^{-1})	Reference
Lake Erie, western basin	20	1 & 10	3–10.5	1.35		Matisoff et al. (2016)
Lake Erie, western basin	20	1, 4	3–10.5		4.57 + −4.87	Matisoff et al. (2016)
Lake Erie, western basin	20	10	3–10.5		9.34 + −6.48	Matisoff et al. (2016)
Lake Erie, central basin	7	12	24	0.45	0.25	This study
Lake Diefenbaker	15	64	20–37	1.49 + −1.8	16.28 + −3.48	Doig et al. (2016)
Lake Diefenbaker	15[a]	64	20–37		13.21 + −1.67	Doig et al. (2016)
Lake Simcoe	10	35			4.3	Nürnberg et al. (2013)
Lake Simcoe	24	23			12.5	Nürnberg et al. (2013)
Lake Simcoe	21	19			7.7	Nürnberg et al. (2013)
Lake Simcoe	24	14			12.8	Nürnberg et al. (2013)
Lakes Mendota	2–23	2–10	5	−1.9 to 83	0.67 to 65	Holdren and Armstrong (1980)
Lake Wingra	4–21	2–10	2 & 3.5	−0.56 to 3.4	0.95 to 2.9	Holdren and Armstrong (1980)
Little John Lake	4–16	2–10		<0.02 to 0.37	0.03 to 3.1	Holdren and Armstrong (1980)
Lake Minocqua	3–18	2–10		<0.02 to 1.1	0.02 to 3.8	Holdren and Armstrong (1980)

[a] Intermediate dissolved oxygen level.

of DRP from the Northeast Ohio Regional Sewer District WWTP effluent, which discharges directly into the Central Basin. The annual average $\delta^{18}O_P$ of the WWTP effluent is 14.8‰ (winter average is 15.5‰, summer average 14.2‰). However, these $\delta^{18}O_P$ signatures are close to the expected equilibrium value for PO$_4$ in the lake, and assuming they are representative of other WWTP effluent, do not explain the high values in the central basin reported by Elsbury et al. (2009). Therefore, with our current information, it appears that the only source consistent with the observation of isotopic signatures in the range of 17‰ in the central basin is internal loading from the sediment. This is in agreement with our calculated diffusive fluxes based on pore water profiles and the core incubations, which suggest input in the range of 2400 MTA or about 20% of the external P load.

Using our isotope data and assuming that river inputs and internal sediment loading are the two major sources of P to lake Erie (about 80% and 20% of the total flux, respectively) and that the isotopic signature of the sources is reflected in the lake water, the expected lake water $\delta^{18}O_P$ would be approximately 12‰ (0.8 ∗ 11‰ + 0.2 ∗ 17‰). Elsbury et al. (2009) report values between 10‰ and 17‰ for lake water, but with the exception of two data points these were all above 12‰ suggesting that PO$_4$ undergoes recycling which resets isotope values within the lake. The expected $\delta^{18}O_P$ equilibrium value for the lake is about 14‰ (ranges from 13.5‰ and 14.5‰) and many of the measured $\delta^{18}O_P$ values in the lake are ~2‰ above expected equilibrium. A simple mass balance calculation suggests that to maintain lake $\delta^{18}O_P$ values at 2‰ above equilibrium if the source of elevated PO$_4$ has an isotopic signature of 18‰ (as in the water extracts of the sediment measured in this study) about 50% of the lake PO$_4$ should be derived from this source. This is more than the 20% based on our diffusive flux calculations, but would be quite reasonable when considering the fluxes reported for the western basin (Matisoff et al., 2016) and contribution from bioturbation and advective fluxes. Obviously this calculation is over simplistic, as many processes in the water column may affect $\delta^{18}O_P$ (uptake, regeneration, intra cellular and extracellular recycling etc.) but it provides an order of magnitude evaluation of the importance of this flux.

When considering the complexities of P cycling in Lake Erie, several key points stand out. Many complex interactions from changing agricultural practices (Baker et al., 2014; Bridgeman et al., 2012; Michalak et al., 2013), to invasive species (Burlakova et al., 2014; Conroy and Culver, 2005) have occurred in Lake Erie and its watershed since the 1990s, and influence nutrient cycling, water quality and the biota. Recent work in the western basin has linked the increase in harmful algal blooms to storm events delivering large pulses of P to the western basin (Michalak et al., 2013; Stumpf et al., 2012). There is also evidence of algal blooms moving east from the western basin into the central basin (Michalak et al., 2013). In addition, the composition of P from the major tributaries has shifted towards a higher percentage of DRP (Baker et al., 2014; Scavia et al., 2014). However, during that same time period, the offshore waters have remained (albeit with rather significant interannual variability) at the 1978 Great Lakes Water Quality Agreement (GLWQA) target goals of mesotrophic (western basin) and oligo-mesotrophic (central and eastern basins) TP concentrations (0.48 and 0.3 μM respectively) (Dove and Chapra, 2015). The introduction in the late 1980s and subsequent extensive invasion of dreissenid mussels, and their significant effects on water quality and nutrient cycling, undoubtedly has impacted P cycling in Lake Erie both directly and indirectly via changes in the food web (Burlakova et al., 2014; Conroy et al., 2005). Burrowing mayflies (*Hexagenia* spp) densities have recovered in the western basin to significant numbers, and can also influence P flux from sediments (Chaffin and Kane, 2010). All of these processes, along with climate change, have likely affected internal P loading from sediments, potentially contributing to the re-eutrophication of the lake and algal bloom events (e.g. (Watson et al., 2016)).

5. Conclusion

Based on pore water diffusive profiles and whole core incubations we estimate a relatively large internal loading flux of P from sediments to the water column in the central basin of Lake Erie. This is consistent with recent reports from the western basin (Matisoff et al., 2016) and the higher than equilibrium $\delta^{18}O_P$ values measured in the lake (Elsbury et al., 2009). This has considerable implications for lake management and conservation measures, as this source of P is hard to regulate or control, and direct measures to reduce this input, such as sediment dredging or capping are not feasible in such a large system and furthermore, have implications to lake benthic ecosystems (Eek et al., 2006). If the sediment flux of bioavailable P is largely derived from historic loading of fertilizers and detergents, then it is expected that this may decrease over time with management actions to reduce the external inputs of P in accordance with recently announced binational targets outlined in Annex 4 of the Great Lakes Water Quality Agreement

(GLWQA). However, the complexity of the system and the changes in nutrient cycling that have occurred over the past couple of decades and projected future climate changes render the system spatially and temporally dynamic and suggest that further investigation into the spatial variability of the sediment based P input and cycling in Lake Erie is warranted.

Author contributions

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Appendix A. Supplementary data

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