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# Using Oxygen Isotopes of Phosphate To Trace Phosphorus Sources and Cycling in Lake Erie

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Water samples collected during three sampling trips to Lake Erie displayed oxygen isotopic values of dissolved phosphate ($\delta^{18}O_p$) that were largely out of equilibrium with ambient conditions, indicating that source signatures may be discerned. $\delta^{18}O_p$ values in the Lake ranged from +10‰ to +17‰, whereas the equilibrium value was expected to be around +14‰. The riverine weighted average $\delta^{18}O_p$ value was +11‰ and may represent one source of phosphate to the Lake. The lake $\delta^{18}O_p$ values indicated that there must be one or more as yet uncharacterized source(s) of phosphate with a high $\delta^{18}O_p$ value. Potential sources other than rivers are not yet well-characterized with respect to $\delta^{18}O$ of phosphate, but we speculate that a likely source may be the release of phosphate from sediments under reducing conditions created during anoxic events in the hypolimnion of the central basin of Lake Erie. Identifying potential phosphorus sources to the Lake is vital for designing effective management plans for reducing nutrient inputs and associated eutrophication.

## 1. Introduction

Lake Erie has had a history of water quality problems, peaking in the early 1970s with eutrophic conditions prevailing in the West and Central Basins. Subsequent regulatory efforts to limit phosphate loading were introduced; however, seasonal anoxia in the bottom waters of Lake Erie's Central Basin has continued (*1*). Bottom water anoxia in the late summer is a result of high nutrient loading that stimulates algal growth; upon decomposition of algal material oxygen is consumed (*2*). Thermal stratification during the summer months inhibits the mixing of oxygen into the hypolimnion, creating conditions favorable to hypoxia.

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Although point source contributions of phosphorus (P) to Lake Erie are strictly regulated (*3*) and nutrient loads in river discharge have not increased, recent research indicates that phosphate concentrations in the Central Basin have begun to increase since 1990, rather than decline (*4*). It is unclear what is causing the rise in phosphate concentrations in the Central Basin. This research utilizes the oxygen isotopic composition of dissolved phosphate ($\delta^{18}O_P$) to assess phosphate sources in Lake Erie. This is the first application of $\delta^{18}O_P$ to identify sources and delineate processes of the P cycle in the Great Lakes, one of the world's most important freshwater systems.

The phosphorus−oxygen bond in phosphate is resistant to inorganic hydrolysis at surface water temperatures and pressures and thus, phosphate only exchanges oxygen with ambient water through biological mediation (*5*−*7*). Therefore, where rates of biological uptake and recycling through the biomass are relatively low compared to the input of phosphate, $\delta^{18}O_P$ values will reflect the isotopic signature of sources. However, as biological uptake and recycling increase, $\delta^{18}O_P$ values will shift toward those expected of isotopic equilibrium between water and phosphate. At equilibrium, the magnitude of fractionation between water and phosphate is only a function of temperature and can be calculated based on temperature, the oxygen isotopic composition of ambient water ($\delta^{18}O_w$), and well-established empirically derived fractionation equations (*5, 6*). In systems limited by phosphate, where phosphate supply falls short of biological demand and P cycling is extensive, it is expected that isotopic equilibrium will be achieved and overwrite the signature of sources or any other process (*8*).

The $\delta^{18}O_P$ values in Lake Erie should be controlled by a combination of simple mixing between distinct sources (and their respective isotopic signatures) and movement toward equilibrium by means of recycling through the biomass. Thus, the $\delta^{18}O_P$ values found in Lake Erie should fall between the source values and the expected equilibrium value. If sources have sufficiently distinct isotopic signatures and if these signatures are not altered considerably by biological turnover, $\delta^{18}O_P$ values can be used as a tracer to distinguish phosphate sources and their relative contribution via simple mixing models (*9, 10*). Alternatively, a value consistent with expected equilibrium indicates a system where all of the phosphate is extensively cycled and turned over by the biomass (*11*).

## 2. Experimental Section

**Sample Collection.** Samples were collected from Lake Erie during three different periods. The first sampling trip took place in early August 2005 in conjunction with the International Field Year on Lake Erie. Sampling stations covered the Western and Central Basins of Lake Erie (www.ifyle.org/stations_map.html). Additionally, seven tributaries to Lake Erie were sampled using a small boat. Two additional sampling trips were conducted in June and October of 2006 in cooperation with the Canadian Center for Inland Waters (CCIW). Samples were collected from several of the CCIW regular monitoring stations (http://www.on.ec.gc.ca/monitoring/water-quality/erie_map-e.html). Additional samples were obtained from the mouths of each of the seven previously sampled rivers. Samples were taken from multiple depths at each lake station on the August 2005 and October 2006 cruises, and from a third of the sampled lake stations on the June 2006 cruise. At locations where a depth transect was sampled, water was taken from the epilimnion, metalimnion, and hypolimnion (when present).


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During the first sampling trip in August 2005, approximately 20 L of water from each lake station and depth and 8 L from each river station was collected in acid-washed polycarbonate bottles. Due to low phosphate concentrations in the Lake (0.03−0.9 $\mu$M; average 0.17 $\mu$M), these volumes were not always sufficient for isotopic analysis. Accordingly, sample size was roughly doubled in subsequent trips, such that ~40 L of lake water and ~20 L of river water were collected during the June and October 2006 sampling trips. Surface water samples were collected using a dedicated bilge pump from the deck and deeper samples were collected using 8 L Van Doran bottles mounted on a rosette. River samples were collected by submerging the collection bottles. River water samples were filtered through 0.45 $\mu$m GF/F filters in the field to remove particulate matter prior to field processing.

In the field, phosphate was quantitatively removed from solution through a process of coprecipitation with magnesium hydroxide ($Mg(OH)_2$) (*12*). About 50 g of magnesium chloride ($MgCl_2$, Fischer, ACS grade) and 220 mL of 1 M sodium hydroxide (NaOH, Fischer, ACS grade) were added to each 20 L container of sample water (final Mg concentration was around 28−30 mM and final pH of ~11.5) to induce magnesium hydroxide precipitation. This procedure was tested previously and was shown to be effective in scavenging soluble reactive phosphate (SRP) (*12, 13*). The precipitate was allowed to settle and the excess water was siphoned off. The precipitates were transferred into 2 L acid-washed high-density polyethylene bottles and kept cool during transport to the laboratory for further analysis.

Samples for $\delta^{18}O_w$ were also collected from each station and depth, and samples for phosphate concentration were collected from the rivers. The respective monitoring programs provided lake water nutrient concentrations. Additionally, sampling time, location, and water temperatures were also recorded.

**Sample Processing.** Samples were processed according to McLaughlin et al. (*13*). The procedure utilizes a series of dissolution and precipitation reactions to isolate and purify dissolved inorganic phosphate as silver phosphate. Briefly, magnesium hydroxide is dissolved and phosphate is precipitated as cerium phosphate. This precipitate is then dissolved and a cation exchange resin is used to remove cerium ions. Finally, silver nitrate is added to the solution, resulting in precipitation of silver phosphate. Typical yield for silver phosphate was ~85%, sample loss was due to the difficulty of precipitate removal from filters (*12, 13*).

The $\delta^{18}O$ value of silver phosphate was determined using a Eurovector Elemental Analyzer coupled to a Micromass Optima mass spectrometer at the U.S. Geological Survey (USGS) in Menlo Park, California. Two internal silver phosphate standards, STDH ($\delta^{18}O_p$ = +20.0‰) and STDL ($\delta^{18}O_p$, +11.3‰), were used for calibration and analyzed in duplicate at the beginning and end of each batch of samples and following each tenth sample. Standards were prepared to span the range of sample weights (0.2−0.3 mg). Samples were run in duplicate, except when the final silver phosphate precipitate mass was insufficient to produce two samples. Analytical precision (1$\sigma$) averaged 0.3‰ for $\delta^{18}O$ based on replicate analyses of standards and some samples. All $\delta^{18}O$ isotopic values are reported using standard delta notation relative to the Vienna Standard Mean Ocean Water (VSMOW) (*14*).

Water $\delta^{18}O$ was measured using a Finnigan MAT 251 mass spectrometer, also at the USGS in Menlo Park. Nutrient concentrations were measured using a flow injection nutrient autoanalyzer system and were provided to us by other facilities (IFYLE, National Environmental Research Laboratories (NERL), UC Davis, and the Marine Science Institute (MSI) at UC Santa Barbara).

**Data Analysis.** The theoretical isotopic equilibrium value expected for each sample was determined by applying the phosphate−water fractionation equation empirically derived by Longinelli and Nuti (*5*),

$$T(°C) = 111.4 - 4.3(\delta^{18}O_p - \delta^{18}O_w) \quad (1)$$

where $\delta^{18}O_P$ is the oxygen isotopic composition of phosphate expected at equilibrium, $\delta^{18}O_w$ is the oxygen isotopic composition of the water, and $T$ is the temperature of the water in degrees Celsius. We used the measured parameters ($\delta^{18}O_w$ and temperature) for each sample to derive the expected equilibrium value. Measured $\delta^{18}O_P$ values were compared to the expected equilibrium values to assess whether the phosphate had been recycled through the biomass. The $\delta^{18}O_P$ values of river samples were compared to the lake $\delta^{18}O_P$ values to determine if river phosphate is an important source to the Lake that could be identified using isotopes.

## 3. Results and Discussion

**Results.** The $\delta^{18}O_P$ values in the surface water of Lake Erie during the three sampling periods were markedly variable both spatially and temporally (Figure 1). Note that the extrapolation between sampling sites is based on a few, sometimes widely spaced, data points, particularly for August 2005. The isotopic values of the rivers sampled are also shown in Figure 1. A table containing all data collected during this study is available as Supporting Information.

*August 2005.* Riverine $\delta^{18}O_P$ values from the Maumee, Cuyahoga, and Chagrin Rivers were quite similar, ranging from +12.3‰ to +12.9‰ (Figure 1a). $\delta^{18}O_P$ values in the Lake showed significant spatial variability with low values in the south and west and higher values in the north and east. Within the shallow West Basin values ranged from +11.7‰ to +13.5‰ at the surface and from +8.4‰ to +14.9‰ at depth whereas in the Central Basin samples values ranged from +13.9‰ to +15.4‰ at the surface and from +12.9‰ to +14.4‰ at depth. Values for $\delta^{18}O_w$ ranged between −7.1‰ and −6.8‰ in the West Basin and between −6.9‰ and −6.7‰ in the Central Basin, with a lakewide average of −6.9‰. Most of the $\delta^{18}O_P$ values were out of equilibrium with respect to temperature and $\delta^{18}O_w$, although the West Basin values are typically closer to the equilibrium compared to the values from the Central Basin samples (Figure 2). No consistent vertical pattern is discernible from the data set; however, because of the small sample size (12 data points), this result may not be representative.

*June 2006.* River $\delta^{18}O_P$ values from the Grand, Chagrin, and Cuyahoga Rivers were very similar to each other and to the signatures measured in 2004: between +12.4‰ and +12.8‰ (Figure 1b). The Detroit River had a lower $\delta^{18}O_P$ value of +10.5‰. Lake water $\delta^{18}O_P$ values ranged from +10.0‰ to +17.1‰, with stations in the Central Basin generally having slightly higher values. The West Basin surface average $\delta^{18}O_P$ value was +14.4‰, whereas the Central Basin surface average value was +14.5‰, though this average is skewed by one particularly low value in the eastern portion of the Central Basin. Samples taken from the hypolimnion in the Central Basin had $\delta^{18}O_P$ values ranging from +12.9‰ to +15.8‰. The hypolimnion values generally had higher $\delta^{18}O_P$ signals relative to the surface value at the same station (Figure 3, station 949). Values for $\delta^{18}O_w$ ranged between −7.3‰ and −7.1‰ in the West Basin and between −7.3‰ and −6.4‰ in the Central Basin, with a lakewide average of −6.9‰. Similar to the samples from August 2005, most of these samples were out of equilibrium, no spatial pattern was discernible with respect to deviation from expected

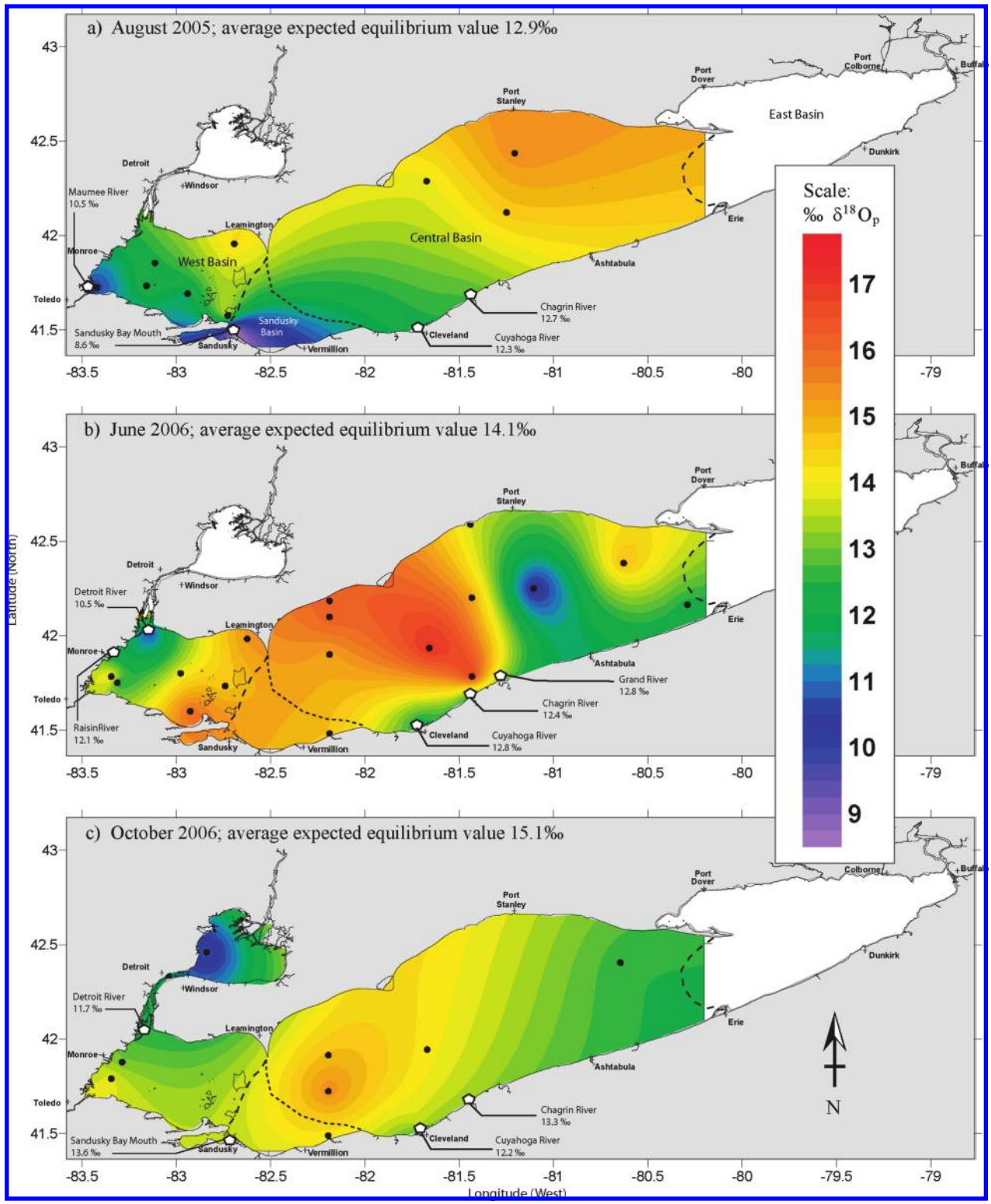


**FIGURE 1. Contour plots of surface oxygen isotopic composition of phosphate in Lake Erie on various sampling trips. Points represent sample stations used to extrapolate contours; white pentagons and labels indicate river mouths sampled with oxygen isotopic composition of phosphate given. Average expected equilibrium values, calculated based on temperature and oxygen isotopic composition of surface water according to ref *3*, are given in the chart title for each sampling trip.**

isotopic equilibrium, and some values in each basin were both greater than and less than those expected at equilibrium (Figure 2).

*October 2006.* Figure 1c shows $\delta^{18}O_P$ values of samples collected during October 2006. The average of the river signatures was +12.5‰, though the river samples exhibit a greater range than those collected in August 2005 or June 2006: from +11.7‰ (Detroit River mouth) to +13.6‰ (Sandusky Bay mouth). Lake St. Clair, which feeds the Detroit River, was added to the sampling plan for the first time during this trip and displays the lowest $\delta^{18}O_P$ value in the October data set (+9.7‰). The West Basin average $\delta^{18}O_P$ value was +13.4‰ for surface waters and +15.0‰ for deeper water samples. The Central Basin average surface and deep $\delta^{18}O_P$

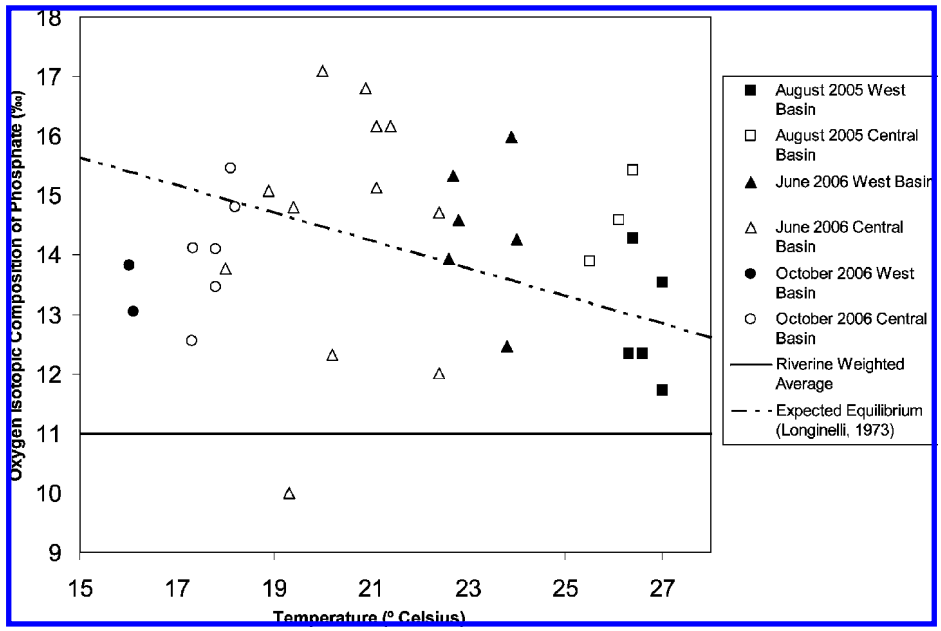


**FIGURE 2. Oxygen isotopic composition of phosphate ($\delta^{18}O_p$) of Lake Erie surface water. Symbols refer to different sampling trips and basins. The line at +11‰ represents the weighted average riverine $\delta^{18}O_p$. The dashed line represents the expected $\delta^{18}O_p$ value calculated based on the temperature for each sample and at the average lake surface $\delta^{18}O_w$ of −6.78‰ (standard deviation 0.3‰). Using the sample-specific $\delta^{18}O_w$ values generally results in less than 0.4‰ deviation from calculations using the average lake water $\delta^{18}O_w$ value.**

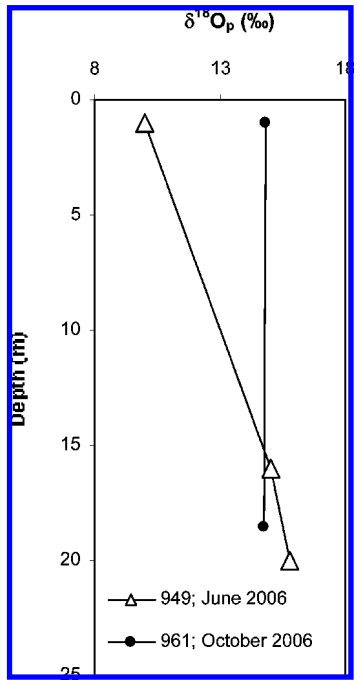


**FIGURE 3. Representative depth profile for June 2006 and October 2006. Station 949 is located at latitude 42.25° N, 81.11 °W in the Central Basin and station 961 is located at 41.1° N, 82.21° W in the Central Basin.**

values were +14.1‰ and +13.1‰, respectively. The Central Basin $\delta^{18}O_P$ values tended to be relatively homogeneous with depth, whereas samples collected at depth in the West Basin tended to be higher than surface values. Values for $\delta^{18}O_W$ ranged between −7.8‰ and −5.2‰ in the West Basin and between −7.2‰ and −5.6‰ in the Central Basin, with a lakewide average of −6.5‰. Most of the October 2006 $\delta^{18}O_P$ values fall between those of the riverine source and values expected at isotopic equilibrium; two data points exceed the equilibrium values (Figure 2).

The relationships between $\delta^{18}O_P$ values in lake water and SRP concentrations and nitrate to SRP ratios (N:P) which could shed light on P cycling processes in the Lake are shown in Figure 4.

**Discussion.** The majority of the $\delta^{18}O_P$ values measured in Lake Erie are higher than those found in the seven rivers sampled, which includes the two rivers, Detroit and Maumee, contributing the largest total P loading to the Lake (Figures 1 and 2). These rivers have a $\delta^{18}O_P$ signature that is fairly consistent through time with an average value of +12.1‰ (±1.7‰) and a weighted average $\delta^{18}O_P$ value (based on phosphate concentration and discharge fluxes) of ∼+11‰. None of the smaller tributaries are expected to have a sufficiently large phosphate flux to result in the higher isotope values observed in the Lake (*15, 16*). Therefore, the lake $\delta^{18}O_P$ composition cannot be explained solely as unaltered riverine phosphate; either additional nonriverine sources (with a higher $\delta^{18}O_P$) and/or some process (involving isotope exchange and fractionation) that would result in high $\delta^{18}O_P$ values in the lake water must be impacting the system.

Notably, however, many of the samples had $\delta^{18}O_P$ values significantly greater than the equilibrium values expected for the temperature range and $\delta^{18}O_W$ in Lake Erie, particularly in the Central Basin (Figure 2). The $\delta^{18}O_P$ values in excess of those at equilibrium cannot be explained by cycling of riverine phosphate through the biomass as biomass-mediated processing drives isotope values toward equilibrium. If rivers are the dominant phosphate source and biological intracellular P cycling within the Lake had altered the $\delta^{18}O_P$ values toward equilibrium, then measured values in the Lake should be distributed only between the lower riverine $\delta^{18}O_P$ values and the equilibrium $\delta^{18}O_P$ values calculated according to eq 1 (Figure 2). This is not the case in Lake Erie.

Extensive biological cycling (leading to isotopic equilibrium) is expected at low phosphate concentrations and high N:P ratios, such as those found in Lake Erie; however, such equilibrium values are not prevalent in Lake Erie and no relation between the deviation from equilibrium and either SRP concentrations or N:P ratios is evident (Figure 4). In the absence of evidence for extensive intracellular biological

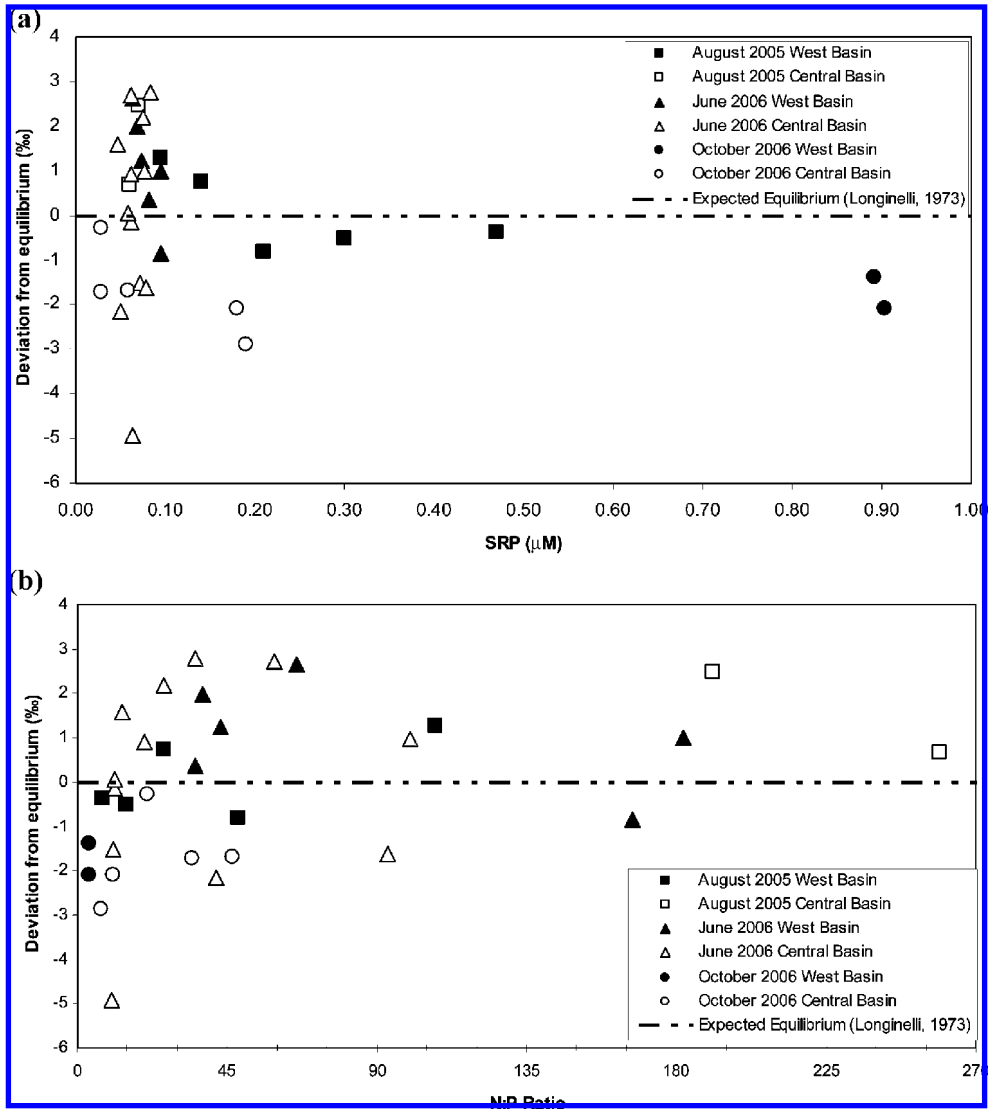


**FIGURE 4. Magnitude and direction of the deviation of the observed $\delta^{18}O_p$ values from the expected equilibrium $\delta^{18}O_p$ value (calculated with sample specific temperature and $\delta^{18}O_w$ values) plotted against (a) soluble reactive phosphate concentration (SRP) and (b) nitrogen-to-phosphorus ratio (N:P).**

recycling (i.e., expected equilibrium), the observed $\delta^{18}O_P$ values can be attributed to either disequilibrium isotopic effects enriching the $\delta^{18}O$ of lake phosphate or end-member mixing which includes at least one phosphate source with a high $\delta^{18}O_P$ value. If caused by mixing, the distribution of $\delta^{18}O_P$ values in Lake Erie would indicate that there is an as yet uncharacterized source of phosphate with an elevated isotopic signature (e.g., higher than +17‰). If driven by disequilibrium processes, the $\delta^{18}O_P$ distribution would indicate a process that shifts the isotopic signature toward values higher than expected at equilibrium.

Blake et al. (*8*) have reported processes resulting in disequilibrium isotopic shifts. Such processes can take place at either high or low inorganic phosphate concentrations. For instance, in an environment with excess phosphate (high SRP concentrations), partial utilization of the phosphate pool will induce kinetic fractionation during nutrient uptake or sediment adsorption (Rayleigh effects) and result in an isotopically heavy residual pool of phosphate. In Lake Erie, where phosphate concentrations are relatively low (average value 0.17 $\mu$M), it is not expected that partial consumption (utilization) of dissolved phosphate will be so prevalent as to have such an impact on the isotopic signature. If indeed partial utilization leading to kinetic fractionation during uptake is the process responsible for the elevated isotope values observed, a consistent relationship would be expected between the SRP and the $\delta^{18}O_P$ values or N:P and $\delta^{18}O_P$ values. Such a relationship is not observed in our data set either when all samples are considered or when only samples with values higher than expected at equilibrium are taken into account (Figure 4).

In phosphorus-limited systems organisms can tap into the dissolved organic phosphorus (DOP) pool utilizing extracellular enzymes such as alkaline phosphatase to convert DOP to phosphate ($PO_4^{3-}$) (*8*). This process can result in "inheritance effects," in which two to three of the oxygen atoms in $PO_4^{3-}$ retain the isotopic signature of the organophosphate source whereas one to two oxygen atoms are replaced from the ambient water with an enzyme-specific fractionation (*8*). The alkaline phosphatase enzyme is associated with a −30‰ fractionation (*8*) and 5′-nucleotidase with a −10‰ fractionation (*17*). This large negative fractionation would typically lower the $\delta^{18}O_P$ value relative to the original organic phosphate pool. Whereas $\delta^{18}O_P$ values of DOP have not yet been reliably determined, we have no reason to suspect that the DOP pool has a high isotopic value. Indeed, if the organophosphate compounds are locally derived, from algae growing in the Lake, their $\delta^{18}O_P$ value is expected to be at or close to equilibrium and inheritance effects due to enzyme conversion of organophosphate would

lower the $\delta^{18}O_P$ signature of the resulting inorganic phosphate. Thus, utilization of DOP most likely cannot explain the elevated values observed in our study relative to those expected at equilibrium.

An alternative explanation for the data is that the isotope values represent mixing of at least two sources: one with a riverine signature and the other with a high $\delta^{18}O_P$ signature near +17‰ or higher. Both source signatures will be altered due to recycling in the Lake and will move toward the equilibrium value. This additional source(s) apparently plays a large role in determining the overall phosphate isotopic composition of the Lake, especially in the Central Basin, as evidenced by higher values there. We hypothesize that the high $\delta^{18}O_P$ signal found in the Central Basin of Lake Erie is from phosphate resuspension and desorption or diffusion from bottom sediments, which is providing the nutrient "pulse" to the Lake. The trend we see in the few offshore depth profiles, where $\delta^{18}O_P$ values typically increased with depth, indicates the possibility of a deep-water phosphate source with a high $\delta^{18}O_P$ value. Under anoxic water conditions—such as those created in the hypolimnion as a result of eutrophication—iron hydroxides at the bottom of the Lake will dissolve and release phosphate adsorbed to their surfaces (*18, 19*). Formation of iron sulfides following the microbial reduction of sulfate aids this process by removing reduced iron from solution, thus precluding the formation of insoluble ferric phosphate (*1*). Therefore, annual anoxic events could be acting to liberate phosphate that had been previously sorbed to bottom sediments (e.g., from historic fertilizer and detergent inputs). This internal loading could be responsible for seasonally elevated phosphate concentrations (*20*) and the high $\delta^{18}O_P$ value seen in this study. At this time, no pore waters or sediments have been analyzed for oxygen isotopes of releasable phosphate, and it is unknown how phosphate resuspension or postburial processing affects the isotopic composition of oxygen in phosphate (*21*).

Although there is little if any vertical transport of water during the thermal stratification common to the summer months, internal waves, mixing during storm events, or coastal upwelling could potentially allow nutrient-rich bottom water to mix into the epilimnion and this could explain the high $\delta^{18}O_P$ values we see in surface waters in June 2006.

Other potential sources of phosphate include detergents, chemical and organic fertilizers, weathering of soil and rocks, atmospheric deposition, groundwater input and sewage effluents, and other point sources of industrial discharge. Detergents (if any used in the basin are phosphate-bearing) are expected to enter the Lake mostly through point source sewage discharge. Sewage effluents, while sometimes having high $\delta^{18}O_P$ values, usually have a low $\delta^{18}O_P$ value (*9, 22, 23*). Indeed, two samples from the Easterly wastewater treatment plant in Cleveland, OH, had $\delta^{18}O_P$ values of +13.6‰, which is lower than the +17‰ value needed to explain our data. These samples may not be representative of all discharging treated wastewater, but if they are representative, this suggests that sewage is not the missing source. Interestingly, two samples with an anomalously low $\delta^{18}O_P$ signature were found near the islands in the West Basin. These low $\delta^{18}O_P$ values (8−9‰) are significantly lower than the riverine signature and are not consistent with biological cycling, which would increase the isotopic signature toward equilibrium. Instead, these values could be reflective of local input source(s) of phosphate with a low $\delta^{18}O_P$ value such as sewage or septic effluent seepage. The proximity of the site to urban centers around the West Basin is such that sewage effluent from municipal wastewater treatment plants could feasibly influence the measured $\delta^{18}O_P$ values. Presence of fecal indicator bacteria in groundwater on South Bass Island shows that sewage effluent does reach the groundwater (*24*) and could potentially be the source of phosphate with low $\delta^{18}O_P$ values seen around the West Basin islands. Clearly, the isotopic signature of the important sewage dischargers and any other known point source discharge to this Lake as well as groundwater seepage sources should be determined before these sources could be dismissed as contributing to local or lakewide phosphate and impacting the observed isotope values.

Marine phosphorites are known to have high $\delta^{18}O_P$ values, but no major phosphorite deposits weather and drain into Lake Erie. If these were dominant, one would expect to see their signature in rivers draining the same bedrock. Some fertilizers are also known to have high $\delta^{18}O_P$ values. Fertilized fields should also primarily drain into Lake Erie through the rivers sampled, yet no high signature was observed in the rivers. Moreover, we observe that high $\delta^{18}O_P$ values rarely occur at the stations nearest to the agricultural southern shoreline and the river mouths, but rather are often found in the middle of the Lake and primarily in the Central Basin. Thus, at present our data do not support present day fertilizer input or soil and rock weathering sources through river discharge as major sources of the observed elevated $\delta^{18}O_P$ signatures. However, historical fertilizer released from the sediments could be a possible source. Particulate matter delivered to the Lake through atmospheric deposition could also have high $\delta^{18}O_P$ values. It is unlikely that the phosphate flux from this source is large enough to solve the mass balance for phosphate in Lake Erie or have a significant effect on bulk phosphate composition. We measured the $\delta^{18}O_P$ value of dry deposition to Lake Erie using two aerosol filters collected in Cleveland, OH, by the EPA Great Lakes National Program Office. Both filters returned $\delta^{18}O_P$ values lower than that of the average riverine signature. Thus, these preliminary results suggest that atmospheric deposition is not responsible for the high $\delta^{18}O_P$, but more systematic work has to be done to characterize and completely rule out an atmospheric source. Groundwater from the drainage basin has not been analyzed for $\delta^{18}O_P$ signatures. Groundwater flux directly to the Lake is a potential input mechanism for phosphate, possibly with a high isotopic signature. However, as groundwater also makes up over 50% of base river flow (*25*), any isotopic signature associated with groundwater should also be observed in the river water $\delta^{18}O_p$ values. It is therefore unlikely that the high $\delta^{18}O_P$ values in the Central Basin are related to groundwater flux.

In conclusion, our data suggest that there is an unaccounted for source of phosphate with a high $\delta^{18}O_P$ signature that contributes to the phosphate load in Lake Erie. Little data on sources other than riverine inputs exist at this stage; thus, a more thorough investigation of potential sources and their respective signatures is needed. Based on our limited data, we speculate that a likely source may be sediment recycling and release of phosphate under reducing conditions created during anoxic events in hypolimnion. Investigation of prevalent phosphorus cycling processes in the Lake and their associated isotopic fractionations will also be useful. Once the specific source(s) and processes that contribute the additional phosphate to the Lake and to isotope fractionation and exchange of oxygen in phosphate are determined, an isotopic mass balance could be constructed such that the relative contributions of the various sources are quantified and the impact of phosphate recycling in the biomass is assessed. Such data will be useful for the management and restoration of lake water quality.

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## Supporting Information Available

A data table that lists all available information for the samples described in the manuscript. The information is available free of charge via the Internet at http://pubs.acs.org.

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