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Review

Tracing phosphorus cycle in global watershed using phosphate oxygen isotopes

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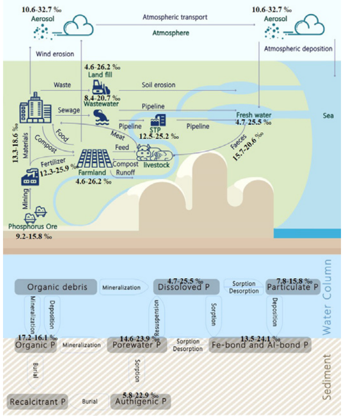
HIGHLIGHTS

- Using the phosphate oxygen isotope technique to trace the P cycle is completely feasible.
- P cycle response to internal P loading and external P input illustrated by isotope data.
- Reducing both internal P loading and external P input to improve water quality are needed.
- Clarifying oxygen isotope fractionation mechanism of phosphate is beneficial for P dynamics prediction.

GRAPHICAL ABSTRACT



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ABSTRACT

The Phosphorus (P) cycle is a crucial biochemical process in the earth system. However, an extensive increase of P input into watersheds destroyed the ecosystem. To explore the effects of internal P loading and external P input in global watersheds, we reviewed the research progress and synthesized the isotope data of experimental results from literatures. An integrated result of the observational and experimental studies revealed that both internal P and external P largely contribute to watershed P loadings in watersheds. Internal P can be released to the overlying water during sediment resuspension process and change of redox conditions near the sediment – water interface. Growing fertilizer application on farmlands to meet food demand with population rise and diet improvement contributed to an huge increase of external P input to watersheds. Therefore, water quality cannot be improved by only reducing internal P or external P loadings. In addition, we found that phosphate oxygen isotope technology is an effectively way to trace the P biogeochemical cycle in watersheds. To better predict the dynamic of P in watersheds, future research integrating oxygen isotope fractionation mechanisms and phosphate oxygen isotope technology would be more effective.

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1. Introduction

Phosphorus (P) forms part of life activities in the ecosystem, the growth, development, and reproduction of organisms cannot go on without P participation (Elser, 2012; Karl, 2000; Westheimer, 1987). The P cycle is essential in the earth system process, this process occurs slowly (Elser and Bennett, 2011; Follmi, 1996; Yuan et al., 2018) in natural conditions. Due to the increasing demand for food and energy, P input to the biosphere by human activities has increased four times in recent decades (Bouwman et al., 2012; Falkowski et al., 2000; Powers et al., 2016), this contributed to the rapidly accelerated P cycle. However, consumption of P by organisms is much less compared to other nutrient elements, like Carbon (C) and Nitrogen (N), with the consumption ratio of C, N and P 106:16:1 (Jaisi and Blake, 2014; Zhang et al., 2018). With the low stoichiometric need but high P input amount into the surface environment (Goyette et al., 2018), generous anthropogenic P loss to the surrounding freshwater by runoff and cause algal bloom, a serious water quality degradation concern globally (Ho et al., 2019).

Internal P loading and external P input can cause excessive high P load (Fig. 1) in watersheds. Internal P loading refers to P released from the sediment by the resuspension process and from suspended particles by the sorption and desorption processes (Fig. 1b). Some researchers found that internal P loading can cause aquatic eutrophication even external P input is effectively controlled (Søndergaard et al., 2012; Wang et al., 2009; Yin et al., 2020). Most P in rivers or lakes is usually stored at the sediment (Horppila, 2019). Therefore, internal P loading from the sediment can delay water quality improvement in eutrophic waterbody even external P input significantly reduced (Søndergaard et al., 2003; Yin et al., 2020). At present, the main concern of external P input to the watershed related to human activities (Fig. 1a), like the mining of phosphate rock, fertilization of farm crops, livestock breeding, food consumption, waste and sewage from urban construction. The elemental P used by humans, such as fertilizer production, for better grow up crops is mainly obtained on digging up geological phosphate reserves (Yuan et al., 2018). Thus, a huge amount of P flowed from ores into agricultural farms and leach to freshwater and oceans, and thereby impairing aquatic ecosystems dramatically (Benitez-Nelson, 2000; Elser and Bennett, 2011; Goyette et al., 2016). Though watersheds can store P as a buffer to prevent the adverse impact of excessive P use, buffering threshold can be rapidly surpassed due to a rapid increase of anthropogenic P input in watersheds (Goyette et al., 2018). In addition, the expanding food demand and diet improvement would also furtherly accelerate this process (Yuan et al., 2018). Hence, reducing P loading into watershed is indispensable to protect water resources, a primary human need for survival (Chen and Graedel, 2016; Goyette et al., 2018).

Substantial progress has been made in tracing the P cycle for better P management in watersheds. For example, analyzing the interference of human activities on P cycle by the numerical models (Elser and Bennett, 2011; Yuan et al., 2018), illustrating the intensification of P cycling resulting from the increase of food demand and population by a life cycle process-balanced model (Liu et al., 2016), or quantifying the different sources of the anthropogenic P by a quantitative budget calculation (Hu et al., 2020; Powers et al., 2016). Among the existing P cycle tracing approaches technologies, the phosphate oxygen isotope technology has received much application. Though P has 23 isotopes, only ^{31}P is stable, the stable isotope technology requires at least two stable isotopes. Therefore, ^{31}P cannot be applied to trace the P cycle in the environment like the other nutrient elements, like C, N, and S, which have two or more stable isotopes. Orthophosphate (PO_4^{3-}) is widely distributed in soil, rock, water, and all organisms, it can migrate in environment as an entirety (Jaisi and Blake, 2014). Based on these, the stable isotope ratios of oxygen in PO_4^{3-} can be used as the tracer to explore the P cycle in the environment (Colman, 2002; Ji, 2017; Liang, 2005; Tian, 2017). The oxygen isotope ratio in PO_4^{3-} is usually expressed as $\delta^{18}O_{PO4}$, this value is calculated by the following equation (Blake et al., 1997; Colman, 2002):

$$\delta^{18}O_{(PO4)}(‰) = \left(R_{sample}/R_{standard} - 1\right) * 1000 \tag{1}$$

where R_{sample} and $R_{standard}$ represents the $^{18}O/^{16}O$ of the sample and standard respectively. The standard often used is VSMOW (Vienna standard mean ocean water). At present, phosphate oxygen isotope technology is one of the most widely used P cycle explorations in watersheds. Previous works have contributed to our understandings of the P migration, but not been evaluated and synthesized to identify future research directions of the P cycle in watersheds.

Therefore, the current paper provides a comprehensive review and evaluates the recent progress of the global watershed P cycle using phosphate oxygen isotope technology. We first reviewed the experimental results to identify the P cycle response to internal P loading and external P input. Further, we evaluated the oxygen isotope fractionation of phosphate and the P cycling pathway illustrated by isotope data in the global watershed. Finally, we highlight the future research needs to understand the P cycle and better predict P dynamics in watersheds in response to multiple P sources.

2. Sampling and experimental evidence

In recent decades, research works have been conducted in identifying and tracing the P cycle in watersheds using phosphate oxygen isotope technique, study areas were all concentrated in the northern hemisphere (Fig. 2), which has an intense population and complex river network than the southern hemisphere. $\delta^{18}O_{(PO4)}$ of potential P sources and fresh water (river and lake) samples showed a wide isotopic composition range, and differences between the value are statistically significant (SI Appendix 1, Table S1). The $\delta^{18}O_{(PO4)}$ ranged from +4.7 to +25.5‰ in freshwater samples, and from +4.2 to +32.7‰ in possible P sources (SI Appendix 1,

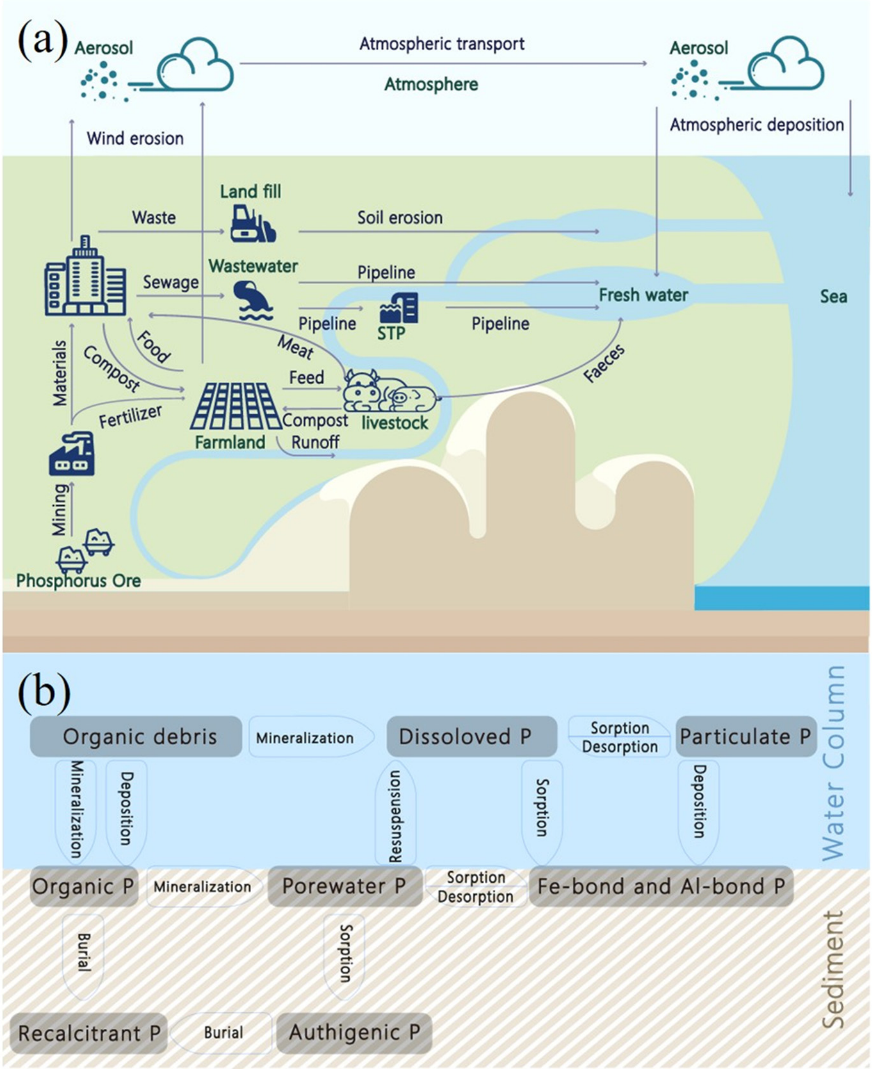


Fig. 1. A schematic diagram of (a) external P input and (b) internal P loadings. Note: Fig. 1(a) refers to (Liu et al., 2016; Yuan et al., 2018); Fig. 1(b) refers to (Cyr et al., 2009; Joshi et al., 2015; Yuan et al., 2019); STP means sewage treatment plant.

Table S2). The average $\delta^{18}O_{(PO4)}$ value in freshwater samples was 15.2 ± 3.7‰, and 16.1 ± 4.2‰ in all samples. The $\delta^{18}O_{(PO4)}$ value of the freshwater falls within the range of $\delta^{18}O_{(PO4)}$ values in the possible P sources, like soil, sediment, fertilizer, etc. This indicates that P in water is derived from multiple sources, and the flow of P from ore to water was a complex process, and needs to be further studied in the future. The $\delta^{18}O_{(PO4)}$ value in soil and sediment have a wider scope, because soil and sediment are the primary sinks of P in watersheds. Soil and sediment have a large P storage capacity, they can retain P as a buffer or release P into watersheds under certain conditions (Ding et al., 2018; Goyette et al., 2018; Søndergaard et al., 2003). The $\delta^{18}O_{(PO4)}$ in fertilizer (Include manure and inorganic fertilizer) and WWTP (wastewater treatment plant final effluent or wastewater) gives an indication of possible contribution of agricultural fertilization and urban wastewater to the P loads in the watershed respectively. Similarly, the $\delta^{18}O_{(PO4)}$ in detergent and faeces can disclose the contribution of domestic sewage and livestock respectively, the $\delta^{18}O_{(PO4)}$ in aerosol can explore the impact of atmospheric deposition into watershed P loads, the $\delta^{18}O_{(PO4)}$ in P ore represent that influence of rock weathering process on P loads in Watersheds (Fig. 2). Due to the overlap of $\delta^{18}O_{(PO4)}$ values in some P sources (Fig. 2), using $\delta^{18}O_{(PO4)}$ for source apportionment of P remains a challenging task. However, due to the broad range of $\delta^{18}O_{(PO4)}$ and significant variation between different sample groups (SI Appendix 1, Table S1), it has received application for tracing the P cycle (Young et al., 2009).

3. Effect and correction of microorganism on P cycle traced by phosphate oxygen isotope technique in watersheds

PO_4^{3-} can migrate into aquatic environment as an entirety without the participation of microorganisms (Colman, 2002; Jaisi and Blake, 2014), therefore, phosphate oxygen isotope technique is an effectively way for tracing P sources in watersheds. However, various microorganisms exist in natural water and participate in the P biogeochemical cycle. These microorganisms preferentially take up P as PO_4^{3-} from the aquatic environment. However, low PO_4^{3-} content limits their biological growth and development (Ehlers et al., 2010; Richardson et al., 2011). Some aquatic plants and microorganisms are forced to exudate extracellular enzymes like phosphatases to hydrolyze the organophosphorus in order to produce inorganic phosphate (Von Sperber et al., 2014). During this process, the exchange of oxygen between PO_4^{3-} and surrounding water interferes with the original $\delta^{18}O_{(PO4)}$ value, and causes difficulty in identifying the possible P sources using phosphate oxygen isotope technique (Blake et al., 2001; Blake et al., 1997; Liang and Blake, 2006). To explore whether the oxygen in PO_4^{3-} has reached equilibrium fractionation with the surrounding water,

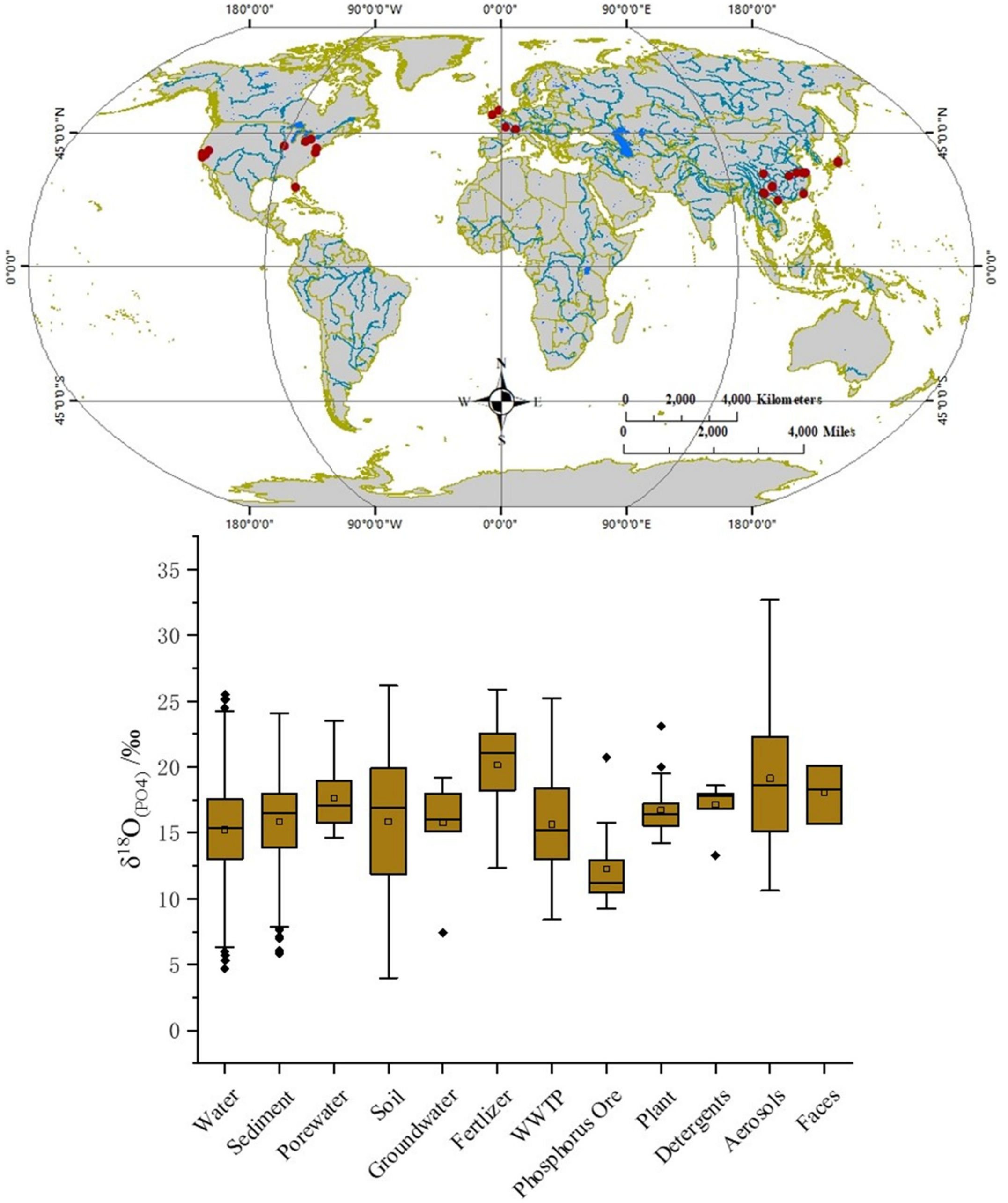


Fig. 2. Sample points and $\delta^{18}O_{(PO4)}$ data in global watershed. Note: the raw data and references cited see SI Appendix 2

studies have focused on equilibrium fractionation caused by enzymatic degradation, several phosphate-water fractionation equations were proposed based on specific researches (Amiot et al., 2017; Chang and Blake, 2015; Kolodny et al., 1983; Lecuyer et al., 2019; Liang and Blake, 2007; Longinelli and Nuti, 1973). Among them, the two most commonly used phosphate-water fractionation equations empirically are given below (Chang and Blake, 2015; Longinelli and Nuti, 1973):

$$T = 111.4 - 4.3*(\delta^{18}O_{(PO4)} - \delta^{18}O_w)\ (r = 0.98) \tag{2}$$

$$\delta^{18}O_{(PO4)} = (\delta^{18}O_w + 1000)e^{\left(14.43*\frac{1000}{T}-26.54\right)/1000} - 1000\ (r^2 = 0.99) \tag{3}$$

where T in Eqs. (2) and (3) is the temperature in degree Centigrade (°C) and Kelvin (K) respectively, $\delta^{18}O_w$ means that the oxygen isotope composition of freshwater. However, Longinelli and Nuti (1973) use fluorination of $BiPO_4$ to measure $\delta^{18}O_{(PO4)}$, an overwhelming majority of recent researchers uses the Ag_3PO_4, which results in a ~2.0‰ increase in $\delta^{18}O_{(PO4)}$ value compared to the Eq. (2). Therefore, the expected equilibrium $\delta^{18}O_{(PO4)}$ values of all samples in global watersheds were calculated according to Eq. (3). We got the raw data ($\delta^{18}O_w$ and T) from literatures (SI Appendix 2), used Eq. (3) to calculate the equilibrium values of $\delta^{18}O_{(PO4)}$. Measured $\delta^{18}O_{(PO4)}$ values in global freshwater range from 4.7‰ to 21.0‰, expected equilibrium values range from 10.0‰ to 23.0‰, the measured $\delta^{18}O_{(PO4)}$ showed a wide variation from the expected equilibrium values in different samples (Fig. 3). Only a few samples (5.7% of the number of sampling points) were close to the expected isotopic equilibrium (within the 95% confidence interval for calculated equilibrium), and thereby, application of phosphate oxygen isotope technology to trace the P cycle in these samples may be difficult due to the extensive oxygen exchange between PO_4^{3-} and water. But this can show the efficient utilization of P by microorganisms and illustrate the biogeochemical cycle of P (Blake et al., 2005). The most sampled sites (94.3% of the number of sampling points) differ significantly from the expected isotopic equilibrium. These samples contain the original information of $\delta^{18}O_{(PO4)}$, the measured $\delta^{18}O$

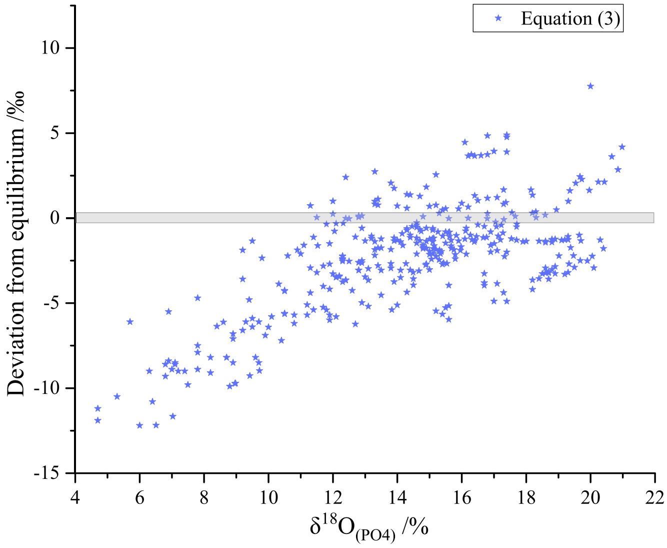


Fig. 3. Deviation of the $\delta^{18}O_{(PO4)}$ values measured from the expected equilibrium $\delta^{18}O_{(PO4)}$ values in freshwater. Note: the grey shadow means that 95% confidence interval for calculated equilibrium.

$_{(PO4)}$ values are useful for tracing the P cycle (Ishida et al., 2019; Pistocchi et al., 2017). P cycle identification using phosphate oxygen isotope technique is highly feasible as 94.3% of the number of sampling points have not reached the expected isotopic equilibrium fractionation. To better understand the biogeochemical cycle of P, previously published works also focused on the fractionation mechanism catalyzed by multiple phosphatases (Fig. 4). In the hydrolysis of phosphomonoesters, about 25% of oxygen from the surrounding water and 75% of oxygen from the substrate; in the hydrolysis of phosphodiester, about 50% of oxygen from the surrounding water and 50% of oxygen from the substrate were involved. These researches support understanding the process of biological metabolism and expand the application field of phosphate oxygen isotope technique. However, combination of the phosphate oxygen isotope fractionation mechanism and the practical application of phosphate oxygen isotope technique for tracing the P cycle provides more accurate information, which no study has yet applied. Therefore, the effect of microorganisms on the P cycle needs further investigation to better illustrate the P migration in the watershed.

4. Internal P loading to watershed

A significant fraction of P in the freshwater ecosystem remains in sediment, these P pools can be released to the overlying water through various mechanisms (Fig. 1 b). Especially in summer, P retention would be negative when internal P loading raise to a high level, and therefore, the P forms like the Labile P are easily released into the freshwater (Pettersson, 1998; Søndergaard et al., 2003; Yin et al., 2020).

4.1. $\delta^{18}O_{(PO4)}$ values in sediment P pools

Most studies focus on four principal P pools in sediment: Dissolved P, Labile P (labile and weakly adsorbed P), Fe-P and Al-P (strongly adsorbed P, Fixation by Fe and Al oxides), and Ca-P (strongly fixed P, Ca-P minerals). Though the P sequential extraction method slightly varied from each other, almost all researches included the four major P pools (Pistocchi et al., 2017; Tiessen et al., 1984; Zohar et al., 2010a). The $\delta^{18}O_{(PO4)}$ differ among the different sedimentary P pools and the four P pools can be arranged based on the average $\delta^{18}O_{(PO4)}$ value as: Fe-P and Al-P > Labile P > Dissolved P > Ca-P (SI Appendix 1, Fig. S1). The $\delta^{18}O_{(PO4)}$ in the Ca-P pool was extremely significantly ($p < 0.01$) lower than the other P pools, while the divergence of $\delta^{18}O_{(PO4)}$ in the other three P pools was not significant ($p < 0.05$). These are originated from that Ca-P is resistant to microbes and do not involved in the metabolic process during the transport through the watershed (Mingus et al., 2019; Tamburini et al., 2010). During the metabolic process catalyzed by multiple enzymes, $\delta^{18}O_{(PO4)}$ enrichment would occur caused by the characteristic of P absorption and utilization by microorganisms: preferential biological uptake of depleted P from the pools (Blake et al., 2005; Tamburini et al., 2010; Zohar et al., 2010b). Therefore, the bioavailable fraction of P in sediments, like Dissolved P and Labile P, would enrich the heavier $\delta^{18}O_{(PO4)}$ in residue phosphate. Fe-P and Al-P are strongly adsorbed P fixed by Fe and Al oxides in sediments, this P pool is generally regarded as moderately or conditionally bioavailable depending on the redox condition of the sediment (Jilbert and Slomp, 2013; Klump and Martens, 1987; Søndergaard et al., 2003; Sondergaard et al., 2001). Especially the Fe-P pool, it is highly sensitive to redox conditions, because the precipitation or dissolution of Fe depends on its valence state, and can be induced by the redox reaction (Jaisi et al., 2007). In sediment, the produced Fe^{2+} induced by anoxic environment could be released to the overlying water, and therefore, the P as iron oxides would be reductively dissolved due to the strong Fe-P coupled pathway of P cycling (Jordan, 2008; Joshi et al., 2015). In addition, the Fe-P and Al-P were the dominant P pool in sediment (Mingus et al., 2019), the adsorption and desorption of P in this form would largely change

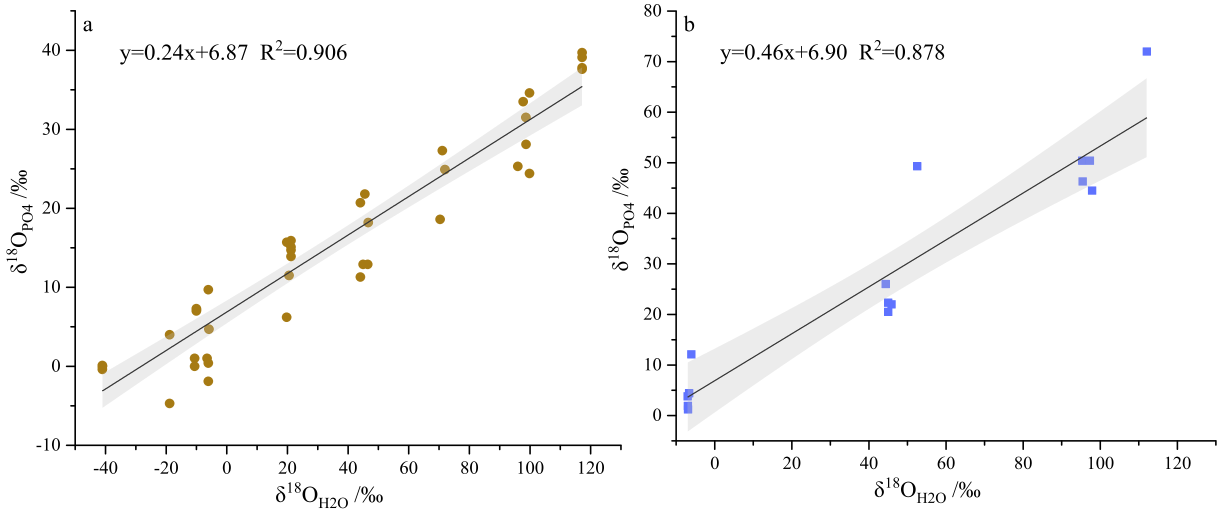


Fig. 4. Equilibrium fractionation mechanism catalyzed by multiple phosphatases. Note: the raw data were from the references (Liang and Blake, 2006; Liang and Blake, 2009; Von Sperber et al., 2014); Fig. 4a represents equilibrium fractionation of phosphomonoesters catalyzed by multiple monoesterase, Fig. 4b represents equilibrium fractionation of phosphodiester catalyzed by multiple diesterase

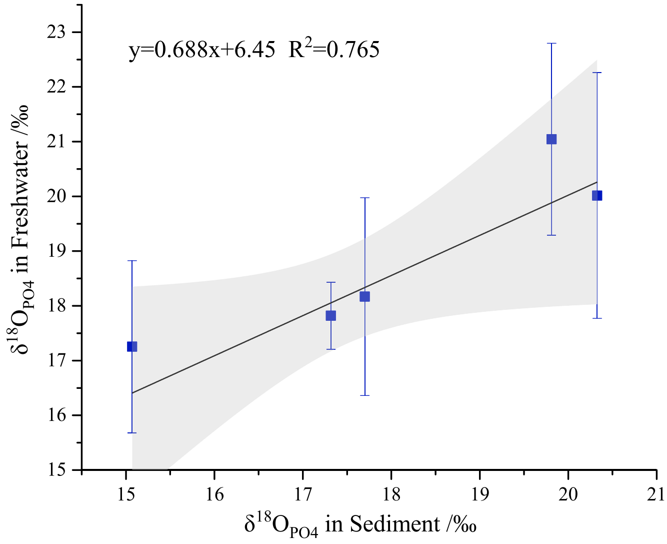


Fig. 5. $\delta^{18}O_{(PO4)}$ values of freshwater vs $\delta^{18}O_{(PO4)}$ values of sediment based on the average isotope data of each watershed in global.

the P loading of the water column and would cause an algal bloom in freshwater (Anshumali and Ramanathan, 2007; Cyr et al., 2009; Jordan, 2008). When all the bioavailable P fractions are consumed, the dominant P form (Fe-P and Al-P) would be utilized by microbes and initiate heavier isotopic values. That is why the $\delta^{18}O_{(PO4)}$ value in Fe-P and Al-P pool was a little higher than that in Dissolved P and Labile P pool (Jaisi et al., 2011).

4.2. Internal P release from sediment

The mean $\delta^{18}O_{(PO4)}$ values in fresh water and sediment of different research areas are shown in Fig. 5. Linear regression analysis showed a significant increase of $\delta^{18}O_{(PO4)}$ values in water with the rise of $\delta^{18}O_{(PO4)}$ values in sediment. The linear regression results implied that sediment can largely contribute to the high P stress on the overlying water. Therefore, water quality cannot be improved as expected by only reducing the external P input (Horppila, 2019; Sondergaard et al., 2001), because P can be released to the overlying water from sediment due to the resuspension process and the change of redox conditions (Rydin, 2000). The data was the mean value in every research area, it may not be enough to illustrate each region's internal P loading accurately. But the global data synthesis and comprehensive analysis can explain the overall impact of internal P loading on the water column. As depicted in Fig. 5, the slope of the linear regression model was 0.688 ($R^2 = 0.765$, $p < 0.05$), indicating that internal P loading can significantly influence water quality and the contribution was large and can lead to that eutrophic water body prevent water recovery even external loading distinctively reduced (Pettersson, 1998; Yin et al., 2020).

Based on the $\delta^{18}O_{(PO4)}$ data and global results of internal P loading, a schematic model (Fig. 6) of P cycling near the sediment-water interface has been built according to the existed research (Joshi et al., 2015; Yuan et al., 2019). P can be stored in sediment or released to water under a defined condition. Dissolved P and Labile P can migrate across the sediment-water interface independent of redox condition, this process is controlled by content or sorption and desorption process. When bioavailable P in the water column is used up, the sediment can produce free P to the overlying water by resuspension and P desorption, which is mainly controlled by the partition coefficient (Kp). Kp depends on water temperature, specific surface area, mineral composition, pH and ionic strength (Huang et al., 2017). But the release of P from Dissolved P or Labile P was far less than the release from the remineralization of organophosphorus and the dissolved P produced by the decoupling of Fe-P biogeochemical cycles (Joshi et al., 2015; Mingus et al., 2019). Therefore, this P pool generated would overwhelm the bottom and surface water.

5. External P input to watershed

The main concern of external P input to watersheds is the anthropogenic P. More P ore mining to produce phosphate fertilizer since the middle of the 20th century, perform a one-way journal from rock to watershed (Elser and Bennett, 2011; Liu et al., 2016). Inorganic fertilizer was the most dominant P source of the multiple external P sources, atmospheric deposition and catchment weathering belonging to background loading were the second-largest sources (Bouwman et al., 2013; Fink et al., 2018). By 2050, approximately 10^9 ha of natural soil would change to farmlands and may enhance the P load by nearly tripled fold (Tilman et al., 2001). However, the P utilization efficiency is very low (only about 22% of P from the environment was consumed in human food) and needs an urgent improvement (Chen and Graedel, 2016). Otherwise, the P-driven eutrophication of terrestrial and freshwater would be more challenging.

5.1. $\delta^{18}O_{(PO4)}$ values in multiple main external P sources

External P sources, as mentioned above, includes soil, Fertilizer, WWTP, detergents, etc. $\delta^{18}O_{(PO4)}$ values varied in multiple groups and have

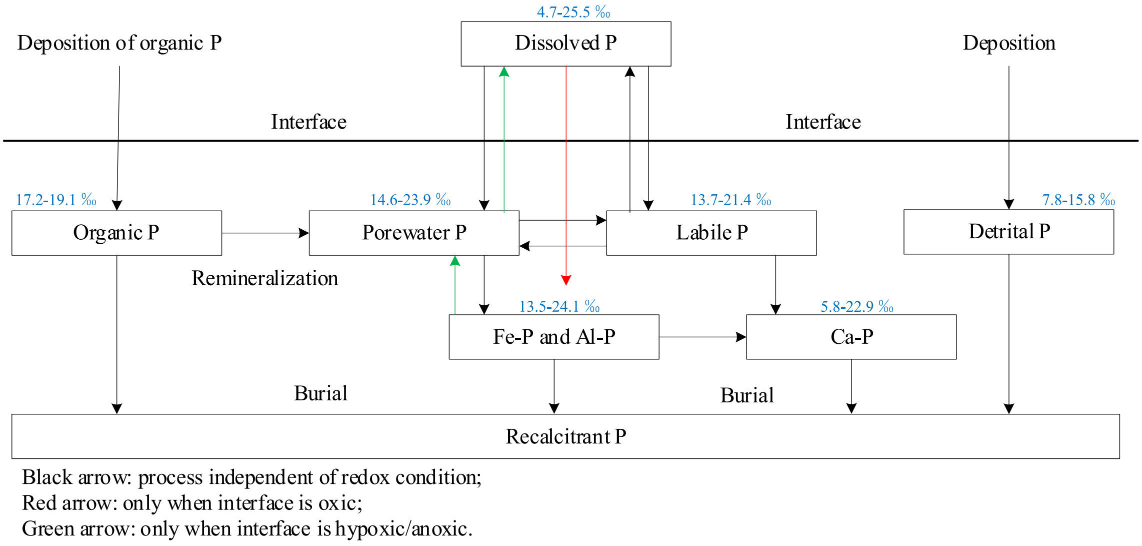


Fig. 6. P cycling near sediment – water interface.

significantly differ among each other (SI Appendix 1, Fig. S2). Soil P pools extraction methods are almost the same as sediment, include Dissolved P, Labile P, Fe-P and Al-P, Ca-P. In soil, the $\delta^{18}O_{(PO4)}$ values in the Ca-P was the lowest (SI Appendix 1, Fig. S2), because Ca-P pool was more stable than other fractions and recalcitrant to plant and microbes (Helfenstein et al., 2018; Parfitt, 1989). Fe-P and Al-P was the dominant pool in soil and conditionally bioavailable to organisms (Maharjan et al., 2018). Dissolved P and Labile P were the absorbable fractions for plant and microbes (Joshi et al., 2016), $\delta^{18}O_{(PO4)}$ values of these P pools were easy to attain equilibrium fractionation with the surrounding water. Fertilizer application enhances crop yield to guarantee food demand for the rapidly increasing population. Therefore, $\delta^{18}O_{(PO4)}$ value can indicate the influence of agricultural activities on watershed P load. The average $\delta^{18}O_{(PO4)}$ value in fertilizer was 20.1 ± 3.6‰, ranging from 12.3–25.9‰ (SI Appendix 1, Table S2). P fertilizer was mainly from P ore, and fertilizer processing can't change the oxygen isotopic composition of phosphate (Gruau et al., 2005). However, $\delta^{18}O_{(PO4)}$ value of fertilizer in this study was significantly higher than that of P ore (11.7 ± 1.8‰). The significant difference could be due to the smaller amount of P ore or man-made P with the heavier isotopes input to fertilizer during processing. In this case, further investigation is needed. WWTP and detergent mainly represent urbanization related P flow to watersheds, and their $\delta^{18}O_{(PO4)}$ values were 15.7 ± 3.5‰ and 16.9 ± 1.7‰, respectively. Aerosol was an important P source which usually ignored by many researches (Bigio et al., 2020; Mahowald et al., 2008; Okin et al., 2011), P in the atmosphere can only transport as aerosol as it can't exist as gaseous phase (Bigio and Angert, 2019). According to research by Fink et al. (2018), atmospheric deposition has a large contribution to watershed P load, these are mainly caused by the climatic conditions due to long-term trends or year-to-year variability or both. The $\delta^{18}O_{(PO4)}$ value in the aerosols ranged from 10.6–32.7‰ with an average value of 19.1 ± 4.7‰ (SI Appendix 1, Table S2). In addition, some isotope data in aerosol was heavier (>27‰) than the other P sources (Fig. 2). Further analysis explored that these heavier isotope data were from pollen samples (Bigio and Angert, 2018), it resulted from isotopic enrichment in the leaf water due to evaporation and followed by the process of heavier oxygen transfer from water to phosphate (Dongmann and Nürnberg, 1974) or the process of organic P compounds synthesis (Pfahler et al., 2013).

5.2. External P input from multiple sources

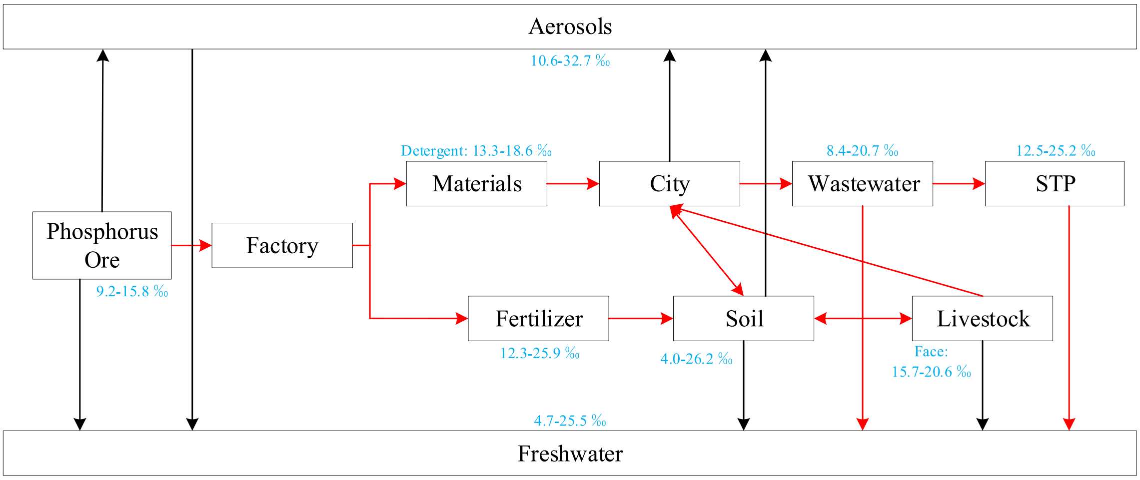
Based on the $\delta^{18}O_{(PO4)}$ data and results of global external P input, a schematic model (Fig. 7) has been built to simulate the P flow from external sources to freshwater. In a natural ecosystem, only a few proportions of P transfer across the system boundary (Newman, 1995). However, due to intense human activities such as phosphate mining, fertilizer usage, livestock breeding, food consumption, garbage and sewage generated by urban construction (Fig. 7), the path of P geochemistry has changed. More active P inputs into terrestrial, enhance P lost from land to freshwater, and the 'tight cycle' was intervened to a much more open cycle (Elser and Bennett, 2011). Fertilizer application in soils is excessively increasing, but P fertilizer utilization efficiency is decreasing. Such a condition indicates a large amount of P entering the environment (Carpenter et al., 1998; Tian et al., 2020). Globally, the P used in feed has doubled, and meat products have increased by 3 folds due to the high demand for meat (Chen and Graedel, 2016). The P emissions from livestock are mainly caused by animal excreta with a quantity of almost the same from the chemical fertilizer application (Bouwman et al., 2013). A large amount of animal excreta accumulates in the surface environment and became a non-point P source. During the process of urbanization, more and more P direct to sewage treatment plant through the pipeline and discharge into the surface water (Forsberg, 1998). The $\delta^{18}O_{(PO4)}$ values in water and WWTP had a small difference (SI Appendix 1, Table S1 and Fig. 7), indicating a close relationship between both. In addition, $\delta^{18}O_{(PO4)}$ values become heavier with the flow of P under human intervene (Fig. 7). This small difference indicated that anthropogenic activities may lead to the enrichment of heavy isotopes. Therefore, we can predict the presence of human intervention in the ecosystem based on $\delta^{18}O_{(PO4)}$ whether it is becoming heavier with P flow compared to the background value (background value can be obtained according to the $\delta^{18}O_{(PO4)}$ values in bedrock).

6. Contribution of internal P loading and external P input

Based on the isotopic mass balance model, we calculated the relative contribution of P from external input and internal loading using the formula shown below (Bigio and Angert, 2018; Gruau et al., 2005):

$$F = \left(\delta^{18}O_{(PO4)}\ \text{in water} - \delta^{18}O_{(PO4)}\ \text{in internal P loading}\right) / \left(\delta^{18}O_{(PO4)}\ \text{in external P input} - \delta^{18}O_{(PO4)}\ \text{in internal P loading}\right) \tag{4}$$

The average $\delta^{18}O_{(PO4)}$ value in water was 18.0 ± 1.3‰, in internal P loading was 17.3 ± 2.0‰, in external P input was 18.5 ± 2.6‰ (Detail calculation process see SI Appendix 1, Part 1). Our results show that external P input contributes 58.7% of P loads to watershed in global. According to the current calculation, external P input contribution was greater than that of internal P loading. Despite the significant effort to reduce the external P input, much effort is needed such as fertilizer P reduction, which is still the most important P source (Fink et al., 2018). In addition, intense efforts are required to minimize internal P loading and improve water quality in eutrophic water (Søndergaard et al., 2003). As depicted in Fig. 8, $\delta^{18}O$



Black arrow: process independent of human activities;

Red arrow: only when human intervene;

Fig. 7. External P input to freshwater.

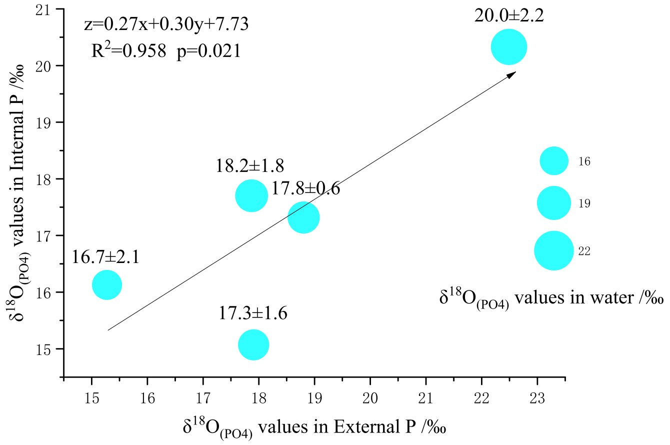


Fig. 8. Contribution of external P and Internal P based on average isotope data of each watershed. Note: x represented the $\delta^{18}O_{(PO4)}$ value in external P, y represented the $\delta^{18}O_{(PO4)}$ value in internal P, z represented the $\delta^{18}O_{(PO4)}$ value in relevant freshwater.

$_{(PO4)}$ of freshwater gradually increased with the increase of $\delta^{18}O_{(PO4)}$ in internal P and external P. Thus, both internal and external P sources have a significant impact on watersheds. Neither of the two sources can be ignored in improving water quality of watersheds.

7. Conclusion

This paper synthesized and evaluated the recent progress of the P cycle in global watersheds through phosphate oxygen isotope technology. Though several published works have been done on the topic, we observed that experimental data and research results were poorly integrated. We, therefore, collected experiment results from published papers and applied multiple models to analyze the P cycle in watersheds. The results showed that internal P (generally refers to the sediment P) can be released to the overlying water during the sediment resuspension process and change in redox conditions near the sediment – water interface. External P input into watershed is increasing due to increase in food demand and diet improvement (more meat products are consumed by human). Both internal P and external P can largely contribute to watershed P loadings. Therefore, efforts to reduce internal P loading and external P input are needed to improve eutrophic water quality.

Our review suggested that phosphate oxygen isotope technology was an effective tool to trace P biogeochemical cycle in the environment. However, oxygen isotope fractionation catalyzed by microbes is a ubiquitous process in natural environment. Thus, we still need a further study on the mechanisms of oxygen isotope fractionation between phosphate and water. When we clarify the fractionation mechanism between phosphate and water, P dynamics in watersheds can be better predicted.

CRediT authorship contribution statement

This work described has not been published previously, that it is not under consideration for publication elsewhere, that its publication is approved by all authors. If accepted, it will not be published elsewhere in the same form, in English or in any other language.

Ziteng Wang: Data collection, Conceptualization, Methodology, Investigation, Writing - original draft, Visualization. Qingjun Guo: Writing - review & editing, Funding acquisition. Liyan Tian: Review.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.154611.

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