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The efficiency of sequential extraction of phosphorus in soil and sediment: insights from the oxygen isotope ratio of phosphate

Xue-Tie Lei[1] · Han Zhang[2] · Min Chen[1] · Laodong Guo[3] · Xi-Guang Zhang[4] · Zhao-Hua Jiang[1] · Ruth E. Blake[5] · Zhi-Gang Chen[1,6]

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Abstract

Purpose Phosphorus (P) occurs in different chemical forms in soil and sediment, and they play different ecological and environmental roles. Thus, separation and quantification of different P pools are essential to the understanding of P dynamics in the environment. Over the past decades, different sequential extraction methods have been used concurrently. However, systematic evaluation of different extraction methods is lacking, making choice of methods and comparisons between results difficult.

Materials and methods We compared the oxygen isotope compositions ($\delta^{18}O_P$) of different phosphate pools that were extracted by two major extraction methods, Hedley (Hedley et al., Soil Sci Soc Am J 46:970-976, 1982) and SEDEX methods (Ruttenberg, Limnol Oceanogr 37:1460-1482, 1992), for both a soil and an estuarine sediment sample. Additionally, Ag_3PO_4 and KH_2PO_4 standards were used to test the fidelity of the extraction and purification procedure. The purity of the precipitated Ag_3PO_4 was also examined.

Results and discussion The $\delta^{18}O_P$ values have large differences among phosphate pools for the soil extracted by the Hedley method and for the sediment extracted by the SEDEX method. The $\delta^{18}O_P$ values of Ag_3PO_4 and KH_2PO_4 standards after extraction, purification, and/or re-precipitation are similar to their original $\delta^{18}O_P$ values. The XRD patterns of the precipitated Ag_3PO_4 are identical to that of Ag_3PO_4 standard. The residual carbon and nitrogen contents in the precipitated Ag_3PO_4 are low.

Conclusions The Hedley method has good efficiency for separating isotopically distinct P_i pools (different sources/bioavailability) in the soil samples, while the SEDEX method has good efficiency for separating isotopically distinct P_i pools (different sources/bioavailability) in sediments that are more marine in character such as for the estuarine sample. The extraction and purification processes do not alter $\delta^{18}O_P$, and the precipitated Ag_3PO_4 has high purity.

Keywords Hedley · Phosphate oxygen isotope · Phosphorus cycling · SEDEX · Sequential extraction

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✉ Zhi-Gang Chen
chzhg@xmu.edu.cn

[1] College of Ocean and Earth Sciences, Xiamen University, Xiamen 361102, China

[2] Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

[3] School of Freshwater Sciences, University of Wisconsin-Milwaukee, Milwaukee, WI 53204, USA

[4] Key Laboratory for Paleobiology, Yunnan University, Kunming 650091, China

[5] Department of Geology and Geophysics, Yale University, New Haven, CT 06520, USA

[6] The Fujian Provincial Key Laboratory for Coastal Ecology and Environmental Studies, Xiamen University, Xiamen 361102, China

1 Introduction

Phosphorus (P) is an essential nutrient for all life forms. Therefore, P deficiency can limit biological growth, while excess P can cause eutrophication and even hypoxia. Soil P plays key roles in plant growth (e.g., crops), and is often the main external source of P entering aquatic systems (Vitousek et al. 2009). On the other hand, sediment is the major sink of P in water, while the sediment P can also diffuse back into the overlying water column (Jensen and Thamdrup 1993; Ruttenberg 2014). Therefore, the dynamics and cycling pathways of P in both soils and sediments (both marine and freshwater—lake/river) have received wide attention.

Phosphorus exists in different pools and chemical forms in soils and sediments. In addition, different P pools have variable reactivity and bioavailability and can be interconverted with each other (Ruttenberg 1992; Joshi et al. 2016; Lin et al. 2018). For example, weakly absorbed P not only can be readily utilized by organisms (Zohar et al. 2010; Jaisi et al. 2011; Joshi et al. 2016), but also easily transported into aquatic environments (Vitousek et al. 2009). Therefore, knowledge of the source, bioavailability, and transformation of different P pools in soils and sediments is essential (Tamburini et al. 2014). Over the past several decades, various sequential extraction methods have been established to address these issues (Cross and Schlesinger 1995; Lukkari et al. 2007). However, all of these extraction methods are highly operationally defined and they extract P with a series of successively stronger reagents. The weaker of the extraction reagents identifies the weaker P adsorption and the higher P bioavailability (Hedley et al. 1982; Cross and Schlesinger 1995). The sequential extraction methods have made a series of contributions to the understanding of P cycling in the environment. However, due to the lack of evaluation, the choice of extraction methods is arbitrary, and comparisons between datasets are difficult (Levy and Schlesinger 1999), thus, preventing a better understanding of P dynamics in the environment.

The oxygen (O) isotopic composition ($^{18}O/^{16}O$ ratio) of phosphate ($\delta^{18}O_P$) has been increasingly used to trace P cycling in aquatic, soil, and sediment systems (Paytan and McLaughlin 2012; Tamburini et al. 2014). The reason for use of $\delta^{18}O_P$ as a tracer is that phosphorus participates in biogeochemical processes primarily as orthophosphate (PO_4^{3-}, hereafter P_i) in nature. Additionally, P_i does not exchange O isotope with water in the absence of enzymatic/biological activity under earth surface environments (Blake et al. 1997; Lécuyer et al. 1999). However, the O isotope exchange is rapid in the presence of enzymatic/biological activity (Blake et al. 1997; Paytan et al. 2002; Chang and Blake 2015), which makes $\delta^{18}O_P$ a good detector and tracer of biological cycling of P. When P_i-water O-isotope exchange reaches steady state, the equilibrium isotope value ($\delta^{18}O_{P\text{-}eq}$) is achieved and is exclusively determined by the temperature and O isotopic composition of ambient water ($\delta^{18}O_W$). The $\delta^{18}O_{P\text{-}eq}$ of dissolved P_i-water O isotope exchange can be calculated using the calibration equation recently determined by Chang and Blake (2015). These chemical and isotopic properties of phosphate enable P_i pools with different sources and bioavailabilities to have different $\delta^{18}O_P$ values (Jaisi et al. 2011; Roberts et al. 2015; Paytan et al. 2017; Jiang et al. 2017; Lei et al. 2019). Therefore, $\delta^{18}O_P$ can be used to evaluate the mixing of different P pools and the efficiency of sequential extraction methods, the aim of which is to separate different P pools with different sources and different bioavailability. For a given method, a larger difference in $\delta^{18}O_P$ values among extracted P_i pools would signify more effective separation of P_i pools—if the P_i pools have widely different initial $\delta^{18}O_P$ values—which is the case for the natural soil and estuarine sediment used in this study.

The methods proposed by Hedley et al. (1982) and the SEDEX method proposed by Ruttenberg (1992) are the two most widely used extraction methods for soils and sediments, respectively. The two methods have similarities. For example, 1.0 M HCl is used by both methods to extract Ca bound P. Citrate-dithionite-bicarbonate (CDB) and acetate buffer in SEDEX method has also been applied to soils to extract iron bound P (Chang and Jackson 1957; Ruiz et al. 1997) and authigenic apatite (Jiang and Gu 1989; Ruiz et al. 1997), respectively. Although both soil and sediment are mixtures of particulate materials, their biogeochemical properties are quite different due to the distinctions of material sources and circum environments. It is equivocal whether each method can be used optimally for both soil and sediment samples. Some recent studies have used Hedley method to extract P from estuarine/coastal sediments (Castañeda-Moya et al. 2010; Yu et al. 2014). In turn, the SEDEX method has also been used for soil samples (Hansen et al. 2004; Moturi et al. 2005). To the best of our knowledge, only Levy and Schlesinger (1999) compared the two extraction methods using 16 types of soil samples. Based on the derived P contents, they concluded that the Hedley method was superior in extracting plant-available P and distinguishing organic and inorganic P, while SEDEX method is optimal in distinguishing $CaCO_3$-bound P and apatite-P. These comparisons evaluated concentrations of different extracted P pools, but not their phosphate O-isotope compositions as done in the present study, which will further reveal the efficiency of these two extraction methods to separate P pools with different $\delta^{18}O_P$ signatures.

To evaluate the efficiency of the two sequential extraction methods for different sample types, both a soil and an estuarine sediment sample were extracted by both methods for the measurements of both contents and $\delta^{18}O_P$ values of extracted P_i. Moreover, the fidelity of the sample treatment procedure and the purity of the precipitated Ag_3PO_4 were also examined. This study provides important insights into the precise $\delta^{18}O_P$ measurement of different P_i pools and the choice and standardization of the P_i sequential extraction method for improved understanding of the biogeochemical cycling of P in the environment.

2 Materials and methods

2.1 Materials

The reagents used in this study include $NaHCO_3$, $NH_3{\cdot}H_2O$, KH_2PO_4, and all are ultra-pure reagents and supplied by Tianjin Guangfu Chemical Co., Ltd. $AgNO_3$, NaOH, $Na_2S_2O_4$, $NaCH_3COO$, $MgCl_2{\cdot}6H_2O$, NH_4Cl, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, HCl, CH_3COOH, all are analytical grade reagents and supplied by Xilong Chemical Co., Ltd. AG50W-X8 cation exchange resin (H^+ form) and AG1-X8 anion exchange resin (OH^- form) are both biotechnology grade and supplied by BIO-RAD Laboratories Inc., USA.

2.2 Collection and processing of the soil and sediment

Surface soil (0~5 cm) was collected from an agricultural field near the campus of Xiamen University (24.610 °N, 118.320 °E) on 22 September 2014. This soil was fertilized by chemical fertilizer and used to cultivate crops. The large particles (e.g., gravels and weeds) were discarded during sampling. The soil was air-dried at 40 °C immediately after sampling and sieved ($\Phi < 150$ μm) for further processing. Surface sediment (0~5 cm) was collected from the Jiulong River estuary (24.408°N, 117.985°E) on 17 April 2014 by a box sampler. The Jiulong River estuary is influenced by regular semidiurnal tides. The annual water depth range of the sampling site is 8.9–18.9 m. The sample was sealed in polyethylene Ziploc bags and stored in an insulation box with ice-bags immediately after collection. The sample was stored at − 20 °C and freeze-dried and sieved ($\Phi < 150$ μm) before extraction.

2.3 Sequential extraction methods

2.3.1 SEDEX method

The modified SEDEX method (Ruttenberg 1992) was used here, in which CDB (citrate-dithionite-bicarbonate buffer) was substituted by BD (bicarbonate-dithionite buffer) (Zhang et al. 2004) (Fig. 1). This is because some studies have shown that BD is more specific to Fe bound P than CDB, which can dissolve some Al-P complexes (Psenner et al. 1984; Nürnberg 1988). Six replicate samples were used and the solid-to-extractant ratio of each step was 1 g:50 mL. The samples were sequentially extracted by $MgCl_2$, BD, acetate buffer (NaAc-HAc), and 1.0 M HCl, and the extracted P_i was generally regarded as exchangeable P, Fe-oxide bound P, authigenic apatite, and detrital apatite, respectively (Ruttenberg 1992; Zhang et al. 2004). Each pool was extracted on a reciprocal shaker at room temperature for a specific time as shown in Fig. 1. The solid residues were resuspended and rinsed with 1.0 M $MgCl_2$ or H_2O for 2 h, then separated from solutions by centrifugation. The P_i concentration of the extractants and the rinsing solutions were measured by the method of Murphy and Riley (1962). Then, the residual extractants and the corresponding rinsing solutions were combined and converted P_i into Ag_3PO_4 by the purification procedure (Fig. 1).

2.3.2 Hedley method

The modified Hedley method (Tiessen and Moir 2008) was used here and the details are shown in Fig. 1 and in our previous study (Jiang et al. 2017). The samples were extracted by 0.5 M $NaHCO_3$, 0.1 M NaOH, 1.0 M HCl, and concentrated HCl (Conc. HCl) sequentially.

2.4 Purification and analysis methods

Several methods have been proposed to purify P_i for $\delta^{18}O_P$ measurements (Blake et al. 2010; Paytan and McLaughlin 2012; Zhang et al. 2015). The method of Blake et al. (2010) is more effective for complex matrix samples and was adopted in this study (Fig. 1). The precipitated Ag_3PO_4 was used for the measurements of $\delta^{18}O_P$ values, C and N contents, and crystal property. The $\delta^{18}O_P$ values were measured by high-temperature conversion–isotope ratio mass spectrometry (HTC-IRMS, Flash EA1112 Series, Delta V Advantage, Thermo Fisher). The Ag_3PO_4 mass, pyrolysis temperature, helium (He) carrier gas flow rate, and gas chromatography temperature are 0.4–0.8 mg, 1380 °C, 80 mL/min and 85 °C, respectively (Yin and Chen 2014; Chen et al. 2015). The $\delta^{18}O$ values were calibrated by two international oxygen isotope reference materials, i.e., the IAEA-601 benzoic acid ($\delta^{18}O_{VSMOW}$ = 23.2‰) and Ag_3PO_4 ($\delta^{18}O_{VSMOW}$ = 21.7‰, Elemental Microanalysis Ltd). The crystal property was measured by powder X-ray diffraction (XRD, Ultima IV, Rigaku) at 35 kV and 15 mA with Cu-Ka radiation (λ = 1.54 Å), and the scanning range and rate were 2θ = 0°~90° and 10°/min, respectively. The C and N contents were measured by an elemental analyzer (EA, Vario EL III) with combustion and reduction temperature of 900 °C and 500 °C, respectively. The He carrier gas flow rate was 250 mL/min and O_2 consumption rate was 0.05 L per sample. Vitamin B5 (Nicotinamide, $C_6H_6N_2O$) was used as a standard.

2.5 Data statistical analysis

One-way ANOVA (analysis of variance) in SPSS (V.20) was used to evaluate the differences in P_i content and $\delta^{18}O_P$ values between P pools. The Tukey HSD-post hoc test was used (p = 0.05) to detect a significant difference between multiple data.

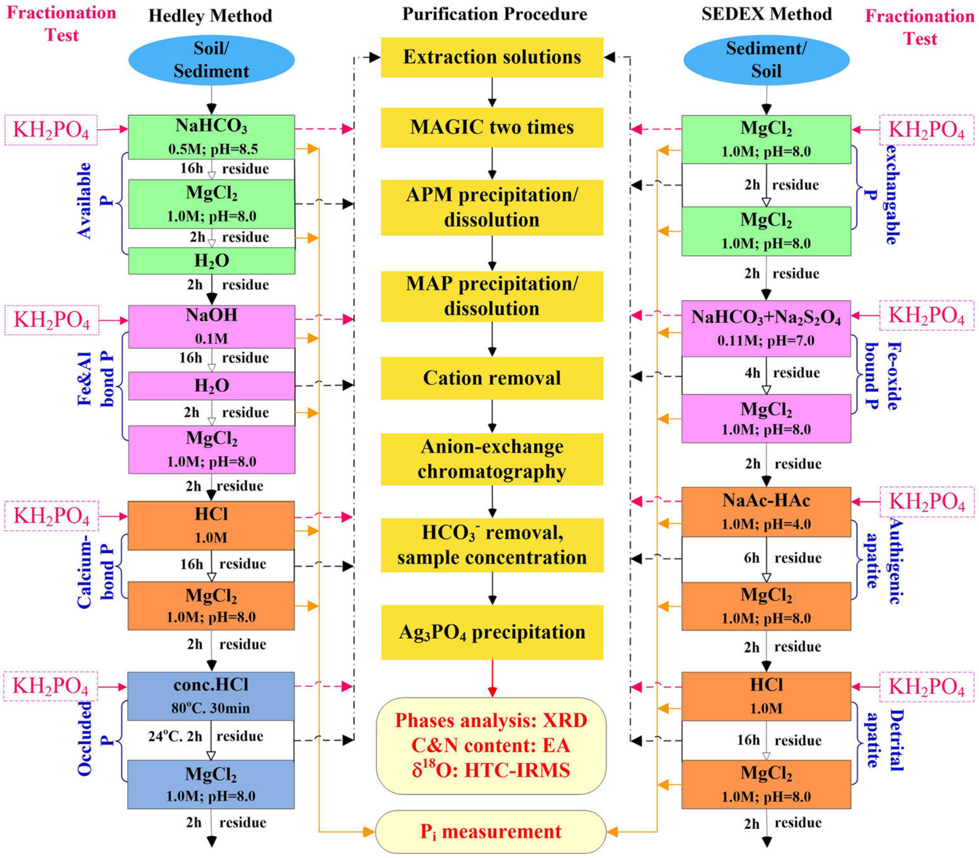

Fig. 1 Sequential extraction and purification procedures for different phosphorus pools in soil and sediment samples. MAGIC: Magnesium-induced co-precipitation; APM: ammonium phosphomolybdate; MAP: magnesium ammonium phosphate

3 Results and discussion

3.1 Isotope fractionation

The fidelity of the extraction and purification processes was examined using procedures shown in Fig. 1. After the Ag_3PO_4 reference was dissolved and directly re-precipitated (without extraction and purification), the mean $\delta^{18}O_P$ value of the re-precipitated Ag_3PO_4 is 8.4 ± 0.4‰ (n = 6) (Table S1, Electronic Supplementary Material—ESM), which is similar, within error, to the original value of the Ag_3PO_4 reference (8.6‰, determined by direct pyrolysis) (Fig. S1; Table S2). This indicates that the precipitation of Ag_3PO_4 does not compromise detectable $\delta^{18}O_P$ values. Figure S1 (ESM) shows that after KH_2PO_4 reagent is extracted by $MgCl_2$, BD and NaAc-HAc buffer, and purified using the procedures depicted in Fig. 1, the $\delta^{18}O_P$ values of the precipitated Ag_3PO_4 are similar, within error, to the original $\delta^{18}O_P$ values of KH_2PO_4 reagent (13.2 ± 0.2‰) determined by direct precipitation of Ag_3PO_4 (without extraction and purification) (Fig. S1; Table S1, S3—ESM). These results are consistent with the study of Jiang et al. (2017), which show that the extraction of $NaHCO_3$, NaOH, 1.0 M HCl, and conc. HCl did not alter the $\delta^{18}O_P$ value of P_i.

3.2 Purity of the precipitated Ag_3PO_4

3.2.1 XRD spectra and the relationship between CO peak area and Ag_3PO_4 mass

Figure 2 shows the XRD patterns of Ag_3PO_4 which was precipitated from the P_i extracted and purified from the soil. They are all identical to the pattern of Ag_3PO_4 standard (JCPDS card NO. 06-0505), indicating the high purity of the precipitated Ag_3PO_4.

The relationship between Ag_3PO_4 mass and CO peak area of the samples is shown in Fig. 3 and is similar to that observed for Ag_3PO_4 standard and the Ag_3PO_4 precipitated after the extraction and purification of KH_2PO_4 reagent (Fig. 3; Tables S2—ESM, S3—ESM). The equations for the Ag_3PO_4 standard, KH_2PO_4 reagent and samples are $y = 473.3x - 12.1$ ($R^2 = 0.966$), $y = 478.4x - 12.5$ ($R^2 = 0.955$) and $y = 488.3x - 23.2$ ($R^2 = 0.909$), respectively. These results again confirm the high purity of the precipitated Ag_3PO_4.

3.2.2 Contents of carbon and nitrogen

After the extraction and purification of P_i from soil and sediment samples, the residual C and N contents (wt%) of the Ag_3PO_4 precipitated from extracted P_i were less than 0.08% and 0.05%

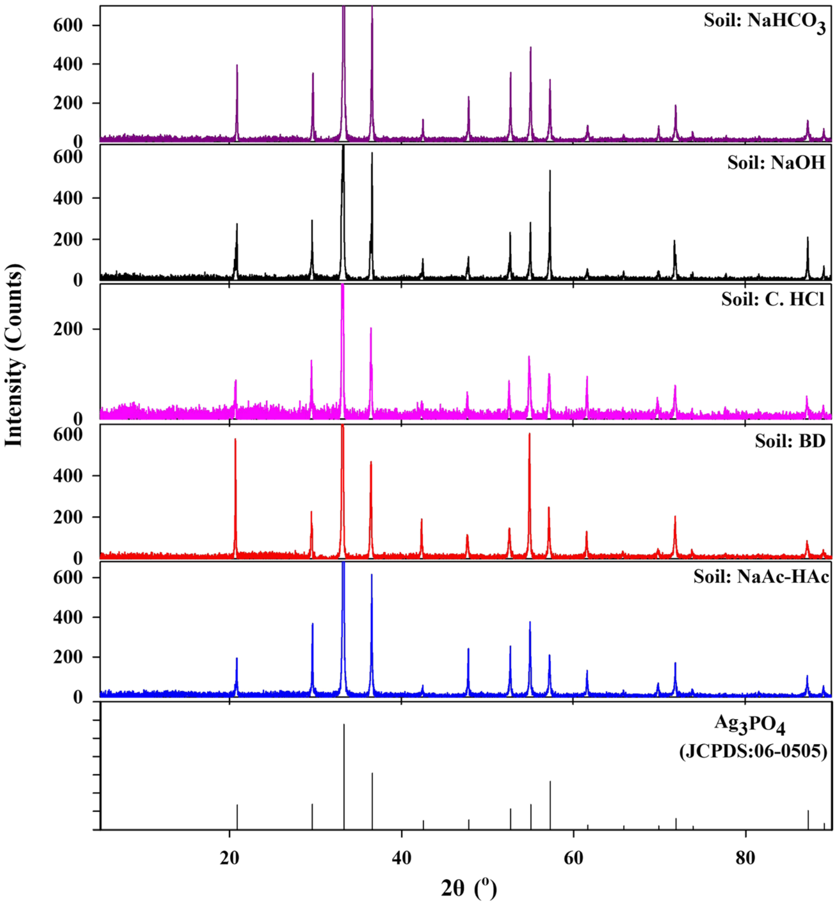

Fig. 2 XRD patterns of the Ag_3PO_4 precipitated from the phosphate extracted and purified from soil. Note part of the upper side of sample panels being discarded for clarity

respectively (Table S4—ESM). The C/N molar ratio was less than 1.22, which is much smaller than that of natural organic matter in sediments (5–20; Ruttenberg and Goñi 1997) and soils (13.5–15.5; Cleveland and Liptzin 2007). To evaluate the effects of residual C and N on $\delta^{18}O_P$ measurements, we, therefore, assumed that extraneous O bonds with C are all from organic matter and O bonds with N are all from NO_3^-. The $\delta^{18}O$-NO_3 values of natural samples range from + 0.5 to + 70‰ (Kendall 1998; Sigman et al. 2009) and the calculated $\delta^{18}O_P$ deviation caused by N ranges from − 0.2 to + 0.5‰. At the same time, if we use the O/C ratio of 0.625 (Xing and Chen 1999) and the $\delta^{18}O$ range of − 5.8 to + 52.7‰ (Sauer et al. 2001; Zech et al. 2014) for natural organic matter, the calculated $\delta^{18}O_P$ deviation caused by C ranges from − 0.1 to + 0.1‰. Therefore, the effects of extraneous O from residual C and N are insignificant.

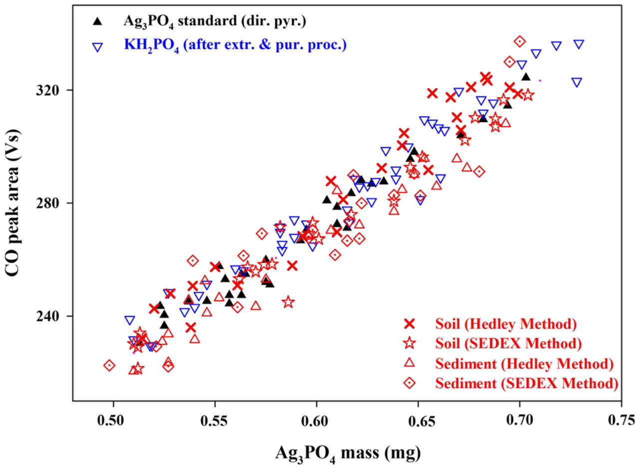

Fig. 3 The relationship between the measured CO peak area and the mass of Ag_3 PO_4

3.3 Comparisons of the sizes of phosphorus pools

3.3.1 Soil sample

Hedley method The mean content of NaOH-P_i is high (800.7 ± 16.7 mg P/kg), while the mean contents of $NaHCO_3$-P_i and 1.0 M HCl-P_i are 400.5 ± 5.3 mg P/kg and 388.4 ± 10.2 mg P/kg, respectively (Fig. 4; Table S5—ESM). The $NaHCO_3$-P_i represents the most easily available P_i that is weakly adsorbed onto the mineral surfaces (Olsen et al. 1954; Cross and Schlesinger 1995). For highly weathered agricultural soils, the main sources of $NaHCO_3$-P_i are the fertilizers and decomposition of organic matter, and its main sinks are biological assimilation, conversions into other P pools, or loss by runoff. Therefore, the $NaHCO_3$-P_i pool is endowed with high

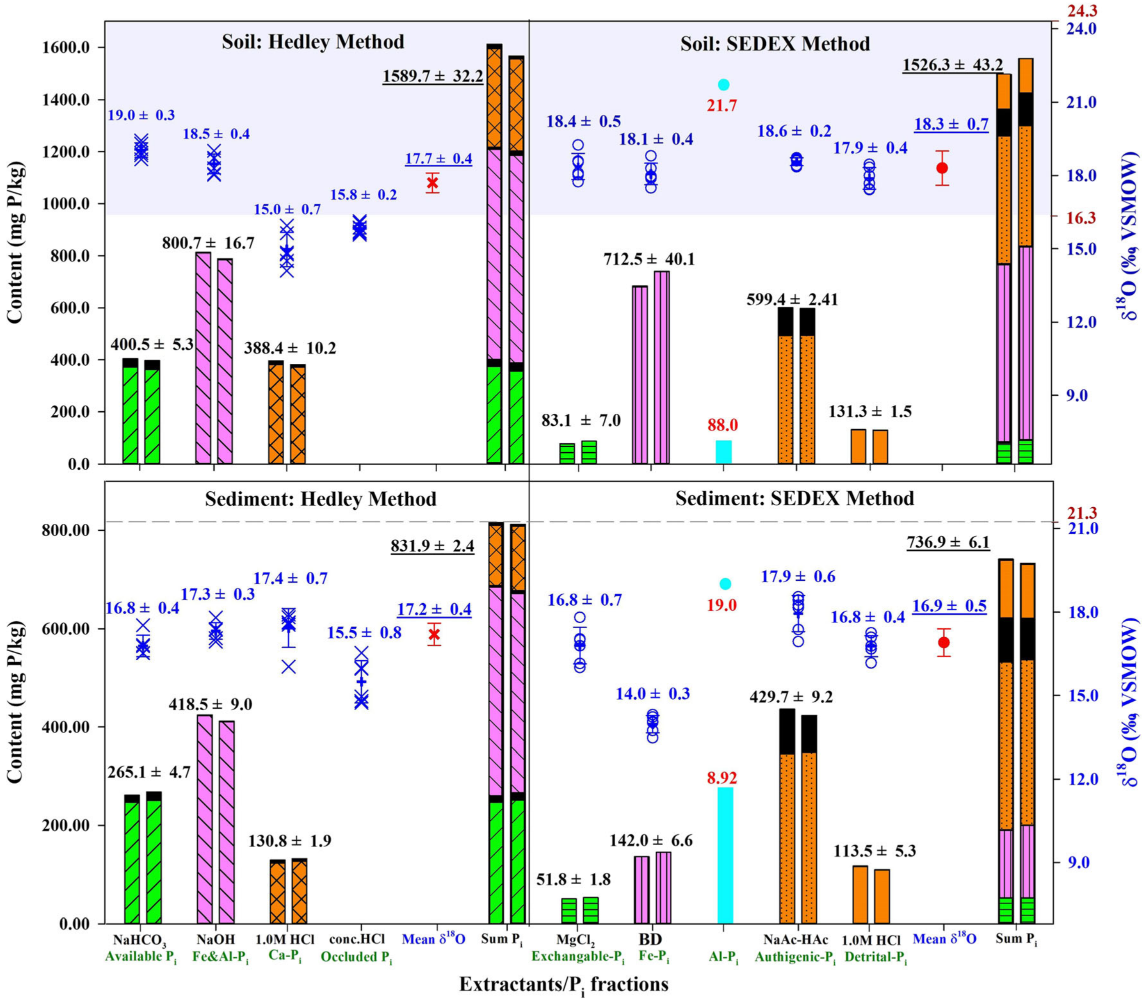

Fig. 4 The $\delta^{18}O_P$ (symbol) and content (bar) of different pools of phosphate in soil (upper panels) and sediment (lower panels). Black bars represent concentrations of phosphate in $MgCl_2$ and H_2O rinsing solution. The mean $\delta^{18}O_P$ value is the $\delta^{18}O_P$ value of bulk sample that was calculated basing on the mass balance of the contents and $\delta^{18}O_P$ values of P_i pools. The content of Al-P_i was calculated by the content difference of BD-P_i and NaOH-P_i, and its $\delta^{18}O_P$ value was calculated by mass balance model. Shaded areas (upper panels) and dash line (lower panels) represent the $\delta^{18}O_{P\text{-eq}}$ values

mobility and variability (Hedley et al. 1982; Cross and Schlesinger 1995). The NaOH-P_i mainly represents Fe and Al bound P_i with moderate bioavailability (Chang and Jackson 1957; Negassa and Leinweber 2009). The 1.0 M HCl-P_i represents Ca bound P_i and has the least bioavailability (Hedley et al. 1982; Cross and Schlesinger 1995; Negassa and Leinweber 2009). In the weakly weathered soils, P distribution is normally controlled by chemical reactions related to Ca-containing minerals, while in the highly weathered soils, it is related to sesquioxides (Cross and Schlesinger 1995). Thus, the content of 1.0 M HCl-P_i usually decreases while NaOH-P_i increases with pedogenesis progress (Cross and Schlesinger 1995; Negassa and Leinweber 2009). Negassa and Leinweber (2009) found that the NaOH-P_i increased with P input in tropical and subtropical soils. The soil used in this study is highly weathered subtropical agricultural soil, so it has high NaOH-P_i and relatively low 1.0 M HCl-P_i.

SEDEX method The BD-P_i and NaAc-HAc-P_i are the dominant pools, and their mean contents are 712.5 ± 40.1 mg P/kg and 599.4 ± 2.4 mg P/kg, respectively, while the mean contents of $MgCl_2$-P_i and 1.0 M HCl-P_i are 83.1 ± 7.0 mg P/kg and 131.3 ± 1.5 mg P/kg, respectively (Fig. 4; Table S5). The extraction mechanism of $MgCl_2$ is the formation of $MgPO_4^-$ complex and/or mass action displacement by Cl^- (Ruttenberg 1992), and for $NaHCO_3$, it is the ionic competition of HCO_3^-, CO_3^{2-}, and OH^- ions and the depression of Ca^{2+} by the relatively high pH (Olsen et al. 1954; Hedley et al. 1982; Tiessen and Moir 2008). Both the results here and those of Levy and Schlesinger (1999) show that the extraction ability of 0.5 M $NaHCO_3$ (pH = 8.5) is stronger than that of 1.0 M $MgCl_2$ (pH = 8.0). The dithionite of BD can reduce Fe- and Mn-oxides/hydroxides, releasing P_i associated with them (Jensen and Thamdrup 1993; Zhang et al. 2004; Lukkari et al. 2007).

Figure 4 shows that the soil has relatively high authigenic apatite but lower detrital apatite contents since the NaAc-HAc-P_i represents authigenic apatite and 1.0 M HCl-P_i represents detrital apatite (Ruttenberg 1992). This is consistent with the high pedogenesis characteristics of the soil. At present, only limited studies used SEDEX method to extract P_i pools from soil, and among those, only the highly weathered soil (Oxisol) and wood-ash had similar distribution patterns as ours, while all other types of soil and aerosol had different distribution patterns (Levy and Schlesinger 1999; Anderson et al. 2010; Hudson-Edwards et al. 2014).

3.3.2 Sediment sample

Hedley method The NaOH-P_i has the highest content (418.5 ± 9.0 mg P/kg), and the mean content of 1.0 M HCl-P_i (130.8 ± 1.9 mg P/kg) is lower than that of $NaHCO_3$-P_i (265.1 ± 4.7 mg P/kg). In general, studies using the Hedley method to extract sediments are limited. Yu et al. (2014) found that the 1.0 M HCl-P_i was the dominant P_i pool (≥ 63%) in sediments of the Yellow River estuary, followed by the resin-P_i (7.4–11.9%). Castañeda-Moya et al. (2010) found that Ca-bound P_i (1.0 M HCl-P_i) and labile-P_i (resin-P_i) had high contents in storm-affected mangrove sediment in the Florida Coastal Everglades, while in normal surface sediment, the NaOH-P_o (organic P), Ca-bound P_i, and labile-P_i were the dominant pools. Therefore, the P_i content and its distribution pattern here is different from those reported in previous studies, which may result from composition differences of the sediments.

SEDEX method The NaAc-HAc-P_i has the highest content (429.7 ± 9.2 mg P/kg), followed by BD-P_i (142.0 ± 6.6 mg P/kg), 1.0 M HCl-P_i (113.5 ± 5.3 mg P/kg), and $MgCl_2$-P_i (51.8 ± 1.8 mg P/kg) in sequence (Fig. 4; Table S5—ESM). This suggests that authigenic apatite is the dominant P_i pool in this specific sediment, which is different from the P_i distribution pattern of the soil extracted by SEDEX method. Similar to the soil sample, the content of $MgCl_2$-P_i is much lower than that of $NaHCO_3$-P_i, suggesting for sediment, the extraction ability of $MgCl_2$ is also much weaker than that of $NaHCO_3$. While different from the soil sample, the content of BD-P_i is much lower than that of NaOH-P_i. The P_i distribution pattern here is similar to that of Great Barrier Reef continental shelf (Monbet et al. 2007) and Florida Bay sediments (Zhang et al. 2004).

3.4 Comparisons of phosphate oxygen isotope compositions

3.4.1 Soil sample

Hedley method The mean $\delta^{18}O_P$ values of the $NaHCO_3$-P_i (19.0 ± 0.3‰) and NaOH-P_i (18.5 ± 0.4‰) are relatively higher than those of the 1.0 M HCl-P_i (15.0 ± 0.7‰) and Conc. HCl-P_i (15.8 ± 0.2‰) (Fig. 4; Table S3—ESM). Based on the mass balance of the contents and $\delta^{18}O_P$ values of P_i pools, the calculated mean $\delta^{18}O_P$ value of the bulk sample is 17.7 ± 0.4‰. The $\delta^{18}O_{P\text{-eq}}$ value represents the complete exchange of oxygen isotopes between P_i and water, which implies active cycling of P by organisms. Therefore, $\delta^{18}O_{P\text{-eq}}$ is a very important parameter reflecting the ambient biogeochemical setting. However, due to the changeable characteristics of surface soil temperature and $\delta^{18}O_W$ of soil water, both the mean temperature and $\delta^{18}O_W$ should be used to calculate $\delta^{18}O_{P\text{-eq}}$ (Lei et al. 2019). The air temperature during the sampling month (8/22~9/22/2014) ranged from 25 to 35 °C, and the mean $\delta^{18}O_W$ of the surface soil at the same site between 9/11/2015 and 9/17/2015 varied from − 4.1 to + 2.2‰ (Table S6—ESM, Lei et al. 2019). Based on these data and the dissolved P_i-water equilibrium equation (Chang and Blake 2015), the estimated $\delta^{18}O_{P\text{-eq}}$ values range from 16.3 to 24.3‰. As shown in Fig. 4, the $\delta^{18}O_P$ values of $NaHCO_3$-P_i and NaOH-P_i are within the range of $\delta^{18}O_{P\text{-eq}}$ value, while the $\delta^{18}O_P$ values of 1.0 M HCl-P_i and Conc.HCl-P_i are slightly lower than the lower end of $\delta^{18}O_{P\text{-eq}}$ values. This distribution pattern is similar to those of previous studies (Zohar et al. 2010; Roberts et al. 2015; Jiang et al. 2017).

For agricultural soils, their $NaHCO_3$-P_i and NaOH-P_i are mainly from fertilizer and have high bioavailability; therefore, their $\delta^{18}O_P$ can be easily affected by biological activities including assimilation, utilization, and release processes (Zohar et al. 2010; Gross and Angert 2015; Roberts et al. 2015). The $\delta^{18}O_P$ values of the two local chemical fertilizers applied to this soil are 13.8‰ and 12.6‰, which are significantly lower than those of $NaHCO_3$-P_i and NaOH-P_i. Therefore, the $\delta^{18}O_P$ data suggest that the fertilizer-derived P_i was intensively cycled (consumed and released) by organisms. Although the $\delta^{18}O_P$ values of the 1.0 M HCl-P_i and Conc.HCl-P_i are relatively low, they are clearly higher than those of igneous rocks (5.3–7.0‰; Taylor 1968; Mizota et al. 1992) and the chemical fertilizers. Previous studies have reported relatively low $\delta^{18}O_P$ values of 1.0 M HCl-P_i in young soils (Tamburini et al. 2012; Roberts et al. 2015), but relatively high ones in mature soils although these reported values are close to or lower than the $\delta^{18}O_{P\text{-eq}}$ values (Angert et al. 2011; Tamburini et al. 2012; Roberts et al. 2015). This implies the proportion of biologically cycled P_i in 1.0 M HCl-P_i and Conc.HCl-P_i increases with the extent of pedogenesis, i.e., more bioavailable P_i can be converted into unavailable P_i during pedogenesis (Joshi et al. 2016). If we assume the mean $\delta^{18}O_P$ value of $NaHCO_3$-P_i and NaOH-P_i represents the $\delta^{18}O_P$ values of biologically cycled P_i (18.8‰), and the $\delta^{18}O_P$ of igneous source P_i is between 5.3 and 7.0‰, using a mass balance model, we can calculate the proportion of biologically cycled P_i to range from 68 to 72% for the 1.0 M HCl-P_i pool and from 75 to 78% for the Conc. HCl-P_i pool. It should be noted that phosphorite also has high $\delta^{18}O_P$ values consistent with origin in marine environment (Shemesh et al. 1983). Because the bedrock of the study area is granite, phosphorite should not be a significant source of P_i.

SEDEX method The mean $\delta^{18}O_P$ values of $MgCl_2$-P_i, BD-P_i, NaAc-HAc-P_i, and 1.0 M HCl-P_i are 18.4 ± 0.5‰, 18.1 ± 0.4‰, 18.6 ± 0.2‰, and 17.9 ± 0.4‰, respectively (Fig. 4; Table S3). Based on the mass balance of the contents and $\delta^{18}O_P$ values of P_i pools, the calculated mean $\delta^{18}O_P$ value of the bulk sample is 18.3 ± 0.7‰. In addition, there is no clear difference between the $\delta^{18}O_P$ values of P_i pools ($p > 0.05$). This is likely due to the weaker extraction abilities of $MgCl_2$ and BD compared to $NaHCO_3$ and NaOH, respectively, i.e., the high $\delta^{18}O_P$ value of the un-extracted P_i causes the increase in the $\delta^{18}O_P$ values of NaAc-HAc-P_i and 1.0 M HCl-P_i. The P_i content of $MgCl_2$-P_i is clearly lower than that of $NaHCO_3$-P_i, and its $\delta^{18}O_P$ value is slightly lower than that of $NaHCO_3$-P_i (Fig. 4). The calculated content and $\delta^{18}O_P$ value of the un-extracted P_i by $MgCl_2$ are 319.0 mg P/kg and 19.2‰, respectively. Some studies (Olsen et al. 1954; Jiang and Gu 1989) have shown that 0.5 M $NaHCO_3$ (pH = 8.5) can dissolve some calcium phosphate due to the depression of Ca^{2+} by the relatively high pH (Olsen et al. 1954). Therefore, the un-extracted P_i by $MgCl_2$ in the SEDEX extraction is probably calcium phosphate. Since the extraction mechanism of BD is the reductive dissolution of Fe oxide/hydroxide, we assume that BD will not dissolve the un-extracted calcium phosphate which is probably extracted by the subsequent NaAc-HAc buffer solution. This can increase the content and $\delta^{18}O_P$ value of NaAc-HAc-P_i.

At the same time, although the extraction mechanism of NaOH is not fully understood, many studies have shown that it mainly extracts Fe and Al-P_i (Williams 1937; Chang and Jackson 1957), while BD mainly extracts Fe-P_i (Jensen and Thamdrup 1993; Zhang et al. 2004; Lukkari et al. 2007). If we follow these assumptions, the content of Al-P_i can be calculated to be 88.0 mg/kg by the difference in contents between NaOH-P_i and BD-P_i, while the calculated $\delta^{18}O_P$ value of Al-P_i is 21.7‰. Thus, if the Al-P_i is extracted by NaAc-HAc buffer and/or 1.0 M HCl, it can also increase their $\delta^{18}O_P$ values. Since the content of Al-P_i is relatively small and certain assumptions are needed, the calculated $\delta^{18}O_P$ value of Al-P_i should be treated with caution. To the best of our knowledge, this is the first data for $\delta^{18}O_P$ of soil P_i pools that were extracted by SEDEX method.

3.4.2 Sediment sample

Hedley method The mean $\delta^{18}O_P$ values of $NaHCO_3$-P_i, NaOH-P_i, and 1.0 M HCl-P_i are 16.8 ± 0.4‰, 17.3 ± 0.3‰, and 17.4 ± 0.7‰, respectively, showing a slight increase trend. However, the Conc.HCl-P_i has the lowest $\delta^{18}O_P$ value (15.5 ± 0.8‰) (Fig. 4; Table S3). Based on the mass balance of the contents and $\delta^{18}O_P$ values of P_i pools, the calculated mean $\delta^{18}O_P$ value of the bulk sample was 17.2 ± 0.4‰. To estimate the $\delta^{18}O_{P\text{-}eq}$ value, the bottom water temperature (25.5 °C) was used here. We did not measure the $\delta^{18}O_W$ of the bottom water. While the salinity and $\delta^{18}O_W$ of the surface water sampled during the same cruise have good linear relationship (Fig. S2—ESM; Table S7—ESM), the $\delta^{18}O_W$ of the bottom water (− 0.7‰) can be calculated by its salinity (28.6) and the fitted equation. Based on these data and the dissolved P_i-water equilibrium equation (Chang and Blake 2015), the calculated $\delta^{18}O_{P\text{-}eq}$ value is 21.3‰. All the measured $\delta^{18}O_P$ values are lower than the calculated $\delta^{18}O_{P\text{-}eq}$ values (Fig. 4).

In natural environments, $\delta^{18}O_P$ approaching the $\delta^{18}O_{P\text{-}eq}$ value is usually the result of biological processes (uptake and release) of P_i, while departure from the $\delta^{18}O_{P\text{-}eq}$ value could be a result of new P_i input. The two main P_i sources with low $\delta^{18}O_P$ are the igneous/metamorphic apatite (Taylor 1968; Mizota et al. 1992) and the decomposition of organic P (Liang and Blake 2009). Since the organic P is more ubiquitous and easy to decompose than igneous/metamorphic apatite, it may be the decomposition of organic P that decreases the $\delta^{18}O_P$ value of $NaHCO_3$-P_i and NaOH-P_i, i.e., lower than $\delta^{18}O_{P\text{-}eq}$ values.

Because different P_i pools have different bioavailability, their $\delta^{18}O_P$ values have different kinetic response to environmental changes, *e.g.*, temperature, such that higher bioavailability leads to a faster response (Zohar et al. 2010; Jaisi et al. 2011; Joshi et al. 2016). Since 1.0 M HCl-P_i has slow response to environmental perturbations, its $\delta^{18}O_P$ value may not have been as affected by the decomposition of organic P; thus, its $\delta^{18}O_P$ value is slightly higher than that of $NaHCO_3$-P_i and NaOH-P_i. The $\delta^{18}O_P$ values of 1.0 M HCl-P_i and Conc. HCl-P_i are also higher than that of igneous/metamorphic apatite, suggesting that they contain some proportion of biologically cycled P_i. Paytan et al. (2017) studied the $\delta^{18}O_P$ of different P_i pools that extracted from a Lake Erie sediment core by the Hedley method. Their dataset showed that the 1.0 M HCl-P_i had the lowest (lower than $\delta^{18}O_{P\text{-}eq}$ value) and most stable $\delta^{18}O_P$ values (mean value is 12.8‰), which is higher than that of igneous apatite but within the range for metamorphic apatites. The $\delta^{18}O_P$ values of H_2O-P_i, $NaHCO_3$-P_i, and NaOH-P_i were all higher than the $\delta^{18}O_{P\text{-}eq}$ value and remained somewhat constant when deeper than 10 cm in the sediment core, although irregular in the upper 10 cm sediment (Paytan et al. 2017). They proposed these high $\delta^{18}O_P$ values may come from chemical fertilizers, detergents, or vegetative organic matter (Paytan et al. 2017). Liu et al. (2019) found NaOH-P_i has the lowest $\delta^{18}O_P$ values for both of two surface sediments of Aha Lake, while $\delta^{18}O_P$ value of $NaHCO_3$-P_i is higher than that of 1.0 M HCl-P_i for one sample, and they are similar for another sample.

SEDEX method The mean $\delta^{18}O_P$ values of $MgCl_2$-P_i, BD-P_i, NaAc-HAc-P_i, and 1.0 M HCl-P_i are 16.8 ± 0.7, 14.0 ± 0.3, 17.9 ± 0.6, and 16.8 ± 0.4‰, respectively (Fig. 4; Table S3—ESM). The $\delta^{18}O_P$ values of NaAc-HAc-P_i and 1.0 M HCl-P_i are higher than or equal to those of $MgCl_2$-P_i and BD-P_i. However, this trend is opposite to what is expected. Because $MgCl_2$-P_i and BD-P_i have higher bioavailability, their $\delta^{18}O_P$ values are expected to be closer to the $\delta^{18}O_{P\text{-eq}}$ value (Jaisi et al. 2011). Similar to the results of the soil sample, the $\delta^{18}O_P$ values of $MgCl_2$-P_i and BD-P_i being smaller than $\delta^{18}O_{P\text{-eq}}$ could result from the decomposition of organic P. For $MgCl_2$-P_i has the fastest response speed, the re-cycling of $MgCl_2$-P_i by organisms can make its $\delta^{18}O_P$ value higher than that of BD-P_i. And the relatively high $\delta^{18}O_P$ values of NaAc-HAc-P_i and 1.0 M HCl-P_i may be the results of their lower bioavailability (i.e., slower response speed) and/or the weaker extraction abilities of $MgCl_2$ and BD compared with $NaHCO_3$ and NaOH, respectively. If we assume that NaOH-P_i contain mainly Fe-P_i and Al-P_i, and BD-P_i is mainly Fe-P_i, the higher $\delta^{18}O_P$ value of NaOH-P_i than that of BD-P_i implies the Al-P_i has higher $\delta^{18}O_P$ value and lower bioavailability than those of BD-P_i and $NaHCO_3$-P_i. The calculated content and $\delta^{18}O_P$ value of Al-P_i is 276.5 mg P/kg and 19.0‰, respectively. Thus, if the Al-P_i is extracted by NaAc-HAc buffer and/or 1.0 M HCl, it can increase their $\delta^{18}O_P$ values. Same as the reason for the soil sample, these calculated values should be treated with caution.

So far, there are only three studies reporting $\delta^{18}O_P$ of marine sediments extracted by the SEDEX method. Jaisi and Blake (2010) found that the $\delta^{18}O_P$ values of authigenic apatite (NaAc-HAc-P_i, 20.2~24.8‰) were higher than detrital apatite (1.0 M HCl-P_i, 7.7~15.4‰). Joshi et al. (2015) found that $\delta^{18}O_P$ values of CDB-P_i (18.7~20.8‰) were much higher than those of NaAc-HAc-P_i (12.7~15.5‰) for a sediment core from the Chesapeake Bay. Yuan et al. (2019) found the $\delta^{18}O_P$ values of Al-P_i, Fe-P_i, exchangeable P_i, authigenic P_i and detrital P_i decreased sequentially for a sediment core from Taihu Lake, and the $\delta^{18}O_{P\text{-eq}}$ values located between the $\delta^{18}O_P$ values of exchangeable P_i and authigenic P_i.

3.5 Implications for the choice and standardization of the sequential extraction method

For both the soil and sediment samples, the distribution patterns of P_i contents are clearly different between the Hedley and SEDEX extraction methods, although the sum content of P_i pools are similar (Fig. 4; Table S5—ESM). For the Hedley method, the P_i distribution pattern of the soil is similar to that of the sediment, while for the SEDEX method, the P_i distribution pattern of the soil is clearly different from that of the sediment. This means that one cannot judge which method is better based on the P_i content alone.

For the soil sample, the standard deviations of the mean $\delta^{18}O_P$ values of P_i pools from the Hedley method and SEDEX method were 1.97 and 0.31, respectively. This indicates the $\delta^{18}O_P$ values of Hedley method have larger variation among P_i pools than the SEDEX method, i.e., the Hedley method is more effective for separating isotopically distinct P_i pools which also likely have different sources/bioavailability for the soil sample used here. While for the sediment sample, the standard deviations of the mean $\delta^{18}O_P$ values of P_i pools from the Hedley method and SEDEX method are 0.87 and 1.67, respectively, suggesting that SEDEX method is more effective for separating isotopically distinct P_i pools which also likely have different sources/bioavailability for the sediment sample used here. These differences are likely to be caused by the inherent isotopic and compositional differences between soil and sediment samples and extraction of different P_i pools targeted by the two methods.

Although SEDEX method has larger variation in the mean $\delta^{18}O_P$ values of P_i pools for the sediment, the extraction ability of $MgCl_2$ and BD is weaker than that of $NaHCO_3$ and NaOH, respectively. The merit of SEDEX method is that it can effectively separate authigenic/biogenic apatite (NaAc-HAc-P_i) from detrital apatite (1.0 M HCl-P_i). Our results show that the contents of NaAc-HAc-P_i are high for both the soil and sediment samples and their $\delta^{18}O_P$ values are different from that of 1.0 M HCl-P_i. This suggests that it is necessary to separate authigenic apatite from detrital apatite. Therefore, combining the merits of two methods should be a better choice, i.e., adding a NaAc-HAc extraction step between NaOH and 1.0 M HCl extraction steps in the Hedley method (Fig. S3—ESM). Meanwhile, both methods hardly separate Fe-P_i from Al-P_i. Tentative calculation of this study shows that Al-P_i has higher $\delta^{18}O_P$ than that of Fe-P_i (BD- P_i), which is consistent with the results of Yuan et al. (2019). Further studies on this topic are warranted. One approach could be to add a BD extraction step between $NaHCO_3$ and NaOH extraction steps of the Hedley method. Therefore, the P extraction procedure established by Jensen et al. (1998) and adopted by Yuan et al. (2019) may be a better choice to separate different P_i pools for both soil and sediment (Fig. S3—ESM). At the same time, for both soil and sediment samples, $NaHCO_3$ has stronger extraction ability than $MgCl_2$, and the $\delta^{18}O_P$ values of $NaHCO_3$-P_i are similar to those of $MgCl_2$-P_i. This suggests that for the study samples, $NaHCO_3$-P_i and $MgCl_2$-P_i have similar source/bioavailability. Since biological respiration can release CO_2, Tiessen and Moir (2008) also suggested that $NaHCO_3$ (0.5 M, pH = 8.5) is a more appropriate measure of plant-available P_i. Therefore, if the amount of available P_i is the concern, extraction using $NaHCO_3$ solution may be a good choice. On the other hand, if P_i runoff from soil or P_i diffusion from sediment to water column is the concern, $MgCl_2$ solution or other extractants such as H_2O or NaCl may be a better choice.

It should be noted that the efficiency of P sequential extraction method derived from $\delta^{18}O_P$ criteria is based on the aim of the extraction (i.e., differentiating P_i source or bioavailability), but not on quantifying the actual P_i forms, which still deserve further studies. Meanwhile, this method also requires the P_i pools of sample having widely different initial $\delta^{18}O_P$ values. Since the types of samples and steps of extraction here are limited, more sample types and extractants should be used in future studies, combining or deleting extraction steps that have similar $\delta^{18}O_P$ values and trying to establish an optimal method that can differentiate more P_i pools and can be used for multiple types of samples.

4 Conclusions

The contents and $\delta^{18}O_P$ signatures of different P_i pools extracted by both Hedley and SEDEX methods for soil and sediment samples were measured to evaluate the efficiency of sequential P extraction methods. The fidelity of the extraction process and the purity of the precipitated Ag_3PO_4 were also tested. The following conclusions have been reached:

1. The extraction and purification processes do not alter $\delta^{18}O_P$, and the precipitated Ag_3PO_4 has high purity for both methods.
2. Based on $\delta^{18}O_P$ data, the Hedley method is more effective for separating isotopically distinct P_i pools (different sources/bioavailability) for soil, while SEDEX method is more effective for separating isotopically distinct P_i pools (different sources/bioavailability) for marine sediment used here.
3. The content of $NaHCO_3$-P_i is higher than that of $MgCl_2$-P_i, while their $\delta^{18}O_P$ values are similar. Therefore, $MgCl_2$ can be substituted by $NaHCO_3$ to better target loosely adsorbed, and biologically available pools of P_i.
4. The $\delta^{18}O_P$ of NaAc-HAc-P_i, 1.0 M HCl-P_i, and Conc.HCl-P_i are all higher than that of igneous apatite, suggesting they all contain portion of biologically cycled P_i. This was caused by either the transforming of the biologically cycled P_i into more stable P_i pools during pedogenesis/diagenesis progress or the incomplete extraction of some prior P_i pools.

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