Optimization framework of sediment phosphate oxygen isotope pretreatment method based on large-scale application: A case study of Fuyang River basin

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A R T I C L E   I N F O

A B S T R A C T

Phosphate oxygen isotope ($\delta^{18}O_P$) technique is an effective tool to identify the source and transformation process of phosphorus. The poor applicability of existing $\delta^{18}O_P$ pretreatment methods for sediments hindered the large-scale application of $\delta^{18}O_P$ technology. This paper presents an optimization framework for the pretreatment of sediment $\delta^{18}O_P$ samples based on large-scale applications, using the Fuyang River Basin as a case study. The typical channel landscape outflow lake, South Lake, was selected as the most favorable point for assessing the applicability and optimizing the mainstream $\delta^{18}O_P$ pretreatment method, which was achieved by clarifying the sediment environmental characteristics of South Lake. To evaluate the suitability of the Blake and McLaughlin methods in South Lake, a comparative study was carried out based on five dimensions: phosphorus recovery rate, removal efficiency of organic matter, removal efficiency of extraction liquid impurity ion, experimental time, and reagent consumption cost. The findings demonstrated that the Blake method outperformed the McLaughlin method across all five dimensions. Based on the environmental characteristics of the sediments of South Lake, the Blake method was optimized from two perspectives, namely the substitution of reagents and adjustment and optimization of experimental procedures. This resulted in an enhancement of phosphorus recovery and organic matter removal efficiency, while also reducing the experimental time required. The optimized method also yielded satisfactory results when applied to the entire watershed. This research paper can thus offer valuable technical support for the widespread application of sediment $\delta^{18}O_P$ technology.

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1. Introduction

Sediment serves as a crucial source of phosphorus in inland waters, and its potential to release phosphorus poses a significant risk factor for river eutrophication [1]. A clear understanding of the migration and transformation processes of phosphorus in sediments, as well as accurate quantitative identification of the sources of phosphorus in sediments, holds the key to curbing river eutrophication [2]. The phosphate oxygen isotope ($\delta^{18}O_P$) technique is an effective tool to identify the source and migration of phosphorus in sediments [3]. The primary method utilized involves collecting sediment samples, extracting the inorganic phosphorus using chemical techniques, purifying it through subsequent processes, and finally obtaining the oxygen isotope ratio of the inorganic phosphorus present in the sediment via stable isotope ratio mass spectrometry after a high-temperature cracking procedure(TC/EA-IRMS) [4,5]. By utilizing the statistical differences in $\delta^{18}O_P$ ratios present in various phosphorus sources and combining it with the fundamental knowledge of incomplete isotopic fractionation of phosphate, it is possible to quantitatively identify the sources of phosphorus in the basin [6].

A significant amount of data is often necessary for the quantitative identification of phosphorus sources using the $\delta^{18}O_P$ technique [7], interpretation of phosphorus sources often involves the use of either end-member mixing models or Bayesian mixing models [8–10]. Nevertheless, the widespread implementation of the $\delta^{18}O_P$ technique requires a well-established pretreatment method for $\delta^{18}O_P$. At present, the pretreatment process for sediment $\delta^{18}O_P$ involves the chemical extraction of inorganic phosphorus, followed by purification of the extracted material to obtain the desired pretreatment end-products (bright yellow Ag_3PO_4 solids). The primary method used for the extraction of inorganic phosphorus is strong acid extraction. As for the purification of the inorganic phosphorus extract, the most commonly adopted techniques are the Blake method [11], the McLaughlin method [12], and their modified variations. Nonetheless, a potential limitation of the sediment $\delta^{18}O_P$ methodology, especially in large-scale watershed studies, is the inadequacy of comparison between different pretreatment methods due to spatial variations in the environmental characteristics of sediment samples. As such, it is not uncommon for the same pretreatment method to encounter limitations when applied to certain samples [13]. Consequently, the precision of the sediment $\delta^{18}O_P$ methodology in tracing phosphorus in watersheds is significantly influenced. Therefore, the pivotal factor for the successful implementation of large-scale $\delta^{18}O_P$ technology application is the identification of appropriate pretreatment methods and the targeted optimization of these techniques to enhance the efficiency of $\delta^{18}O_P$ technology in the targeted water body.

At present, the main approach to optimize $\delta^{18}O_P$ pretreatment methods for sediment involves adjusting experimental procedures [4], optimizing experimental parameters [14], replacing experimental reagents [15], and repeating experimental operations [16] to enhance the effective removal of organic matter and other impurity ions, to improve the applicability and convenience of the $\delta^{18}O_P$ pretreatment method. However, such optimization is often performed based on the specific environmental characteristics of sediments, in an effort to establish a universal pretreatment method that can be extrapolated to other target water bodies. Although this idea has the potential to enhance the effectiveness of the method, it still faces limitations in terms of applicability due to spatial variations in organic matter and impurity ions present in sediment samples across the entire watershed [17]. Regarding sediments derived from watersheds, identifying the most unfavorable location and conducting applicability evaluation and optimization of the $\delta^{18}O_P$ pretreatment method based on its environmental characteristics represents the optimal solution for enabling widespread application of the $\delta^{18}O_P$ pretreatment method at present.

As of now, there is no feasible optimization plan available for the pretreatment method to support the large-scale employment of $\delta^{18}O_P$ technology in the context of watershed scale. This paper illustrates the establishment of an optimization framework for sediment $\delta^{18}O_P$ pre-treatment, using Fuyang River in Handan City as a case study, aiming to bridge the gap in knowledge pertaining to this research area. After conducting a comprehensive survey of the basin, the channel landscape outflow lake known as South Lake was selected as the most unfavorable point for conducting an applied assessment of mainstream $\delta^{18}O_P$ pretreatment methods. Furthermore, by taking into account the sediment characteristics of South Lake, we refined the current $\delta^{18}O_P$ pretreatment methods to more aptly align with the sediment of the Fuyang River Basin.The optimization framework we built in this paper can also be applied to other watersheds which can greatly promote the application of the $\delta^{18}O_P$ technique in inland watersheds.

2. Material and methods

2.1. Study area

The Fuyang River Basin represents one of the tributaries of the Ziya River system located in the Haihe River Basin. The river originates from the Fengfeng Black Dragon Cave, flowing through the urban area of Handan, where it merges with the Zhu and Qin Rivers. From there, it travels northwards to reach the Yongnian District, before eventually ending up in Quzhou County. To enhance flood control and landscape management, the Fuyang River Basin is equipped with a number of essential features, including the Dongwushi Reservoir, South Lake, and the Zhizhang River (which is primarily used for flood discharge) [18]. The South Lake is situated to the south of Handan's urban area, where it serves as the confluence point for the Fuyang River, Zhu River, and Zhizhang River. To cater to the requirements of urban flood control and landscape ecology, the South Lake was excavated in 2010 on the foundation of the Fuyang River channel. The lake boasts a water surface area of 0.2 km^2, an average depth of 1.3 m, and is abundant with a vast array of aquatic plants.

After conducting a detailed watershed survey, it was determined that South Lake may be the most unfavorable point due to the following reasons: (1) The water supply of South Lake primarily relies on Fuyang River runoff. It serves as both a flood detention basin and a pollutant trap, allowing pollutants from upstream inflows to be heavily trapped in the lake. (2) The short water retention time

resulting from the large lake discharge limits the aquatic plants' ability to purify water quality. Additionally, the buffer capacity for upstream inflow pollutants is weak, which often results in high sediment pollution levels [19].

2.2. Sample collection

As shown in Fig. 1, the sampling sites utilized in the investigation of South Lake's sediment environment were displayed, support of South Lake as the most unfavorable point within the wider Fuyang River Basin, and the subsequent assessment of the applicability of the two pretreatment methods. Five sampling sites (A, B, C, D, E) were established within South Lake, while four additional sites (W1, W2, W3, W4) were established-upstream (Fuyang River), upstream (Zhu River), downstream (Fuyang River), and downstream (Zhizhang River). To evaluate the feasibility of the optimized pretreatment approach, 29 sampling sites (S1–S29) were established throughout the Fuyang River Basin. Totally 37 sediment samples were collected.

A Grab bucket sediment harvester was used to collect the surface sediments (10 cm–15 cm), three parallel samples of 200 g around each sampling site were collected and fully mixed. The mixed samples were placed in a ziplock bag and transported to the laboratory as soon as possible for drying, grinding, 100 mesh screen, and air drying in the oven at 25 °C [20].

2.3. Sample analysis

2.3.1. Sediment environment characteristics and extraction liquid index

(1) Loss on ignition (LOI)

The combustion loss was measured by the burning method to characterize the content of organic matter in the sediment sample [21]. The drying sample was weighed with 0.5g sediment and placed in a porcelain crucible with known weight in Muffle furnace. The temperature was set at 550 °C and heated for 6h. After cooling to room temperature, the crucible and sediment were weighed and the content of organic matter was calculated according to the mass difference before and after. Each sediment sample was assessed thrice and the mean value was calculated to reduce the measurement error.
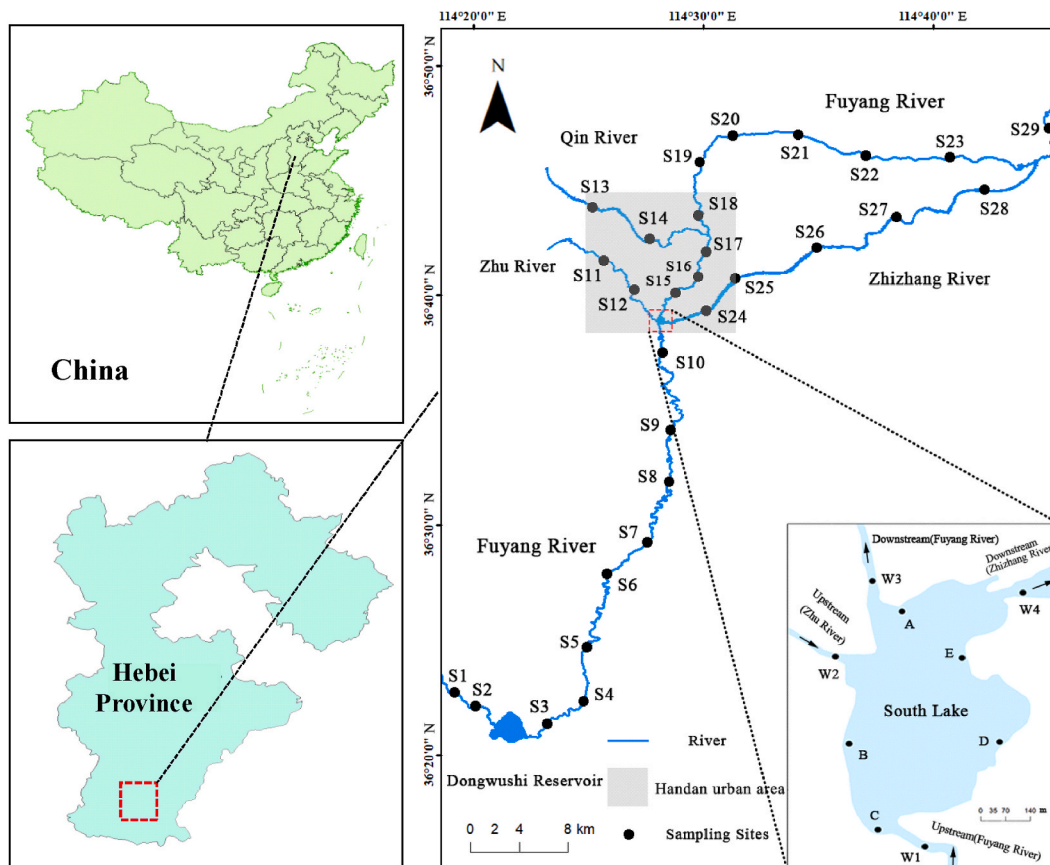

Fig. 1. Sampling sites in Fuyang River Basin.

(2) Conductivity (COND)

Water was added to screened sediment samples at a ratio of 1:5 (m/V), the samples were fully oscillated in a thermostatic oscillator for 5 min, and then left for 30 min after removal. The COND meter was used to measure the COND in the sediment extract after standing [22], and each sample was repeated three times to take the average value as the COND value. The COND value in the extract was measured by the COND meter as well.

(3) Dissolved Organic Carbon (DOC)

The extract of sediment after acid extraction was filtered by a 0.45 μm filter membrane and a TOC analyzer was used to determine the content of dissolved organic carbon in the extract [23]. Each extract was assessed thrice and the mean value was calculated to reduce the measurement error.

(4) Phosphorus speciation in sediments

The SMT method proposed by the European Commission for Testing was adopted to extract different forms of phosphorus from sediment samples [24]. SMT method divides total phosphorus (TP) into organophosphorus (OP) and inorganic phosphorus (IP), among which inorganic phosphorus was further divided into calcium-bound phosphorus (Ca–P) and iron-aluminum bound phosphorus (Fe/Al–P). Each sediment sample was assessed thrice and the mean value was calculated to reduce the measurement error.

(5) phosphate in sediment extract

Molybdenum-antimony spectrophotometry was used to determine phosphate content in sediment extract [25]. Each sediment sample was assessed thrice and the mean value was calculated to reduce the measurement error.

2.3.2. Pretreatment method

At present, there are two main pretreatment methods for sediments: the Blake Method and the McLaughlin Method. The detailed experimental procedures are described below.

(1) Blake Method [11].
① Inorganic phosphorus was extracted from sediments with 1 M HCl
② $MgCl_2 \cdot 6H_2O$ and NaOH were added to form $Mg(OH)_2$ co-precipitation (MAGIC) after 0.45 μm filtration membrane. After centrifugation, the supernatant was discarded and HNO_3 was added to dissolve precipitation (extraction solution), repeat this step once.
③The extraction solution was heated in a water bath at 50 °C, and then the ammonium molybdate solution was introduced to produce a precipitate of ammonium phosphomolybdate. The precipitation was separated from the solution using a 0.45 μm filtration membrane. The solution was rinsed with 10% ammonia solution two to three times, and a small amount (30–50 mL) citric acid-NH_4OH solution was used to dissolve the ammonium phosphomolybdate crystal.
④ Adjust the pH of the solution to 8–9, added magnesium reagent to generate magnesium ammonium phosphate precipitation, used 0.45 μm filtration membrane to separate from the solution, rinsed with pure water for two to three times, and used HNO_3 to dissolve precipitation.
⑤ The solution was passed through the cation resin column two or three times to remove the metal cations.
⑥ The solution was passed through the anion resin column two or three times to remove the organic matter.
⑦ The pH of the solution was adjusted to 7–8, followed by the addition of $AgNO_3$ to induce the precipitation of Ag_3PO_4. Subsequently, the sample was dried at 60 °C prior to measurement.
(2) McLaughlin method [12].
① Inorganic phosphorus was extracted from sediments with 1 M HCl.
② $MgCl_2 \cdot 6H_2O$ and NaOH were added to form $Mg(OH)_2$ co-precipitation (MAGIC) after 0.45 μm filtration membrane. After centrifugation, the supernatant was discarded and HNO_3 was added to dissolve precipitation, repeat this step once.
③ Acetic acid and sodium acetate solution were added to adjust the pH of the solution to 5.5. $Ce(NO_3)_3$ solution was added to generate $CePO_4$ precipitation. After centrifugation, the supernatant was discarded.
④ The solution was passed through a cation resin column two or three times to remove the metal cations.
⑤ The solution was passed through the anion resin column two or three times to remove the organic matter.
⑥ The pH of the solution was adjusted to 7–8, followed by the addition of $AgNO_3$ to induce precipitation of Ag_3PO_4. Subsequently, the sample was dried at 60 °C prior to measurement.

2.3.3. Indicator calculation

(1) Phosphorus recovery rate

$$R = \frac{r1}{r2} \times 100\%$$
(1)

Where R is the phosphorus recovery rate; r_1 is the phosphorus content measured in the solution at the end of a step; r_2 is the phosphorus content measured in the solution after the previous step.

(2) Organic matter removal efficiency

$$W = \frac{W_1 - W_2}{W_1} \times 100\%$$
(2)

Where W is organic matter removal efficiency; w_1 is the content of organic matter measured in inorganic phosphorus extract; w_2 is the content of organic matter in the solution measured after anion removal.

(3) Removal efficiency of impurity ions in solution

$$Z = \frac{z_1 - z_2}{z_1} \times 100\%$$
(3)

Where Z is the removal efficiency of impurity ions; z_1 is the COND value of inorganic phosphorus extract, z_2 is the COND value in solution after removal by adding cation resin.

3. Results

3.1. Characteristics of sediment environment in South Lake

The environmental characteristics of the sediments in South Lake were shown in Table 1. The organic matter, COND, TP and IP at the upstream points (W1 and W2) were all higher than those at the downstream points (W3 and W4). The average contents of organic matter, COND, TP, and IP in South Lake sediments were 6.24%, 670.58 μS/cm, 2.38 mg/g, and 1.16 mg/g, respectively, which were higher than the corresponding indicators of upstream and downstream points. It can be seen that the South Lake, as a river landscape outflow lake, effectively assists in the retention of various river pollutants.

SMT method was adopted to determine the content of different forms of phosphorus in sediments, and the results were shown in Fig. 2. It was found that the average TP content in the sediments of the South Lake was 2380 mg/kg, which was generally higher than that of the sediments from enter(W1, W2) and exit rivers(W3, W4), and the TP content of the enter rivers was higher than that of the exit rivers, suggesting South Lake is effective in retaining TP from the river. At the same time, the percentages of OP in TP of sediments from South Lake, enter rivers and exit rivers were all higher than 50%. On average, the percentage of OP in South Lake sediments was 51.29%, which is notably greater than the OP percentages observed in sediments from both enter and exit rivers.

3.2. Applicability evaluation of different pretreatment methods

Blake and McLaughlin method were used to process each 5g of 3 parallel samples collected around each point in South Lake. The phosphorus recovery rate, organic matter removal efficiency, removal efficiency of impurity ions from the extraction solution, experimental time and reagent consumption cost in key steps of the two methods were recorded and analyzed, and the average value of each individual data point was calculated. The difference and stability between the two methods were compared and the applicability of the two pretreatment methods was evaluated.

3.2.1. Phosphorus recovery in key steps

For the sediment in South Lake, the phosphorus content in the key steps of Blake method and McLaughlin method was determined and analyzed, and the phosphorus recovery rate was calculated by Eq. (1). We repeat our analysis three times for each sample and the results were shown in Table 2. The total recovery of phosphorus by Blake method was 71.53% ± 9.23%, and that by McLaughlin

Table 1
Mean values of environmental characteristics of sediment in South Lake.

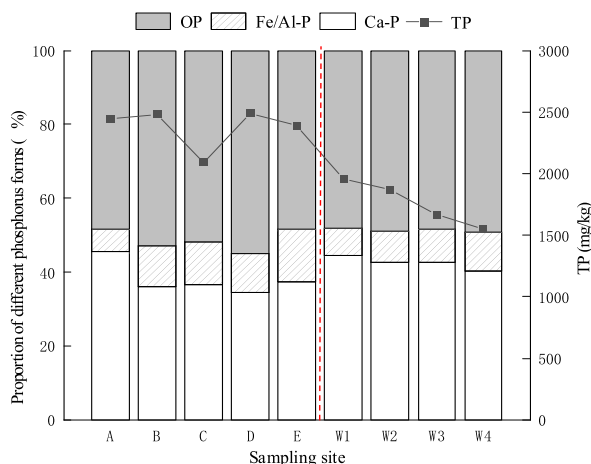| Sampling sites	LOI(%)	COND(μS/cm)	TP(mg/g)	IP(mg/g)
A	5.25	635.7	2.44	1.26
B	4.54	684.7	2.48	1.17
C	10.19	654.3	2.1	1.02
D	6.05	667.8	2.49	1.12
E	5.16	710.4	2.39	1.23
W1	3.62	512.5	1.95	1.01
W2	3.41	486.1	1.86	0.95
W3	1.21	364.7	1.54	0.78
W4	3.01	494.8	1.66	0.86

Fig. 2. P speciation in sediments of South Lake, entering and exiting rivers.

Table 2
Phosphorus recovery in key steps of Blake method and McLaughlin method.

Blake method		McLaughlin method	
Key Steps	Recovery Rate	Key Steps	Recovery Rate
Twice MAGIC	96.08% ± 1.34%	Once MAGIC	91.83% ± 4.17%
APM + MAP	81.17% ± 4.95%	CePO$_4$ precipitates	75.29% ± 8.91%
Cationic resins remove metal ions	89.93% ± 4.82%	Cationic resins remove metal ions	89.70% ± 6.93%
Anion resins remove organic material	87.73% ± 8.08%	Anion resins remove organic material	64.34% ± 10.88%
Total	71.53% ± 9.23%	Total	61.77% ± 12.02%

method was 61.77% ± 12.02%. The total recovery of phosphorus by McLaughlin method fluctuates greatly. The principal disparities between the two methods were the frequency of employment of MAGIC co-precipitation and the distinctive precipitation of phosphate.

3.2.2. Organic matter removal efficiency

Blake method and McLaughlin method used BioRadAG1-X8 anion resin to remove organic matter. The concentration of DOC in the sediment extract(1 M HCl) was determined before and after the addition of anion resin. The results were shown in Fig. 3, the organic matter removal efficiency calculated by Eq. (2) of BioRadAG1-X8 anion resin by Blake method and McLaughlin method in South Lake was 60.59% ± 3.06% and 46.66% ± 4.54%, respectively. The organic matter removal efficiency of Blake method was better than that of McLaughlin method. The removal effect of Blake method was also more stable than that of McLaughlin method.

3.2.3. Removal efficiency of impurity ions in extraction solution

The sediment extract obtained using 1 M HCl at different sampling points in South Lake was taken as the starting point, and the extract before adding AgNO$_3$ was taken as the end point. Blake method and McLaughlin method were respectively used to purify the
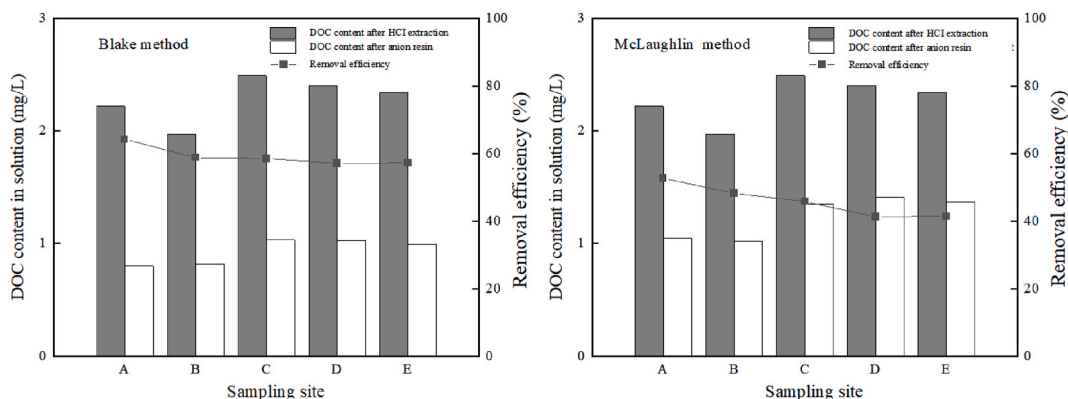

Fig. 3. Content and removal efficiency of organic matter by Blake method and McLaughlin method.

sediment extract obtained using 1 M HCl, and COND values were determined after different steps. The results were shown in Fig. 4. The removal efficiency of Blake method for impurity ions in the sediments of South Lake calculated by Eq. (3) was 89.61%, while that of Mclaughlin method was 74.29%.

3.2.4. Time consumption

The experimental time of key steps in Blake and McLaughlin method was recorded. The results were shown in Table 3. The overall time of Blake method was 40h, while that of McLaughlin method was 35h. The most significant difference between the Blake method and the McLaughlin method lies in their characteristic phosphate precipitation. For the characteristic precipitation of phosphate in Blake method, ammonium molybdate solution was used to generate the characteristic precipitation of ammonium phosphomolybdate. In the experimental operation, the pH of the solution was not high, but the time of precipitation generated by heating at 50 °C water bath was longer, which increased the experiment time. The characteristic precipitation of phosphate in the McLaughlin method used cerium nitrate solution to generate the characteristic precipitation of cerium phosphate, which had a high requirement on the pH value of the solution, low rate of success, and unstable precipitation of cerium phosphate.

3.2.5. Reagent dosage and cost

Reagent consumption in key steps of Blake method and McLaughlin method was recorded and the cost of both methods was estimated. The results were shown in Table 4. The reagent consumption cost of Blake method for each sample was about 1124.14 yuan, and that of McLaughlin method was about 1152.82 yuan. The reagent consumption of Blake method and McLaughlin method was different in the MAGIC precipitation times and the characteristic precipitation of phosphate, while the reagent consumption of other steps was similar. Among them, the cost of resin agent was relatively high.

The differences of Blake and McLaughlin method in phosphorus recovery rate, organic matter removal efficiency, removal efficiency of impurity ions in extraction solution, experimental time, and reagent dosage were comprehensively compared. The results showed that Blake method had better stability than McLaughlin method, and was more suitable for $\delta^{18}O_P$ pretreatment method in South Lake sediments. However, there are still some problems in Blake method, such as long experiment time and tedious operation. Moreover, The total phosphorus recovery rate and organic matter removal efficiency need to be further improved.

3.3. Pre-treatment method optimization

The classic Blake method was optimized and compared the phosphorus recovery rate, organic matter removal efficiency, extraction liquid impurity ion removal efficiency, experimental time, and reagent dosage in key steps before and after the optimization. The average values of the indicators from each sampling site at South Lake were utilized to assess the differences and stability between the two methods, and to evaluate the suitability of the optimized method.

3.3.1. Method optimization

(1) Reagent replacement

Since the strong acid cannot destroy the P–O bond in phosphate and isotope fractionation will not occur, HNO_3 was tried to replace HCl for inorganic phosphorus extraction [26]. The contents of inorganic phosphorus and organic matter in the HCl and HNO_3 extraction solution in the classic Blake method were compared(Fig. 5). The extraction efficiency of inorganic phosphorus from HCl and HNO_3 extraction was determined, and the extraction efficiency of HNO_3 was similar to that of HCl. The content of organic matter in the extraction solution of HNO_3 was less than that of HCl. Applying HNO_3 to extract inorganic phosphorus can avoid the introduction of Cl^- and prevent the formation of AgCl in the subsequent purification process, which was conducive to the efficient formation of the
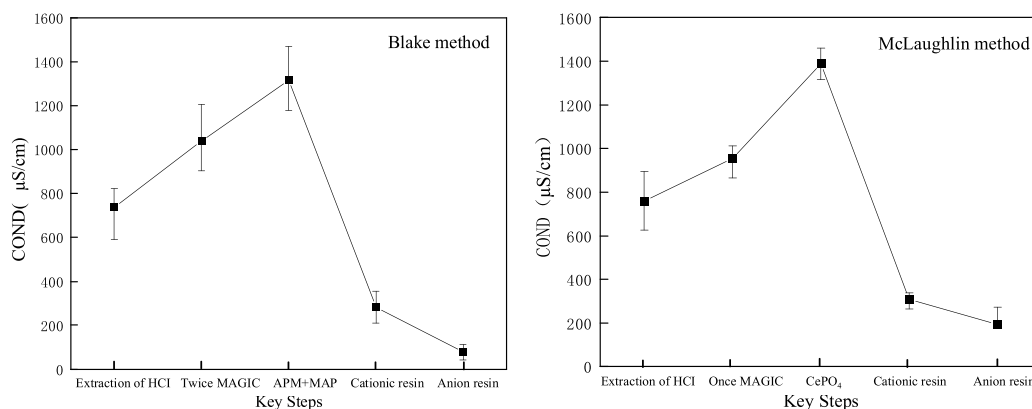

Fig. 4. COND values at different purification stages in Blake and McLaughlin method.

Table 3

Time consumption in key steps of Blake method and McLaughlin method.

Blake method		McLaughlin method	
Key Steps	Time consuming experiment	Key Steps	Time consuming experiment
Extraction of inorganic phosphorus	24 h	Extraction of inorganic phosphorus	24 h
Twice MAGIC	5 h	Once MAGIC	2 h
APM + MAP	8 h	CePO$_4$ precipitation	6 h
Cationic resins remove metal ions	1 h	Cationic resins remove metal ions	1 h
Anion resins remove organic material	1 h	Anion resins remove organic material	1 h
Ag$_3$PO$_4$ precipitates are generated	1 h	Ag$_3$PO$_4$ precipitates are generated	1 h
Total time consuming	40 h	Total time consuming	35 h

Table 4

reagent consumption and cost in key steps of Blake method and McLaughlin method.

| Blake method			McLaughlin method		
Key Steps	Consumption of medicine	Cost (yuan)	Key Steps	Consumption of medicine	Cost (yuan)
Extraction of inorganic phosphorus	100 ml 1 M HCl	10	Extraction of inorganic phosphorus	100 ml 1 M HCl	10
Twice MAGIC	60 ml 4 M NaOH 100 ml 1 M MgCl$_2$	8.64	Once MAGIC	30 ml 4 M NaOH 50 ml 1 M MgCl$_2$	4.32
APM + MAP	40 ml 0.5 M (NH$_4$)$_2$MoO$_4$ 50mlCA-NH$_3$·H$_2$O 40 ml 1 M MgCl$_2$	32	CePO$_4$ precipitation	40 ml 1MCH$_3$COONa 10 ml 10%CH$_3$COOH 20 ml 1MCePO$_4$	65
Cationic resins remove metal ions	10 g	512	Cationic resins remove metal ions	10 g	512
Anion resins remove organic material	10 g	545	Anion resins remove organic material	10 g	545
Ag$_3$PO$_4$ precipitates are generated	35 ml 0.2 M AgNO$_3$	16.5	Ag$_3$PO$_4$ precipitates are generated	35 ml 0.2 M AgNO$_3$	16.5
Total	1124.14 yuan		Total		1152.82 yuan
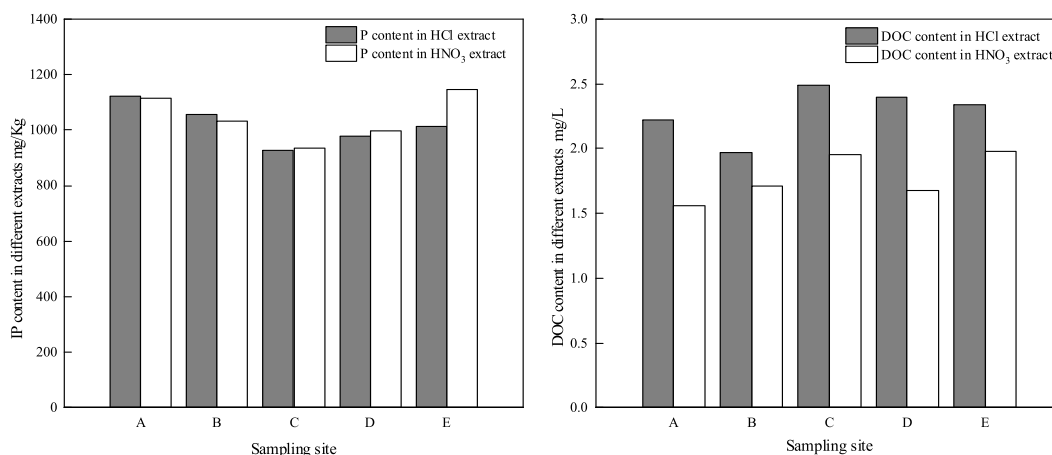
Fig. 5. Comparison of IP content and organic matter content between HCl and HNO$_3$ extraction.

final Ag$_3$PO$_4$ precipitation. The inorganic phosphorus in South Lake sediments can be extracted by HNO$_3$ instead of HCl.

At the same time, in order to effectively reduce the cost of the experiment, domestic 732 cation resin was used to replace Biorad AG50W-X8 cation exchange resin to remove impurity ions in the solution, and DAX-8 resin to replace BioRad AG1-X8 anionic resin to remove organic matter in the solution.

(2) Adjust and optimize the experimental procedure
   ① Remove one step of magnesium hydroxide co-precipitation in the Blake method (MAGIC)

Remove one step of magnesium hydroxide co-precipitation to avoid the introduction of impurity ions, reduce the loss of phosphorus, and shorten the experimental process and time-consuming.

② Adjust the sequence of steps for removing organic matter with DAX-8 resin

After extracting inorganic phosphorus from sediments with HNO_3, DAX-8 resin was used to remove organic matter from the solution. The HNO_3 extraction solution was passed through DAX-8 resin 5 times.

③ APM operation details optimization

During the APM precipitation step in the classic Blake method, the 45 °C water bath was heated and waited for the precipitation of ammonium phosphomolybdate for a long time within 4–5 h. The temperature of the water bath was adjusted to 45 °C, 60 °C and 75 °C respectively by using a constant temperature water bath, and the APM precipitation typically took 4–5 h, 2–3 h, and 1.5–2 h to generate, respectively. With the increase of water bath heating temperature, the time of APM precipitation was shortened. However, when heating the mixture in a water bath at 75 °C, APM precipitates tend to adhere to the walls of the beaker during formation, making them difficult to dissolve in citric acid-ammonia solution. This often leads to a significant amount of phosphate loss, which can negatively impact the subsequent MAP precipitation process and even prevent its formation altogether. This can greatly compromise the stability of the pretreatment method. Under heating conditions of 60 °C and 75 °C in a water bath, the formation time of APM precipitation was similar. However, it was found that there was no adhesion of APM to the beaker walls when the water bath temperature was increased to 60 °C. This is important as such sticking would have a negative impact on subsequent experimental steps. Therefore, the precipitation formation of APM was promoted by heating at 60 °C water bath to shorten the overall time of the experiment. The specific process of the optimized Blake method was shown in Fig. 6.

3.3.2. Feasibility evaluation

(1) Effect comparison

The optimized Blake method was used to enrich and purify the sediment samples from South Lake, and the production of bright yellow Ag_3PO_4 was taken as the experimental endpoint. The results were compared with the classic Blake method in five dimensions, including phosphorus recovery rate, organic matter removal efficiency, impurity ion removal efficiency, time consumption, and reagent cost (Table 5). It is evident that the improved Blake method has a superior effect in comparison to the classical Blake method.

(2) Verification and effect verification of isotope fractionation

To validate whether the optimized pretreatment method induces isotopic fractionation, pure Ag_3PO_4 was produced directly by adding silver nitrate to potassium dihydrogen phosphate. The resulting oxygen isotopes were analyzed and compared with those obtained using the optimized Blake pretreatment method. The oxygen isotope values of Ag_3PO_4 samples obtained by the two methods are 13.45 ± 0.15‰ and 13.64 ± 0.26‰, respectively. These results indicate that the optimized pretreatment method did not induce oxygen isotope fractionation, which is consistent with the conclusion that P–O bonds in phosphate are resistant to inorganic hydrolysis and do not exchange oxygen with water in the absence of microbial activity. We applied the optimized Blake method to Fuyang River Basin (S1–S29) and obtain satisfactory results.

4. Discussion

4.1. Reasons for differences in applicability of different pretreatment methods

The complexity and limited applicability of the $\delta^{18}O_P$ pretreatment method in sediments are primary factors that hinder the broad application of this technique. In particular, when facing large-scale applications in river basins, the heterogeneous characteristics of sediments can impact the suitability of various pretreatment methods. The differences in applicability are associated with both the environmental properties of the sediments and the purification process of the pre-treatment methods. These differences manifest in the
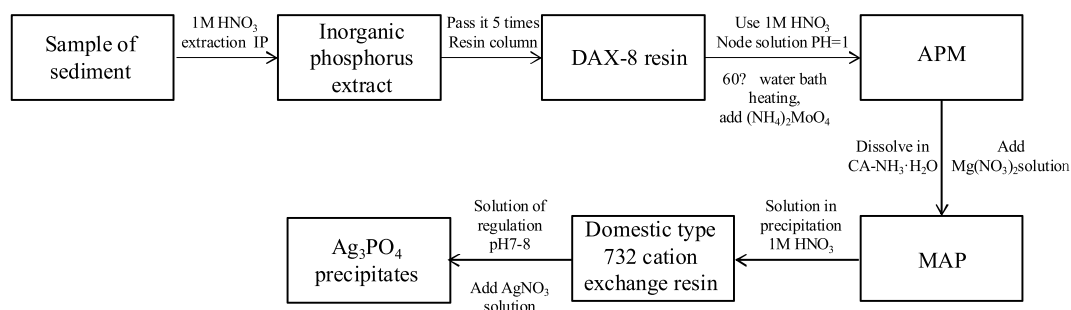
Fig. 6. Flow chart of optimized Blake method.

Table 5
Effect comparison between optimized Blake method and classic Blake method.

Dimension	Optimized Blake method	Classic Blake method
P recovery rate	$78.23 \pm 2.05\%$	$66.42\% \pm 2.87\%$
Organic material removal efficiency	61.25%	59.68%
Impurity ion removal efficiency	89.93%	89.61%
Time consumption	33–34h	40h
Reagent cost	139.90 yuan	1124.14 yuan

following aspects: (1) The characteristic precipitation of Blake and McLaughlin methods exhibit noteworthy differences. In the Blake method, the AMP and MAP precipitants are relatively lenient compared to the $CePO_4$ precipitant in the McLaughlin method. Additionally, an increase in the pH level can result in incomplete $CePO_4$ precipitation by increasing the solution volume. This results in the difference of phosphorus recovery rate [27]. (2) In comparison to AMP and MAP precipitation in the Blake method, the adsorption capacity of $CePO_4$ precipitation for organic matter in the McLaughlin method is stronger. This may cause a higher organic matter content in the subsequent experimental phases, and make organic matter removal efficiency unstable. When organic matter is present in a solution, it can adsorb some of the phosphates that are also in the solution. Differences in the efficiency of organic matter removal due to different purification processes can also result in differences in the phosphorus recovery rate [28]. (3) When exposed to strong acids, strong bases, and buffer reagents, the valence of metal ions in solution is subject to change, and metal ions are also prone to forming metal hydroxide precipitates, such as $Mg(OH)_2$, $Al(OH)_3$, $Mn(OH)_2$, $Fe(OH)_2$ and other white precipitates. The formation of Cu $(OH)_2$ blue flocculent precipitates and $Fe(OH)_3$ reddish-brown flocculent precipitates can increase the consumption of experimental reagents or interfere with the formation of target precipitates, resulting in differences in reagent consumption costs and phosphorus recovery rates. Insufficient initial sediment or the presence of organic matter and impurity ions can lead to low phosphorus recovery rates, making it difficult to generate enough Ag_3PO_4 through this method [29]. During the pre-experiment process of this method, we encountered numerous failures. With persistence, we were able to accumulate valuable insights into the operational details required for South Lake sediment.

4.2. Optimization framework of sediment phosphate oxygen isotope pretreatment method based on large-scale application

Currently, two primary approaches are being considered to address the issue of scaling up the application of various $\delta^{18}O_P$ pretreatment techniques.: The first approach involves optimizing existing pretreatment methods and conducting verification using sediment samples from the target water body. Currently, numerous researchers both domestically and abroad have developed a significant number of $\delta^{18}O_P$ optimization methods to enhance the efficiency and convenience of the techniques. Although these methods exhibit strong versatility for small-scale research applications, discrepancies in sediment environmental characteristics hinder consistent utilization of the same method for treating certain sediment samples when research is scaled up [30]. Secondly, selective adsorption materials for phosphate were employed to concentrate phosphate in sediments and diminish the impact of organic matter and impurity ions on the subsequent purification process [31]. The recent rapid advancement of phosphate in-situ enrichment materials provides a foundation for implementing this idea. The utilization of phosphate selective adsorption materials can effectively eliminate the impact of organic matter and various impurities on each step of the pretreatment method [32]. This approach has been initially applied to the pretreatment method of $\delta^{18}O_P$ in water bodies. However, the transfer efficiency of inorganic phosphorus from sediments to phosphate selective adsorption materials is limited due to the abundant presence of metal-based oxides, thereby posing substantial constraints to the application of this approach in sediments. For large-scale application of sediment $\delta^{18}O_P$, it is essential to ensure that the $\delta^{18}O_P$ pretreatment method is not only applicable but also cost-effective in terms of time and reagent consumption. To achieve this, a framework for optimizing the pretreatment method based on the large-scale application of sediment $\delta^{18}O_P$ was proposed in this study. (Fig. 7). The proposed optimization framework identified the most challenging locations in the target watershed, where the sediment contained the highest levels of organic matter and impurity ions. Typically, identifying these points required field investigations and comprehensive assessments. Based on the environmental characteristics of the sediment at these challenging locations, the framework evaluated the applicability of the two mainstream pretreatment methods. Building upon the optimal method, method optimization was conducted to enhance its applicability, reduce the consumption of reagents and time, and expand its applicability to the entire basin, ensuring the effectiveness of the pretreatment method at the watershed scale. Research on the extensive implementation of $\delta^{18}O_P$ at a watershed scale is currently inadequate. This study addresses this shortfall in the field and furnishes the fundamental procedural support required for the large-scale utilization and subsequent indexing of $\delta^{18}O_P$.

5. Conclusion

The paper outlines an optimization framework for pre-treatment techniques for the extensive application of sediment $\delta^{18}O_P$. The Fuyang River Basin is utilized as an example, with South Lake as the most unfavorable point. An examination of South Lake sediment's environmental characteristics showed that its organic matter, COND, TP, and IP content were higher than those in the enter river and exit river. South Lake, as a river landscape outflow lake, played a significant role in the Fuyang River Basin. Based on South Lake sediment's environmental characteristics, the applicability of mainstream $\delta^{18}O_P$ pre-treatment methods was evaluated. The Blake method was found to be the most suitable method considering differences in phosphorus recovery rate, organic matter removal
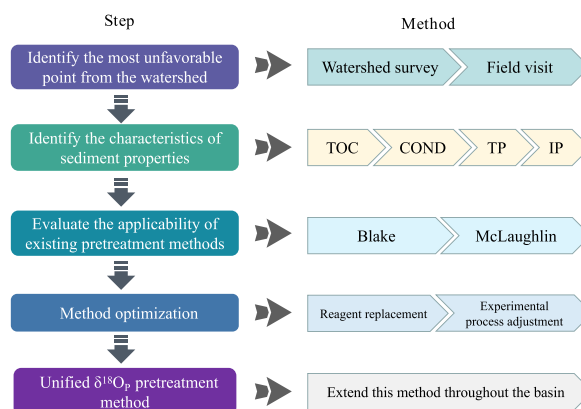
Fig. 7. Optimization framework of pretreatment methods based on large-scale application of sediment $\delta^{18}O_P$.

efficiency, impurity ion removal efficiency, experimental time, and reagent cost. The classic Blake method was subsequently optimized by the replacement of experimental reagents and adjustments to the experimental process. Feasibility evaluations showed that the optimized Blake method could be better applied to South Lake sediments. The optimized Blake method yielded satisfactory results when applied to the entire Fuyang River Basin. This paper thus provides a feasible methodological framework for the large-scale utilization of $\delta^{18}O_P$ in sediments and forms a foundation for its potential use in sediment at the catchment scale.

Author contribution statement

Jing Yang: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.
Chengyu Du, Hengtong Lu, Qingqing Chan, Jiaxuan Zhang, Hailong Ma, Huiying Zeng: Performed the experiments.
Xin Jin: Contributed reagents, materials, analysis tools or data; Wrote the paper.
Simin Li: Contributed reagents, materials, analysis tools or data.

Data availability statement

Data included in article/supp. material/referenced in article.

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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