Optimized digestion methods: organic phosphorus sequential extraction, total phosphorus, and nitrogen simultaneous determination in sediments

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Abstract
Purpose The organic phosphorus (OP) that is found in sediments influences the water quality of the overlying water. Accurate methods for OP extraction are important to identify phosphorus fractions in the sediments. We optimized the following: (1) the pH range of solutions after digestion; (2) the amounts of TP, H₂SO₄, and K₂S₂O₈ in the digestion; and (3) the digestion efficiency between acid K₂S₂O₈ and alkaline K₂S₂O₈ in total phosphorus (TP) and total nitrogen (TN) measurements. Moreover, we explained the related experimental phenomena and the results with an in-depth mechanism.

Materials and methods Sediments samples were taken from three locations (Yellow Sea, Jiehe River, and Jiaolai River, China). Each sample was analyzed to optimize sequential OP extraction based on the Ivanoff method.

Results and discussion We focused on the digestion step and digestion efficiency between acidic K₂S₂O₈ and alkaline K₂S₂O₈, total phosphorus (TP), and total nitrogen (TN) measurements. The results indicate that the optimal pH range of solutions after digestion is from 3 to 5.5. The TP digestion efficiency in combination with H₂SO₄ + K₂S₂O₈ (acid) is, on average, 8% higher than that of NaOH + K₂S₂O₈ (alkaline). However, the results for TN suggest the opposite. Optimal amounts of TP, H₂SO₄, and K₂S₂O₈ for digestion were also clearly determined.

Conclusions The pH of solutions after digestion affects the color development necessary for effective phosphorus (P) determination. The TP and TN could be determined simultaneously using the alkaline K₂S₂O₈ digestion system under the experimental conditions. Finally, the optimal orthogonal combinations and mass ratios of P, K₂S₂O₈, and H₂SO₄, respectively, were determined to be ~ 1.5 × 10⁻⁵:1:8 (NaHCO₃, 16 h), ~ 5.6 × 10⁻⁵:1:3 (HCl, 3 h), ~ 1.6 × 10⁻⁵:1:5 (NaOH, 16 h), and ~ 1.4 × 10⁻⁵:1:8 (NaOH, 16 h, pH = 0.2). We improved the accuracy and precision of the Ivanoff method using an optimized sequential extraction method.

Keywords Organic phosphorus · Sequential extraction method · Simultaneous determination · Total phosphorus · Total nitrogen

1 Introduction

Phosphorus (P) is an important and limiting nutrient for primary production in aquatic environments (Kaiserli et al. 2002; Ahlgren et al. 2005; Fowdar et al. 2017). However, excessive P from industrial and agricultural emissions has already caused some serious environmental pollution problems (Smi 2000). Phosphorus pollution can trigger eutrophication, biodiversity loss, and oxygen depletion in water (Chowdhury et al. 2017). According to figures from the US EPA, it costs communities approximately US$2.2 billion every year to remedy drinking water and recreational water and to protect endangered species that are threatened by algal blooms (Dodd et al. 2009).
Sediments that adsorb large amounts of P are thought to be an important source of P for overlying water (Monbet et al. 2007; Hu et al. 2011). The P in sediments can be divided into inorganic P (IP) and organic P (OP), of which OP accounts for 12–42% of the total P (TP) (Ding et al. 2010). Studies have shown that considerable quantities of released P are from OP found in sediments (Suzumura and Kamatani 1995; Slomp et al. 2002). Under certain conditions, the decomposition of OP in sediments becomes an important source of soluble reactive P (SRP) in water (Bostrom et al. 1989). Similar to the sequential extraction of IP (Hieltjes and Lijklema 1980), OP can also be divided into many fractions (Zhu et al. 2013). However, the fractions and distributions of OP in sediments are poorly understood because there are currently no effective fractionation and characterization approaches (Zhang et al. 2008). Bowman and Cole (1978) developed a chemical fractionation method for OP in soil, and they divided OP into four distinct fractions using a sequential extraction method: labile OP, moderately labile OP, moderately resistant OP, and highly resistant OP. However, there are some problems associated with this method, such as the incomplete removal of high concentrations of phytate in most soils and sediments (Oluyedun et al. 1991; Golterman et al. 1998; Turner et al. 2002). Their fractionation method has been further improved by Tiessen et al. (1983), Sharpley and Smith (1985), and Ivanoff et al. (1998). For example, Ivanoff et al. (1998) developed a sequential extraction method for OP in soils. The OP recovery was improved by using an additional step to determine residual OP and biomass OP. Currently, there are no unanimously accepted fractionation procedures for analyzing OP in sediments (Li et al. 2013), and the sequential extraction procedure is still being improved and modified to estimate the fractionation of P in soil or sediment (Waterlot 2018). Although it is a classical method, there are still some problems with the Ivanoff method. For example, the proportions of OP, H2SO4, and persulfate in the digestion are uncertain. In addition, the concentration of P during extraction and digestion are determined without pH adjustments. Furthermore, a pH range for the effective measurement of TP by the ascorbic acid-molybdenum blue method is not obtained (Murphy and Riley 1962; Tiessen et al. 1983). The previous problems could affect the accuracy of OP determination. Therefore, it is essential to optimize the fractionation method of OP in sediments. Additionally, during the determination process, OP might be converted to IP under the K2S2O8 digestion condition. There is a similar scenario for TN measurement where different forms of N change to nitrate nitrogen (NO3-N) when TN is affected by K2S2O8. Therefore, the feasibility of determining TN using a TP digestion system is worth studying. There have been studies of the simultaneous determination of TP and TN using either an alkaline or acid peroxydisulfate, but those authors did not give an in-depth description of the mechanisms or phenomena (Worsfold et al. 2005).

The objectives of this study are to (1) investigate and optimize the pH range of the digestion solution for TP measurement by the phosphor-molybdate colorimetric method; (2) identify the digestion efficiency of TP and TN using the two digestion systems H2SO4 + K2S2O8 and NaOH+ K2S2O8; (3) investigate the feasibility of determining TP and TN using the same digestion system; and (4) investigate the relationship between the TP digestion efficiency and the concentration of P, as well as dosages of H2SO4 and K2S2O8. Moreover, the aims of this study are to explain the related experimental phenomena and results with an in-depth mechanism and to improve the accuracy and precision of the classical Ivanoff OP sequential extraction method by using an optimized method.

2 Materials and methods

2.1 Study site and sampling

The Jiehe River and Jiaolai River are located in the northwest of the Shandong Peninsula, and they flow northwest into the Laizhou Bay of the Bohai Sea, China (Fig. 1). Both rivers have been heavily contaminated. Pollution in the Jiehe River is mainly caused by local mining and smelting activities (Bi and Zhao 2017). Pollution in the Jiaolai River is mainly caused by upstream industrial effluent (Cai et al. 2015; Li et al. 2016). Sediment samples were collected using a Van Veen grab sampler (Fig. 1). Composite surface sediment samples were stored in sealed plastic bags in an adiabatic box and then frozen at −24 °C until the analysis was performed. The samples were freeze dried and sieved (100 mesh) prior to the analysis.

2.2 Measurements

The TP was measured by calcination in a muffle furnace (550 °C) and was then extracted using a solution of 1 mol L−1 HCl. Total IP (TIP) was measured by extraction with 1 mol L−1 HCl (16 h) without calcination. The difference between TP and TIP was total OP (TOP) (Aspila et al. 1976). The three solid-phase fractions of OP determination (readily labile OP, moderately labile OP, and nonlabile OP) in the sediment samples were based on the Ivanoff method (Ivanoff et al. 1998).

1. Readily labile OP: A total of 1.0-g sediment samples that had been sieved through a 100-mesh sieve was initially extracted with 50 mL of 0.5 mol L−1 NaHCO3 at pH 8.5 for 16 h and was then centrifuged at 4000 g for 15 min. After the centrifugation, the extract was collected to determine both IP and TP. The difference between TP and IP was readily labile OP.
2. Moderately labile OP: The residue from the NaHCO$_3$ extraction was extracted with 50 mL of 1.0 mol L$^{-1}$ HCl for 3 h. The residue from the HCl extraction was rinsed with deionized water and then extracted using 50 mL of 0.5 mol L$^{-1}$ NaOH for 16 h. The NaOH extract was acidified to pH 0.2 with concentrated HCl to separate the nonlabile fraction (humic acid-P) from the moderately labile fraction (fulvic acid-P). All extracts were centrifuged and analyzed for TP and IP. The HCl-OP and fulvic acid-OP were moderately labile OP.

3. Nonlabile-OP: The rinsed residue from the NaOH extraction was ashed at 550 °C for 1 h and then extracted with 1 mol L$^{-1}$ H$_2$SO$_4$ for 24 h. After centrifugation, the extract was analyzed for TP. The sum of H$_2$SO$_4$-TP and humic acid-OP was nonlabile-OP.

Total extracted OP is the sum of the three solid-phase fractions of OP described previously. The P concentration in all extracts was determined according to the molybdenum blue method (Murphy and Riley 1962). Total organic carbon (TOC) and TN in the sediment samples were analyzed using a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan). The TN in all solutions was measured using a spectrophotometry method that is based on the reaction of diacetylmonoxime and urea in an acidic solution (Zhao et al. 2011). The nitrite determination method was based on the reactions of sulfanilic acid and naphthylethylenediamine dihydrochloride (NED) (Pandurangappa and Venkataramanappa 2007). Triplicates were analyzed for all samples, and the results are expressed as their average. The relative standard deviation (RSD) of the measurements is ≤ 5%.

2.3 The pH gradient experiments of digestion solutions

The eight parallel solutions containing OP (P < 30 μg) derived from sediment extraction were added to eight 50-mL colorimetric tubes. The eight parallel solutions were digested for TP determination (Bowman 1989). The parallel digestion solutions were spiked with 2.5 mol L$^{-1}$ NaOH or 2.5 mol L$^{-1}$ H$_2$SO$_4$ to adjust pH to approximately 1, 2, 3, 5, 7, 9, 11, and 13 after digestion. The previous mixtures were diluted by adding Milli-Q water to the 50-mL comparison tubes for P determination. The reported results are the average values of three parallel experiments.
2.4 The TP digestion by systems of $\text{H}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_8$ and NaOH+ $\text{K}_2\text{S}_2\text{O}_8$

To compare the digestion efficiency of TP using $\text{H}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_8$ and NaOH+ $\text{K}_2\text{S}_2\text{O}_8$, 12 parallel solutions containing OP (Sect. 2.3) of accurately measured aliquots ($P < 30 \mu g$) were added into 12 colorimetric tubes (50 mL). The tubes were divided into three series: (1) tubes A–E were spiked with different amounts of 2.5 mol L$^{-1}$ NaOH (0.5, 1, 2, 4, and 6 mL) and 3 mL of 5% $\text{K}_2\text{S}_2\text{O}_8$ (wt%); (2) tube F was not spiked with 5% $\text{K}_2\text{S}_2\text{O}_8$ (wt%), $\text{H}_2\text{SO}_4$, or NaOH addition and tube G was spiked with 3 mL of 5% $\text{K}_2\text{S}_2\text{O}_8$ (wt%) without the $\text{H}_2\text{SO}_4$ or NaOH addition. Group G is the standard method published by the Chinese EPA (2002); (3) tubes H–L were spiked with different amounts of 2.5 mol L$^{-1}$ $\text{H}_2\text{SO}_4$ (0.5, 1, 2, 4, and 6 mL) and 3 mL of 5% $\text{K}_2\text{S}_2\text{O}_8$ (wt%). Milli-Q water was added to these 12 tubes until they were filled to the 25-mL tick mark for digestion (Halstead et al. 1999). The resulting concentration of TP was used to represent digestion efficiency. After digestion, the pH values of the 12 parallel digestion solutions were adjusted to the effective colorimetric pH range by adding 1 or 6 mol L$^{-1}$ NaOH and 1 or 6 mol L$^{-1}$ $\text{H}_2\text{SO}_4$, and then the tubes were diluted by Milli-Q water to the 50-mL tick mark for the determination of P.

2.5 TN digestion by $\text{H}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_8$ and NaOH+ $\text{K}_2\text{S}_2\text{O}_8$

Generally, the digestion system of NaOH+ $\text{K}_2\text{S}_2\text{O}_8$ is used for the determination of TN in water because the digestion efficiency can be promoted by the alkalinity associated with $\text{K}_2\text{S}_2\text{O}_8$ (Halstead et al. 1999). To investigate whether the digestion system of $\text{H}_2\text{SO}_4 + \text{K}_2\text{S}_2\text{O}_8$ can be simultaneously applied to the digestion and determination of TN and TP, an experiment that compared the digestion efficiency of TN was performed.

The standard artificial solution containing 5 mg L$^{-1}$ organic nitrogen, 5 mg L$^{-1}$ NH$_3$-N, and 5 mg L$^{-1}$ NO$_x$-N was from analytically pure urea (CO(NH$_2$)$_2$), NH$_4$Cl, and KNO$_3$. In natural water, urea is a common type of organic nitrogen and a significant part of the nitrogen from agricultural fertilizer and animal metabolism sources. It is also common in the laboratory. Consequently, urea was selected to represent organic nitrogen. Then, the standard N solutions (2 mL) were added into 12 colorimetric tubes (25 mL). The tubes were divided into three series: (1) tubes 1–5 were spiked with 5 mL of different concentrations (0.025, 0.125, 0.25, 0.375, and 0.5 mol L$^{-1}$) of NaOH solutions containing 4% $\text{K}_2\text{S}_2\text{O}_8$ (wt%), (2) tube 6 was a blank group that did not contain $\text{H}_2\text{SO}_4$ or NaOH but contained 4% $\text{K}_2\text{S}_2\text{O}_8$ (wt%), tube 7 was spiked with 4% alkaline $\text{K}_2\text{S}_2\text{O}_8$ (wt%) and was analyzed with a standard oxidation digestion-UV spectrophotometry method for TN determination as published by the Chinese EPA (Zhou et al. 2012), and (3) tubes 8–12 were spiked with 5 mL of different concentrations (0.025, 0.125, 0.25, 0.375, and 0.5 mol L$^{-1}$) of $\text{H}_2\text{SO}_4$ solutions that contained 4% $\text{K}_2\text{S}_2\text{O}_8$ (wt%). Milli-Q water was added to the 12 tubes until the 10-mL tick mark for TN digestion (Halstead et al. 1999). Then, 1 mL of HCl (1 + 9) was added and diluted by Milli-Q water to the 25-mL tick mark for TN determination after digestion.

2.6 Orthogonal experiment of TP digestion efficiency

To investigate the optimal conditions of TP digestion (where the TP value was regarded as an index), an orthogonal experiment of three factors at four levels was designed using the SPSS 19.0 software (SPSS, IBM Statistics 19.0 edition, USA) (Table 1).

3 Results and discussion

3.1 Sediment characteristics

The chemical components and fractions of P of the sediment samples are shown in Table 1. The concentrations of TP in the sediments range from 297 to 2797 mg kg$^{-1}$. The concentration of IP dominates the P fraction, ranging from 271 to 1197 mg kg$^{-1}$ (60–91.2% of the TP). Additionally, OP content ranges from 26 to 380 mg kg$^{-1}$, accounting for 8.8–40% of the TP. Concentrations of TOC and TN in sediments range from 0.11 to 2.3 and 0.04 to 0.36 (wt%), respectively.

The Jiaolai River is a freshwater deficient river. Its water volume is mainly dependent on the influx from marine environments. As a consequence, marine silt and sand have been deposited at the sediment-water interface in the river. Therefore, sediments that are close to the estuary are dominated by larger particles in the Jiaolai River than the Jiehe River. However, the Jiehe River is a normal freshwater river that flows into the sea. There is more clay in Jiehe River sediments (Fig. 2). These findings suggest that the rivers have different compositions that contained 4% $\text{K}_2\text{S}_2\text{O}_8$ (wt%). Milli-Q water was added to the 12 tubes until the 10-mL tick mark for TN digestion (Halstead et al. 1999). Then, 1 mL of HCl (1 + 9) was added and diluted by Milli-Q water to the 25-mL tick mark for TN determination after digestion.

Table 1 Design of orthogonal experiment

| Levels | A P extracting solution (mL) | B $\text{H}_2\text{SO}_4$ (mL) | C $\text{K}_2\text{S}_2\text{O}_8$ (mL) |
|--------|-----------------------------|-----------------------------|---------------------------------|
| 1      | 1                           | 1                           | 1                               |
| 2      | 2                           | 2                           | 2                               |
| 3      | 3                           | 3                           | 3                               |
| 4      | 5                           | 5                           | 5                               |

*The moderately labile OP extracting solution (1 mol L$^{-1}$ HCl, 3 h) was 1, 2, 3, and 4.
likelihood that more pollutants (such as TP, IP, OP, TN, and TOC) will be in a river (Fig. 2).

In the present study, the characteristics, origins, and pollution degrees of these sediment samples are different, which is a better representation in order to verify the reliability of the optimized OP sequential extraction method.

### 3.2 The optimal pH range of a solution after digestion for TP determination

The relationship between TP concentrations and solution pH is shown in Fig. 3. Triplicates were analyzed, and the average values are expressed in the results. Figure 3 shows that measured TP concentrations are low (close to zero) when the pH is lower than 2 or higher than 12. Generally, the redox activity of ascorbic acid depends on pH, so molybdenum phosphates could be reduced by ascorbic acid under strongly acidic conditions (Snehalatha et al. 1997; Mowry and Ogren 1999). Additionally, ascorbic acid is more likely to be oxidized under alkaline conditions than acidic conditions (Hou et al. 2017). Therefore, the ascorbic acid has possibly been oxidized because the pH is higher than 12. In addition, TP is still not strictly consistent with the digestion solution pH values (2–12). As shown in Fig. 3, the experiment reveals that the optimal pH range for TP measurement is 3–5.5 (weak acid conditions). The low concentration of TP at high pH (6.5–12) levels may be due to ascorbic acid being more likely to be oxidized under alkaline conditions.

### 3.3 The digestion efficiency of H$_2$SO$_4$ + K$_2$S$_2$O$_8$ and NaOH+ K$_2$S$_2$O$_8$

Figure 4 shows that the TP digestion efficiency with H$_2$SO$_4$ + K$_2$S$_2$O$_8$ is relatively higher than with NaOH+ K$_2$S$_2$O$_8$. For group F, the background concentration of IP is 70.8 mg kg$^{-1}$ in the sediment. For groups A–C, the TP digestion efficiency is not promoted with amounts of 2.5 mol L$^{-1}$ NaOH lower than 2 mL (3 < pH < 5) compared to group G. However, the TP digestion efficiency increases as the amount of NaOH increases (groups D and E). This finding is because the thermal decomposition of persulfate was promoted by OH$^-$ (H$^+$ can be neutralized by OH$^-$), which can enhance O$_2$ with strong oxidizing properties (Halstead et al. 1999).

$$\text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 1/2\text{O}_2 + 2\text{H}^+; \quad (1)$$

$$\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \quad (2)$$

### Table 2 General chemical characteristics of the studied sediments

| Parameters | YS1  | L1   | L2   | L3   | J1   | J2   | J3   | Ja   | Jb   |
|------------|------|------|------|------|------|------|------|------|------|
| TP (mg kg$^{-1}$) | 533  | 409  | 297  | 695  | 539  | 715  | 677  | 1197 | 2797 |
| IP (mg kg$^{-1}$) | 441  | 361  | 271  | 445  | 429  | 630  | 488  | 1007 | 2417 |
| OP (mg kg$^{-1}$)$^b$ | 92 (17.3) | 48 (11.7) | 26 (8.8) | 250 (40) | 110 (20.4) | 85 (11.9) | 189 (27.9) | 190 (15.9) | 380 (13.6) |
| TOC (%)   | 0.217 | 0.140 | 0.110 | 1.975 | 0.933 | 0.289 | 0.524 | 0.656 | 2.302 |
| TN (%)    | 0.063 | 0.049 | 0.044 | 0.314 | 0.209 | 0.073 | 0.085 | 0.111 | 0.363 |

$^b$ Values in the parentheses are the percentage of TP in sediments (%)
For groups H–L, the OP digestion efficiency was promoted with 2.5 mol L$^{-1}$ H$_2$SO$_4$, and the efficiency of promotion was higher than the groups with added NaOH. This result was due to the following two reactions ((Eqs. (3) and (4)) (Fuller et al. 2016)

$$S_2O_8^{2-} + 2H_2SO_4 \rightarrow H_2S_2O_8 + 2HSO_4^{-} - SO_4^{2-}$$ \hspace{1cm} (3)

$$S_2O_8^{2-} + H_2O \rightarrow 2SO_4^{2-} + 1/2O_2 + 2H^+$$ \hspace{1cm} (4)

Because SO$_4^{2-}$ and O$_2$ are strong oxidizing radicals, the OP digestion efficiency of H$_2$SO$_4$ + K$_2$S$_2$O$_8$ is higher than that of NaOH+ K$_2$S$_2$O$_8$. Additionally, the pH of the digestion solution in all groups (A–L) was adjusted to the optimal pH range after digestion and prior to effective TP measurement (3 < pH < 5.5) as shown in Fig. 4.

Based on these results, the digestion system of H$_2$SO$_4$+ K$_2$S$_2$O$_8$ is more effective than NaOH+ K$_2$S$_2$O$_8$ for determining TP in a sediment extraction. However, both the alkaline and the acid peroxydisulfate can be recommended for TP determination rather than the Chinese EPA standard method (group G).

For TN determination, the digestion efficiency of NaOH+ K$_2$S$_2$O$_8$ is significantly higher than that of H$_2$SO$_4$+ K$_2$S$_2$O$_8$ (Fig. 5a). For groups 1–5, the TN digestion efficiency is similar to group 7. This result suggests that the alkaline K$_2$S$_2$O$_8$ digestion method for TN is a stable and reliable. In addition, NH$_4^+$ is more easily oxidized with increasing pH, so NH$_3$(aq) is more easily oxidized than NH$_4^+$.

$$3S_2O_8^{2-} + 2NH_3(aq) \rightarrow N_2 + 6H^+ + 6SO_4^{2-}$$ \hspace{1cm} (5)

In groups 8–12, the TN digestion efficiency was suppressed with H$_2$SO$_4$, and the efficiency decreased as H$_2$SO$_4$ increased. Different forms of N were measured in the five acidic groups (Fig. 5b). The amounts of NH$_3$-N first increased and then decreased as the amounts of H$_2$SO$_4$ increased (from 7.2 to 8.9 and finally to 8.5 mg L$^{-1}$). However, the concentrations of urea-N (CO(NH$_2$)$_2$-N) and NH$_3$-N concentrations in the standard artificial solution before digestion.
consensus as to whether HNCO is produced or not (Alzueta et al. 1998). Therefore, CO(NH2)2-N was decomposed to NH3-N and BX-N, thereby increasing the amount of NH3-N in the solution. Then, the X-N was oxidized to NO3−-N, increasing the content of NO3−-N. The original NH3-N in the acid tubes was not oxidized during the digestion. Finally, all forms of N added up to ~15 mg L−1 in each tube after digestion, observing the N conservation law. Hence, the mechanisms of digestion for NH3-N, CO(NH2)2-N, and NO3−-N are most likely the following reactions (Eqs. (7) and (8)):

\[ \text{H}_2\text{N-CO-NH}_2 \rightarrow \text{NH}_3 + \text{HNCO} \quad (6) \]
\[ \text{H}_2\text{N-CO-NH}_2 \rightarrow \text{NH}_3 + \text{X-N} \quad (7) \]
\[ \text{X-N} \rightarrow \text{NO}_3^- \text{-N} \quad (8) \]

Based on these results, the digestion system of H2SO4+K2S2O8 should not be selected for TN measurement. The alkaline K2S2O8 method can be selected over the Chinese EPA standard method (group G for TP and group 7 for TN) for simultaneous determination of TP and TN, under certain conditions (Worsfold et al. 2005). However, understanding what types of oxidation agents or conditions could convert NH3-N to NO3−-N directly (no N2 production) in strong acid conditions and understanding whether there are other digestion agents that could simultaneously oxidize all forms of P to IP (for TP determination) and all forms of N to NO3−-N (for TN measurement) remains to be discovered.

### 3.4 The orthogonal experiment of OP digestion efficiency

Based on the results, the orthogonal experiment L16 (43) of OP was designed to investigate the impact of the amount of OP, H2SO4, and K2S2O8 on the OP digestion efficiency (Table 3). The values of TP1, TP2, TP3, and TP4 represent the P concentrations in four kinds of OP extracting solutions.
(0.5 mol L⁻¹ NaHCO₃, 16 h; 1 mol L⁻¹ HCl, 3 h; 0.5 mol L⁻¹ NaOH, 16 h; HCl added into 0.5 mol L⁻¹ NaOH extraction to adjust, pH = 0.2) after digestion.

According to the results of the orthogonal polar difference analysis, the order of influence of the factors is A > B > C (Table 4). Therefore, the amount of P is the major factor that influences the digestion efficiency, followed by H₂SO₄ and K₂S₂O₈. The optimal combinations of the extracting solution for P by NaHCO₃, HCl, NaOH, and NaOH (pH = 0.2) are A₁B₄C₃, A₁B₂C₃, A₁B₃C₃, and A₁B₄C₃, respectively. After calculating the optimal combinations, the mass ratios of P, K₂S₂O₈, and H₂SO₄, respectively, are ~1.5 × 10⁻⁵:1.8 (NaHCO₃, 16 h), ~5.6 × 10⁻⁵:1:3 (HCl, 3 h), ~1.6 × 10⁻⁵:1:5 (NaOH, 16 h), and ~1.4 × 10⁻⁵:1:8 (NaOH, 16 h, pH = 0.2). The digestion solution pH values were adjusted to the optimal pH range prior to analysis (pH 3–5.5).

Nine types of sediments from different sampling areas (Fig. 1) were analyzed to determine the OP concentrations under the established optimal conditions. The recovery (%) of OP was measured as the ratio of total extracted OP to TOP (Zhang et al. 2008). Table 5 shows that the recoveries were 92–103%. There is high recovery and reproducibility when using the optimized method.

### 4 Conclusions

A method of digesting OP in sediments using a sequential extraction based on the Ivanoff method was optimized in this study. The pH of solutions after digestion affects the color development necessary for effective P determination. The optimal pH for digestion ranges from 3 to 5.5. Additionally, the OP digestion efficiency using H₂SO₄ + K₂S₂O₈ is, on average, 8% higher than that of NaOH+ K₂S₂O₈. The alkaline K₂S₂O₈ digestion method can be selected for simultaneous determination of TP and TN, under certain conditions. Finally, the optimal orthogonal combinations and the mass ratios of P, K₂S₂O₈, and H₂SO₄, respectively, are ~1.5 × 10⁻⁵:1.8 (NaHCO₃, 16 h), ~5.6 × 10⁻⁵:1:3 (HCl, 3 h), ~1.6 × 10⁻⁵:1:5 (NaOH, 16 h), and ~1.4 × 10⁻⁵:1:8 (NaOH, 16 h, pH = 0.2). The accuracy and precision of the optimized Ivanoff method are improved in the present study.

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