Phosphorus fractions and its summer flux from sediments of deep reservoirs located at a phosphate-rock watershed, Central China
Yufei Bao, Yuchun Wang, Mingming Hu and Qiwen Wang

ABSTRACT

Huangbai River, including four enchained reservoirs, is located in a phosphate-rock watershed in Yichang City, Central China. Previous studies showed that pollution levels due to activities of phosphate mining (PM) were extremely high and the water quality of reservoirs was severely affected by sedimentation. Yet, detailed knowledge of the sediment is lacking at that high phosphorus (P) concentration basin. Therefore, the different P fractions and its diffusion fluxes at the water-sediment interface of four deep reservoirs have been investigated for the first time to understand the internal P loading. The results indicated that the concentrations of total P, ranging from 9,631.5 to 581.6 mg kg$^{-1}$, exhibited an apparent spatial trend from the upstream to the downstream reservoirs, which corresponded with the activities of P mining in this basin. The P-fraction concentrations obtained from the sites were mainly ranked in this order: P associated with calcium (Ca-Pi) > organic P (Po) > P bound to aluminum (Al), ferrum (Fe) and manganese (Mn) oxides and hydroxides (Fe/Al-Pi). The orthophosphate diffusion fluxes ranged from $-0.40 \pm 0.09$ to $0.95 \pm 0.14$ mg m$^{-2}$ d$^{-1}$ which were positively related to P fraction concentrations while negatively related to oxidation-reduction potential and dissolved oxygen values. These results implied the dynamics role of internal P loading. The principle component analysis suggested that PM activities and internal P loading were the most reactive factors in this river system.

Key words | Huangbai River, orthophosphate diffusion fluxes, phosphate mining (PM), phosphorus fraction, sediment

INTRODUCTION

Eutrophication, defined as the enrichment of nutrients in water body, is one of the main problems in water management (Elser & Bennett 2011). Among these nutrients, phosphorus (P) is a key controlling factor for primary productivity in aquatic ecosystems because P is one of the natural growth-limiting factors in most reservoirs or lakes (Kaiserli et al. 2002; Bertrand et al. 2015). According to the research of the Organization for Economic Co-operation and Development (OECD), about 80% of the problems of lake eutrophication were limited by P, while another 10% were related to both P and nitrogen (N) and the remaining 10% were controlled by N and other factors (Wang 2001). Accordingly, the most common strategy for restoration of eutrophic lakes focused on reducing external P loading. This method, however, achieved limited effects because bottom sediments could also release it to the overlying water, especially when P input was reduced (Mlynarczyk et al. 2013; Qin et al. 2016). Therefore, systematic studies of internal P loading are indispensable to understand the process of P circulation and support the effective policies to manage eutrophication (Elser & Bennett 2011; Zhang et al. 2016a).
Huangbai River, a branch of the Yangtze River, is located in the west of Yichang City, Central China. Its mainstream is 162 km with a watershed area of 1,902 km² (111°04′–111°30′E, 30°43′–31°29′N). The average annual rainfall and runoff is 1,150 mm and 870 × 10⁶ m³, respectively. The known P ore reserved in the basin is 1.137 × 10¹² kg. Since 2003, the scale of phosphate mining (PM) has kept increasing (i.e. 4.74 × 10⁹, 6.05 × 10⁹, 8.76 × 10⁹, and 14.1 × 10⁹ kg in 2004, 2005, 2008 and 2014, respectively) and about 0.218–0.554 kg d⁻¹ total phosphorus (TP) was generated for one unit of PM productivity (i.e. 2.74 × 10⁹ kg d⁻¹) (Wang et al. 2016). Serious pollutions of PM operations have aggravated the problem of eutrophication. Thus, algae bloom occurred frequently in reservoirs, and ‘black spots’ events (in which the decay of algal left the water column black) are occurrence along the river, causing problems such as the drinking water crisis of 2013 in Yichang City.

Confronted with these challenges, Wang et al. (2016) investigated the influence of large-scale PM on water quality in Huangbai River basin, and found that P concentrations of the water body and TP in the sediment greatly increased during the period of PM. However, Wang et al. (2016) had no detailed data on different P forms from which the potential P release capacity of sediment could be estimated. A further limitation is that the simple measurement of TP in sediment contributes little to illuminate internal P cycling (Ramanathan 2007). Nowadays, many studies assessed internal P loading in shallow water bodies such as Taihu Lake, Hongze Lake, Yangzi River and Bützow Lake (Dai & Pan 2014; Yao et al. 2016; Zhang et al. 2016a) and concluded that the internal loadings of P were the main factor initiating algal blooms. However, deep reservoirs or lakes (mean depth > 5 m) with PM activities around have received less attention (Qin et al. 2016). Furthermore, in deep reservoirs, stratification is a basic and vital phenomenon. It is probable that the potential for internal P loading will increase as stratification patterns strengthen (North et al. 2014). Therefore, it is necessary and important to study internal P loading in deep reservoirs.

Consequently, in this study, the P fractions, the P diffusion fluxes and the relationships with environmental factors of four deep reservoirs in Huangbai River have been investigated for the first time to enhance the knowledge of P cycling in this high P concentration basin, so that algal growth and PM operations can be controlled better in the future.

MATERIALS AND METHODS

Study areas and sediment sampling

Huangbai River includes four en chained reservoirs: Xuanmiaoguan (XMG), Tianfumiao (TFM), Xibeikou (XBK), and Shangjiahe (SJH), built by dams in the upstream, upper-middle stream, midstream and downstream areas of the river, respectively (Figure 1). In the catchment areas of XMG and TFM reservoirs, there were 45 PM sites and the mining practices influenced an area of 408.5 km² which was about 72.6% of the areas. In XBK catchment area, there were 11 PM sites and they affected an area of 30.2 km², which was about 10% of the catchment area. The catchment area of SJH reservoir had no mining sites (Wang et al. 2016). The soils of this basin, rich in iron (Fe), aluminum (Al) and organic matters, are constructed by carbonate yellow-brown soil, muddy yellow-brown loam and a
small amount of brown calcareous soils. Basic information about the reservoirs is provided in Table 1.

Duplicated samples of superficial sediments (about 0–5 cm deep) and the corresponding overlying water (about 0–4 cm above the interface) were collected using a gravity corer (diameter 6.5 cm and length 60 cm) (Wang 2000) at three points in each reservoir (Figure 1): the river end of the reservoir, the middle part, and the head of the reservoir. Stratified overlying water was injected into PVC bottles at an interval of 2 cm. The sediments were sampled into sections of 2 cm length and packed in polyethylene centrifuge tubes and sealed to avoid sediment oxidation. Each reservoir was sampled for one day and the sampling dates were 23–26 June 2016 for XMG, TFM, XBK and SJH reservoirs, respectively. All samples were collected in triplicates, taken in air-sealed plastic bags and kept at 4°C until analyses (within 24 h).

Water chemistry

The parameters of water such as the temperature (T), dissolved oxygen (DO), electrical conductivity (EC), oxidation–reduction potential (ORP), and pH values were measured in situ using a YSI (Yellow Springs Instruments, USA) EXO2 multisensor sonde. The overlying water and pore water (extracted from sediment by centrifuging at 4,000 rpm for 30 min) samples were filtered through 0.45 μm G/F filter membranes. The concentration of orthophosphate (PO₄³⁻-P), the most bioavailability P form, was determined by molybdenum blue method (APHA et al. 1998).

Sediment sample analysis

One sample of sediments was used to calculate the water content by weighing the weight loss after drying the sediments at 105°C. Meanwhile, the water volume of the sediment was approximately regarded as the pore volume, and the porosity of sediment was the ratio between pore volume and total sedimentary volume. The dried samples were homogenized and separated by a laser diffraction particle size analyzer (LS I3 320, Beckman Coulter Company, USA) into three grain size fractions: the sand fraction (62.5–500 μm), the silt fraction (3.9–62.5 μm), the clay fraction (0.5–3.9 μm).

Other sediment samples were freeze-dried, homogenized and sieved through a 100-mesh sieve. Total organic carbon (TOC) and total nitrogen (TN) were detected by an elemental analyzer (Vario EL III, Elementar Company, Germany) after pretreatment in 1 mol L⁻¹ hydrochloric acid (HCl) to remove inorganic carbon. P fractions were classified into TP, inorganic P (Pi), organic P (Po), P associated with calcium (Ca) (Ca-Pi) and P bound to aluminum (Al), ferrum (Fe) and manganese (Mn) oxides and hydroxides (Fe/Al-Pi), and determined by the SMT (Standards Measurements and Testing) protocol (Zhang et al. 2016b). For all samples, triplicates were analyzed and the average or ‘mean value ± standard deviation’ of data were reported.

Flux estimation and data analysis

For deep reservoirs, wind is not the primary driving factor for the interchange of water-sediment interface. Instead, P concentration gradient may dominate the exchange process. Therefore, Fick’s first law, based on the principle holding that concentration gradient initiates the exchange, was used to estimate the theoretical release flux of PO₄³⁻-P at the interface of water and sediment (Berner 1980).

Table 1 | Summary of the sampled reservoirs

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Position</th>
<th>Catchment area (km²)</th>
<th>Storage capacities (m³)</th>
<th>Mean depth (m)</th>
<th>Water retention (d)</th>
<th>PM sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xuanmiaoguan</td>
<td>31°18′N 111°21′E</td>
<td>380</td>
<td>40.5 x 10⁶</td>
<td>28.7</td>
<td>81–84</td>
<td>45⁵</td>
</tr>
<tr>
<td>Tianfumiao</td>
<td>31°12′N 111°21′E</td>
<td>554</td>
<td>64.2 x 10⁶</td>
<td>35.8</td>
<td>87⁶</td>
<td></td>
</tr>
<tr>
<td>Xibeikou</td>
<td>31°05′N 111°20′E</td>
<td>862</td>
<td>210 x 10⁶</td>
<td>45.9</td>
<td>130–171</td>
<td>11⁸</td>
</tr>
<tr>
<td>Shangjiahe</td>
<td>31°00′N 111°23′E</td>
<td>937</td>
<td>16.9 x 10⁶</td>
<td>13.5</td>
<td>7–14²</td>
<td>0²</td>
</tr>
</tbody>
</table>

*The data of water retention were calculated from the ratio between effective capacity (or total capacity) and its average flow.

¹Number of sites for PM came from the report of Yichang government in 2013.
\[ J = -\phi D_s \left( \frac{\partial C}{\partial x} \right)_{x=0} \]  

(1)

where \( J \) is the diffusion flux (mg m\(^{-2}\) d\(^{-1}\)); \( \phi \) is the porosity of surface sediment; \( \left( \frac{\partial C}{\partial x} \right)_{x=0} \) is the concentration gradient at the water–sediment interface. It takes the slope value of the best fitting line of distribution profile of PO\(_4^{3-}\)-P concentrations in the overlying water and sediment. \( D_s \) is the effective diffusion coefficient, which is calculated from \( D_0 \) by the following equations (Berner 1980). \( D_0 \) (cm\(^2\) s\(^{-1}\)) is the theoretical diffusion coefficient of infinite dilution solution and it is calculated according to Krom & Berner (1980). The \( T \) in Equation (4) is the temperature of the overlying water (°C).

\[ D_s = \phi D_0, \quad \phi \leq 0.7 \]  

(2)

\[ D_s = \phi^2 D_0, \quad \phi > 0.7 \]  

(3)

\[ D_0 \times 10^{-6} = 7.34 + 0.16 \times (T - 25 \degree C) \]  

(4)

The mean values and standard deviations were calculated by Microsoft Excel 2007 and the figures were plotted by Origin 8.0. Analysis of variance (ANOVA), correlation statistical analyses and principal components analysis (PCA) were tested with SPSS 22 (Statistical Program for Social Sciences 22).

### RESULTS AND DISCUSSION

#### Physicochemical properties of overlying water and interstitial water

The physicochemical properties of overlying water and PO\(_4^{3-}\)-P concentrations of interstitial water are listed in Table 2. The parameters gave pH values that ranged from 7.79 to 8.64, owing to the alkaline geochemical environment of the soil (Wang et al. 2016). EC, a measure of the ionic strength, ranged from 385.4 to 496.5 \( \mu \)S cm\(^{-1}\). The ORP values were found to be 124.7 ± 20.9 mv and the DO concentrations were 5.9 ± 2.3 mg L\(^{-1}\). The PO\(_4^{3-}\)-P concentrations (mg L\(^{-1}\)) of the overlying water and the interstitial water ranged from 0.14 ± 0.04 to 2.85 ± 0.09 and from 0.03 ± 0.01 to 4.58 ± 0.24, respectively. It was much higher in the first two reservoirs than the last two ones.

#### Characteristics of the surface sediment

The physical and chemical properties of sediments are shown in Table 3. Water content of sediment reflects its resuspension ability: the higher the value is, the easier it is to suspend. According to Table 3, the surface sediment contained a large percentage of water (56.4 ± 7.0%) which

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>T (°C)</th>
<th>EC (( \mu )S cm(^{-1}))</th>
<th>ORP (mv)</th>
<th>DO (mg L(^{-1}))</th>
<th>PO(_4^{3-})-P (mg L(^{-1}))(^{a})</th>
<th>PO(_4^{3-})-P (mg L(^{-1}))(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>XMG-1</td>
<td>8.64</td>
<td>19.23</td>
<td>410.7</td>
<td>113.1</td>
<td>5.8</td>
<td>2.85 ± 0.09</td>
<td>4.58 ± 0.24</td>
</tr>
<tr>
<td>XMG-2</td>
<td>8.59</td>
<td>18.09</td>
<td>385.4</td>
<td>132.2</td>
<td>4.4</td>
<td>1.58 ± 0.07</td>
<td>2.19 ± 0.13</td>
</tr>
<tr>
<td>XMG-3</td>
<td>7.97</td>
<td>15.56</td>
<td>441.7</td>
<td>117.9</td>
<td>2.9</td>
<td>1.96 ± 0.13</td>
<td>3.61 ± 0.17</td>
</tr>
<tr>
<td>TFM-1</td>
<td>8.20</td>
<td>17.66</td>
<td>411.1</td>
<td>135.8</td>
<td>6.5</td>
<td>1.15 ± 0.09</td>
<td>1.50 ± 0.09</td>
</tr>
<tr>
<td>TFM-2</td>
<td>7.92</td>
<td>10.11</td>
<td>496.5</td>
<td>142.0</td>
<td>2.3</td>
<td>0.86 ± 0.06</td>
<td>1.41 ± 0.15</td>
</tr>
<tr>
<td>TFM-3</td>
<td>7.79</td>
<td>9.84</td>
<td>488.7</td>
<td>118.0</td>
<td>3.1</td>
<td>0.82 ± 0.09</td>
<td>1.92 ± 0.12</td>
</tr>
<tr>
<td>XBK-1</td>
<td>8.30</td>
<td>18.88</td>
<td>428.5</td>
<td>148.7</td>
<td>8.1</td>
<td>0.67 ± 0.03</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>XBK-2</td>
<td>8.09</td>
<td>13.84</td>
<td>462.7</td>
<td>132.6</td>
<td>5.3</td>
<td>0.14 ± 0.04</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>XBK-3</td>
<td>8.13</td>
<td>10.60</td>
<td>466.6</td>
<td>112.6</td>
<td>6.7</td>
<td>0.21 ± 0.03</td>
<td>0.32 ± 0.06</td>
</tr>
<tr>
<td>SJH-1</td>
<td>8.26</td>
<td>13.67</td>
<td>488.3</td>
<td>137.9</td>
<td>8.7</td>
<td>0.39 ± 0.03</td>
<td>0.30 ± 0.05</td>
</tr>
<tr>
<td>SJH-2</td>
<td>8.22</td>
<td>12.71</td>
<td>484.0</td>
<td>121.4</td>
<td>8.2</td>
<td>0.20 ± 0.06</td>
<td>0.43 ± 0.08</td>
</tr>
<tr>
<td>SJH-3</td>
<td>8.11</td>
<td>11.83</td>
<td>472.7</td>
<td>141.6</td>
<td>8.1</td>
<td>0.42 ± 0.09</td>
<td>0.26 ± 0.07</td>
</tr>
</tbody>
</table>

\(^{a}\)Represents the mean values of PO\(_4^{3-}\)-P concentrations of the overlying water (0–4 cm).

\(^{b}\)Represents the mean values of PO\(_4^{3-}\)-P concentration of interstitial water of the surface sediment (0–4 cm).
would facilitate the diffusion of P through its suspension under external disturbance. The average value of the porosity of surface sediment was 77.1 ± 5.1%. Particle size analysis indicated that most surface sediments were high in proportion to the clay and silt fractions, on average of 96.1%. Higher porosity and smaller sediment particle are more reactive due to increased surface area (Caden-Menun 2005).

As presented in Table 3, both TN and TOC concentrations, showed no significant difference \((p > 0.05)\) among the reservoirs (TN varied from 0.22 to 0.49% and TOC varied from 1.61 to 3.85%). However, TP ranged from 6,555.0 to 9,631.5 mg kg\(^{-1}\) in XMG, from 4,468.7 to 2,740.2 mg kg\(^{-1}\) in TFM, and finally from 581.6 to 860.9 mg kg\(^{-1}\) in SJH, respectively. It was obvious that TP decreased dramatically among the reservoirs, and one-factor ANOVA showed that there were significant differences \((p<0.05)\) of TP among the reservoirs. Higher values of the samples were collected from the former three reservoirs (XMG, TFM and XBK) located in the upstream and midstream areas. The TP content of the downstream reservoir (SJH) was approximately one order of magnitude smaller than that of former two ones (XMG, TFM).

The C/N (TOC/TN) ratios ranged from 7.4 to 11.4 with the average of 8.8. Po was related to both TOC and TN, indicating that Po may originate from both endogenetic and anthropogenic source (Zhang et al. 2016b). The C/N ratio varied from 2.6 to 4.3 in bacteria, and 7.7 to 10.1 in aquatic plants, whereas this ratio of terrestrial plants or materials was higher than 20 (Meyers & Lallier-Vergès 1999). Almost all C/N ratios in the sampling sediments of Huangbai River were lower than 10, suggesting a much higher contribution of endogenetic source for sedimentary Po.

### Phosphorus fraction composition

As presented in Figure 2, the fractions of different P varied greatly. For ten sampling sites \((n = 30)\), the rank order of P fractions concentrations was HCl-Pi > Po > Fe/Al-Pi while the rank order was Po > HCl-Pi > Fe/Al-Pi at the two left sites (SJH-1 and SJH-2). The former distribution pattern

![Figure 2](https://iwaponline.com/ws/article-pdf/18/2/688/2068846/ws018020688.pdf)
was similar to most reservoirs (rivers) of the Three Gorges (Wang et al. 2015).

Po showed the P fraction bound to organic matters and its stability was relative to the different Po structures (Zhang et al. 2014a). Po contents in the surface sediments varied from 286.2 to 544.2 mg kg$^{-1}$, which was not significantly different ($p > 0.05$) among reservoirs. However, it contributed 5.03–50.59% to the TP and the percentage of each reservoir showed significant difference in the following order: SJH (44.61%) > XBK (22.01%) > TFM (12.89%) > XMG (6.05%) (Figure 3), which mainly resulted from the difference of TP contents.

Fe/Al-Pi, was considered as algal available, could be easily affected by pH and ORP, and consequently was released into pore water under reductive conditions (Kaiserli et al. 2002). About 2.13–18.61% of the sedimentary TP was Fe/Al-Pi, which ranged from 94.8 to 315.9 mg kg$^{-1}$. The highest amount was detected in XMG-3 (315.9 mg kg$^{-1}$), which was about 3 times of that in SJH-3 (94.8 mg kg$^{-1}$). The ANOVA showed a difference ($p < 0.05$) among the reservoirs in the following order: XMG (272.9 mg kg$^{-1}$) > XBK (184.6 mg kg$^{-1}$) > TFM (160.1 mg kg$^{-1}$) > SJH (109.2 mg kg$^{-1}$) (Figure 3).

Ca-Pi was assumed to mainly consist of apatite P (natural and detritus) (Kaiserli et al. 2002). The Ca-Pi contents ranged from 236.3 to 8,962.9 mg kg$^{-1}$, and its relative contribution ranged at 34.84–92.84% of TP, which decreased dramatically from the upstream to downstream reservoirs (Figure 3). According to Wang et al. (2016), one of the main chemical compounds from PM in the Huangbai River basin is carbonate fluorapatite (Ca$_5$(PO$_4$)$_3$(CO$_3$F)). Therefore, for the XMG, TFM and XBK reservoirs with PM in the catchment areas, apatite produced from the mining areas was accumulated in the reservoirs. Besides, dams’ foundation along the river, which made the water body flow much lower, probably resulted in the difference distributions of Ca-Pi (Maavara et al. 2015). This inorganic fraction was a subject of debate because it had long been considered of little mobilization. However, many researches have shown that this fraction could be mobilized with the decreased pH and the specific biochemical effects (Kaiserli et al. 2002; Zhang et al. 2016a).

**Estimated diffusion fluxes of PO$_4^{3-}$-P**

Figure 4 showed the typical distribution profiles of PO$_4^{3-}$-P concentrations in the overlying water and sediments of four reservoirs. The variations of PO$_4^{3-}$-P diffusion fluxes across the water-sediment interface in the sampling sites were presented in Figure 5. The fluxes (mg m$^{-2}$ d$^{-1}$) ranged from 0.39 ± 0.08 to 0.95 ± 0.14 in XMG, from 0.19 ± 0.05 to 0.40 ± 0.07 in TFM, from 0.40 ± 0.09 to

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**Figure 3** | The average concentrations and percentages of different P forms in the four reservoirs.

**Figure 4** | PO$_4^{3-}$-P concentrations of pore water and the corresponding overlying water.
0.05 ± 0.01 in XBK and from −0.06 ± 0.01 to 0.10 ± 0.04 in SJH. The fluxes were positive for the former two reservoirs, which mean that the migration direction of PO$_3^-$/C$_0$ was from the sediment to the water column. However, most parts of the sediment in XBK and SJH might be a sink for PO$_3^-$/C$_0$ (negative fluxes).

This phenomenon can be explained from two aspects. On the one hand, the ratios of Fe to TP of the sediment in XBK and SJH (19.3–63.9) were above the threshold of 15 which was established by Jensen & Andersen (1992) for P retention under aerobic conditions. If this ratio holds true across the reservoir, internal P loading could be controlled by keeping surficial sediments oxidized in XBK and SJH. However, the ratios of Fe to TP of the sediment in XMG and TFM (2.4–12.7) were below that threshold, which indicated that the sediments could not adsorb more PO$_3^-$/C$_0$ of the overlying water. On the other hand, Compared with XBK and SJH reservoirs, XMG and TFM reservoirs contented much higher concentration and percentage of Ca-Pi (Figure 3). Combining with the statistical analysis (Table 4), we hypothesize that the microbial degradation of Ca-Pi is driven by the microorganism to absorb reactive P nutrients from the environment for its own use. So, it may be controlled within a certain range by some related enzymes (Perez et al. 2007; Yuan et al. 2014). The P diffusion fluxes of TFM are a little similar to that of Hongze Lake which was in the medium eutrophication stage (Yao et al. 2016). Instead, XBK and SJH reservoirs are under relatively lower P diffusion conditions.

Statistical analysis

Relationship of sediment characteristics and P fractions

The correlations of characteristics and different P forms of the surface sediments are listed in Table 6. A non-parametric test is performed since environment data do not usually follow a good normal distribution. The pairs of Ca-Pi with TP, with Fe/Al-Pi, and with Po clearly showed a strong association or conversion among them and implied an external Ca-Pi input to reservoirs (Table 6) (Sudha & Ambujam 2015). The coefficients of variation (mean value/standard
deviation) of Ca-Pi and TP were 1.15 and 1.07, respectively, also indicating that the variance of TP concentrations was mainly related to the Ca-Pi contents. In addition, there was a positive correlation among C/N, Ca-Pi and TP, which reflected the sediments probability mainly came from the same origin (Zhang et al. 2016b).

### PCA of data

PCA is a powerful pattern recognition technique that intends to explain the variance of a large number of intercorrelated variables with a smaller set of independent variables (Kaiserli et al. 2002). The factors rotated iteratively by varimax method and the eigenvalues greater than 1.0 were selected. The degree of association between each variable and each factor is given by its loading on that factor.

In total, three factors were identified, accounting for 83.39% of the variance of the data from Hungbai River. The first factor, accounting for 42.02% of the total variance, was correlated with P diffusion flux, Po, Fe/Al-Pi, Ca-Pi and TP (Figure 6). These factors represented the

![Figure 6](https://iwaponline.com/ws/article-pdf/18/2/688/206946/ws018020688.pdf)
pollutions from sediment, mainly the precipitated apatite produced from PM activities (Wang et al. 2016). The second factor accounting for 28.78% was correlated with TN, TOC, C/N, EC, moisture content, which mainly resulted from the sedimentary characters. The third factor was represented by ORP and DO with 12.60% of the variance, which implied that ORP and DO values in overlying water might greatly influence the sedimentary properties (Qiu et al. 2016).

CONCLUSIONS

This study showed that different P-forms and $\text{PO}_4^{3-}$-P diffusion fluxes of the surface sediments varied with reservoirs and decreased sharply from upstream to downstream reservoirs, which corresponded with the pollutions of PM in this basin. The rank order of P-fraction concentrations obtained from most sample sites was Ca-Pi > Po > Fe/Al-Pi. Ca-Pi, varying from 34.84 to 92.84% of TP, was the primary driver of variation in TP. The C/N ratios ranged from 7.4 to 11.4 which suggested that Po mainly originated from endogenetic source. The analysis of environmental factors indicated that there was a strong association among P-forms. $\text{PO}_4^{3-}$-P diffusion fluxes had significant positive correlations with each P-form concentration but negative correlations with ORP and DO values of the overlying water. PCA test suggested that PM activities and internal P loading acted as the most reactive elements in the four deep reservoirs. Thus, for water eutrophication management in this basin, both the pollutions from PM activities and internal P loading of sediment should be paid attention to. Future work on biological characterization of the sediments would provide more information on the status of this river.

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