Comparison of phosphorus fraction distribution and influencing factors of suspended and surface sediments in the Tiaoxi watershed, China

Hongmeng Ye, Xuyin Yuan, Lei Han, Heng Yin and Jing Jin

ABSTRACT

Suspended and surface sediments from the Tiaoxi watershed, fed by the Xitiaoxi and Dongtiaoxi rivers, were analyzed for total phosphorus (TP) and the inorganic P fractions of loosely adsorbed P that were extractable with NH₄Cl (NH₄Cl-P), reductant P (BD-P), metal oxide-bound P extractable with NaOH (NaOH-P), and calcium-bound, HCl-extractable P (HCl-P), while other physicochemical compositions were also determined. The spatial variations of P fractions in these sediments were investigated, and the major factors influencing the various fractions were explored by multivariate statistics. Compared to surface sediments, suspended sediments contained considerably higher concentrations of total nitrogen, TP, organic matter, Al, Fe, Mn and biologically available P (BAP, given as NH₄Cl-P, BD-P and NaOH-P combined) and lower concentrations of Si, Ca and HCl-P in the studied catchments. Dongtiaoxi sediments had higher TP, inorganic phosphorus and HCl-P concentrations and a lower BAP content compared with Xitiaoxi sediments, trends that were associated with local geological backgrounds, landscapes and anthropogenic characteristics. The results of principal component analysis showed different effects of sediment properties on P fraction distributions for Xitiaoxi and Dongtiaoxi sediments. The sediment components and structure exert a strong influence on BAP in Xitiaoxi sediments, in contrast to Dongtiaoxi sediments, where P fractions are mainly affected by urbanization and other anthropogenic activities such as shipping.

Key words | influencing factor, phosphorus fractions, surface sediments, suspended sediments, Tiaoxi watershed

INTRODUCTION

Eutrophication as a result of water pollution is a universal problem in many countries, and China is no exception (Hu et al. 2009; Baken et al. 2015). In most cases, the eutrophication of rivers or lakes is related to elevated concentrations of phosphorus (Schindler 2002). Algal bloom is the result of serious eutrophication, and since phosphorus (P) is a key-limiting factor of algal growth (Kerr et al. 2011), this element is highly important and significant to the eutrophication of water bodies.

Previous research has shown that phosphorus from non-point sources contributes to 66–93% of the whole input into the aquatic ecosystems of China (Ongley et al. 2010), and the majority of this phosphorus enters water bodies as a result of runoff from eroded soil (Liang et al. 2004).

In aquatic ecosystems, suspended as well as surface sediment particles are important carriers of phosphorus. Two quantitative parameters are of importance: inorganic phosphorus (IP) and total phosphorus (TP). Phosphorus present in the form of IP is highly available to living organisms and is the most important contributing factor for eutrophication (Zhou et al. 2014). For this reason, quantification of IP has been widely used to identify and measure the potential availability of P to algae, and this is a more effective parameter to evaluate the trophic status of a water body than quantification of TP (Han et al. 2011). However, different IP fractions have different release potentials in an aquatic environment, in particular IP presents in suspended as opposed to surface sediments (Wang et al. 2006). The phosphorus fractions in suspended or surface sediments can be influenced by the sediment compositions (e.g., metals oxides or hydroxides), the presence of organic matter (OM), and the sediment particle size, all of which
influence the bio-availability of IP (Kerr et al. 2011; Su et al. 2014). The properties of suspended and surface sediments are further dictated by the local geological setting, land use, rainfall and other environmental factors (Kaiserli et al. 2002; Sun et al. 2009). However, only a few studies have been conducted to correlate the levels of aquatic sediment phosphorus with local terrestrial sources, to address the impacts of such environmental factors (Haygarth 2005; Kerr et al. 2011). A spatial distribution analysis of phosphorus fractions in suspended and surface sediments would be required to identify such factors.

Most previous studies that reported phosphorus fractions focused on the surface sediments of rivers or lakes, but less attention has been paid to suspended sediments (Bibby & Webster-Brown 2005; Kerr et al. 2011). However, since suspended sediments are more bio-available and easier to remove and mitigate than surface sediments (Su et al. 2014), determining the phosphorus fraction in suspended sediments is more effective for evaluation of water quality. In conclusion, there is a high need to analyze the spatial differentiation of phosphorus fractions in suspended and surface sediments, as well as to explore the main factors influencing sediment phosphorus fractions under different catchment environmental conditions, taking into account such variables as source, geological background and land use. Systematic, comprehensive analysis in a watershed is less reported.

This study was performed on the Tiaoxi watershed, which provides the main water supply of eutrophic Taihu Lake, the third largest freshwater lake in China. The whole watershed is divided into two sub-catchments formed by the rivers Xitiaoxi and Dongtiaoxi, which display distinct differences in their geological nature, geomorphology, land use and anthropogenic activities. An analysis of the spatial distribution of sediment phosphorus fractions in these two sub-catchments was conducted to evaluate the role of environmental conditions that apply in the Tiaoxi watershed, and provide an important reference value for improving the water quality in Taihu Lake.

The main objectives of this study were: (1) to characterize the spatial variations of TP contents and fractions in the fluvial suspended sediments and surface sediments of the Tiaoxi watershed; (2) to evaluate the bio-availability of sediment phosphorus and analyze the environmental characteristics in different river reaches; and (3) to analyze the relationships between phosphorus fractions and sediment properties, and reveal the main influencing factors for phosphorus fraction distributions in the sediments.

**MATERIALS AND METHODS**

**Study area and sampling procedure**

The Taihu basin is located in the Changjiang Delta Region in eastern China. During the last few decades, the waters and sediments of Taihu Lake and the conjoint rivers have suffered from increasing pollution as a result of domestic, industrial and agricultural activities. It is estimated that the TN and TP load from non-point sources contributes up to 83% and 84% of the whole input of Taihu Lake basin, respectively (Zhang et al. 2004). As a result of nutrient overload, Taihu Lake has eutrophic status, with frequent occurrence of blue algae outbreaks (Li et al. 2013a), resulting in a severe decrease in water quality and restriction of the sustainable development of the local economy.

The Tiaoxi watershed belongs to the Taihu basin and is an economically developed area within China’s Zhejiang province. The geomorphology of the Tiaoxi watershed from southwest to east and northeast varies from mountainous to hilly and ends in a plain area, and the corresponding height ranges from 1,500 m to 5–5 m. The rainfall varies widely, both spatially and temporally, with peaks from April to September. The influxes of total nitrogen (TN) and TP from rivers in the Tiaoxi watershed feeding into Taihu Lake reach 2,077 t/yr and 88 t/yr, respectively, which are the main sources of eutrophication in the southwest part of Taihu Lake (Wang et al. 2011). Non-point sources of nutrients dominate in the whole watershed (Liang et al. 2008), and they have a strong positive correlation with landscape characteristics, so that land use plays the most important role in the nutrient distribution, followed by soil characteristics and other factors (Li & Li 2008). For example, the TP export coefficient for cropland was calculated as 0.0896 mg/L, and for woodland 0.0075 mg/L in the surface runoff of the studied area (Li et al. 2007).

Two main rivers, the Xitiaoxi River and Dongtiaoxi River, feed into the Tiaoxi watershed, which ends in Taihu Lake. The Xitiaoxi River (50° 23′–31 11′N, 119° 24′–120° 29′E) belongs to the district of Huzhou City, Zhejiang, and covers 2,200 km², with a mainstream length of 157 km. Its annual average runoff discharge is approximately 1.58 billion m³ with a river flow of 46.5 m³/s. The Dongtiaoxi River (50° 05′–50° 57′N, 119° 28′–120° 08′E) covers 2,265 km² and has a length of 151.4 km, with an annual average runoff discharge of 1.51 billion m³ and a river flow of 47.7 m³/s. According to the statistical information from remote sensing images, the major land covers in the study area are woodland and cropland. The land use around the...
Xitiaoxi catchment differs from that in the Dongtiaoxi catchment, as the latter has more urban and construction land (Liang et al. 2008; Li et al. 2013b).

In the summer of 2014, during the wet season, the Xitiaoxi and Dongtiaoxi rivers were sampled, resulting in 46 samples of suspended as well as surface sediments. The sampling locations are shown on a map (Figure 1), where for the Xitiaoxi River the upstream sites X1 to X5 are mainly located in woodland, the midstream locations X6 to X10 are dominated by cropland, and the downstream sites X11 to X13 are urban land. For the Dongtiaoxi River, the upstream sites D1 to D4 are mainly urban areas, the midstream sites D5 to D7 are located in cropland and grassland, and the downstream D8 to D10 sites are surrounded by urban and construction land. Combined with field investigation, there is a municipal sewage outlet upstream of the Dongtiaoxi catchment, but not upstream of the Xitiaoxi catchment, which is mainly covered by woodland. Surface sediments (0–10 cm in depth) were collected by a grab sampler. Triplicate sub-samples were collected for an integrated sample at one site. Organic debris and coarse gravel were manually removed before samples were bagged and stored. At the same time, 200 L water samples were collected at a depth of 50 cm for suspended sediment collection, when the depth of the river was not exceeding 5 m. The suspended sediments were filtered in a filter flask using Millipore nitrocellulose membranes (0.45 μm) with a vacuum pump, dried at 40°C and stored at 4°C before analysis.

**Experimental quantitative analyses**

Sediment samples were analyzed for TN measured using the concentrated H₂SO₄ digestion method (Institute of Soil Science, Chinese Academy of Sciences 1978) and TP was determined by the molybdate colorimetric method with perchloric acid digestion (Tian et al. 2010). OM in the sediments was determined after treatment with K₂Cr₂O₇/H₂SO₄ according to the Walkley-Black method (Kim 1995). Al, Fe, Ca, Mn and Si contents were determined using an X-ray fluorescence spectrometer (PW2440, Philips, The Netherlands). In all analyses, triplicate samples were determined, giving an analysis error within 10%. The size distribution of sediments including clay (0.45–4 μm), silt (4–63 μm), and sand fractions (63–500 μm) was determined by a laser particle size analyzer (Han et al. 2014).

A sequential extraction method following Hupfer et al. (1995) was used to obtain the geochemical P fractions (Wang et al. 2006). The phosphorus present in the samples was divided into loosely adsorbed phosphorus, which can be extracted with 1.0 M NH₄Cl (here called NH₄Cl-P); reductant phosphorus, which was extracted using 0.11 M Na₂S₂O₄/NaHCO₃ (BD-P); phosphorus bound to metal oxides, which could be extracted with 1.0 M sodium hydroxide (NaOH-P); and calcium-bound phosphorus, which was released by 0.5 M HCl hydrochloric acid (HCl-P) (Wang et al. 2006). Each extraction step was performed at room temperature in an orbital shaker, shaken at 4,500 r/min for 2 h using 25 mL.

Figure 1 | Map showing sampling sites (a) and land use patterns (b) in the Tiaoxi watershed.
Comparing the sediments from the two rivers, the mean values of TN and OM were higher in the Xitiaoxi sediments while the TP content was higher in the Dongtiaoxi sediments (Table 1), which reflected their differences in land use. The major land cover types for the Xitiaoxi catchment were woodland and cropland, together occupying over 90% of the total area, while more urban and construction land is present in the Dongtiaoxi catchment (Li et al. 2015b). A study comparing different land uses reported that the concentrations of phosphorus from cropland and urban land are higher than from cultivated land (Liang et al. 2004). It was notable that sediments from the Xitiaoxi River contained more fine particles (silt and clay) and Al, Fe and Mn components, and less Si and Ca components than the sediments from the Dongtiaoxi River. This would suggest that the Xitiaoxi sediments include more clay minerals and iron and manganese oxides, while the Dongtiaoxi sediments contain more silicate and carbonate minerals. In addition, we observed that the Si/Al ratios of sediments were lower in the Xitiaoxi River than in the Dongtiaoxi River (3.6 and 4.3 for suspended and surface sediments respectively in the Xitiaoxi River, compared to 4.1 and 5.1 for suspended and surface sediments in the Dongtiaoxi River). A previous study using the Si/Al ratio to chemically characterize sediments from the Pakuranga stream found that the highest ratio was observed when Si-bearing materials such as biogenic diatoms and quartz were abundant (Bibby & Webster-Brown 2005). This is consistent with our observations that aquatic diatoms were abundant midstream and dispersed by shipping activities to the downstream parts of the Dongtiaoxi River.

In the Xitiaoxi River, on average 80% of TP in suspended sediments was present in the form of IP; for surface sediments this was 75%. Lower percentages were found for the Dongtiaoxi River, with 71% for suspended and 68% for surface sediments. Thus, IP was always the dominant P fraction and mostly regulated TP changes in the Tiaoxi watershed. Previous work has shown that particulate IP was the most important P fraction in sediments from basins dominated by agricultural land use (Russell et al. 1998). In addition, it has been described that IP has a higher bio-availability and thus makes a higher contribution to water eutrophication (Wang et al. 2010). Therefore, research on P fractions should be focused on the IP fraction for water quality assessments.

Distributions and variations of phosphorus fractions in Xitiaoxi sediments

Previous studies have demonstrated that the different P fractions in sediments are greatly affected by land use and the
Table 1 | Compositions and other parameters in suspended sediments and surface sediments from the Xitiaoxi and Dongtiaoxi rivers

<table>
<thead>
<tr>
<th>Item</th>
<th>Xitiaoxi River (n = 13)</th>
<th>Dongtiaoxi River (n = 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Suspended sediment mean (Range)</td>
<td>Surface sediment mean (Range)</td>
</tr>
<tr>
<td>TN (mg·g⁻¹)</td>
<td>2.28 (1.51–2.75)</td>
<td>1.68 (1.28–2.31)</td>
</tr>
<tr>
<td>TP (mg·g⁻¹)</td>
<td>1.22 (0.96–1.51)</td>
<td>1.04 (0.76–1.37)</td>
</tr>
<tr>
<td>IP (mg·g⁻¹)</td>
<td>0.97 (0.80–1.13)</td>
<td>0.78 (0.65–0.95)</td>
</tr>
<tr>
<td>OM (%)</td>
<td>2.55 (1.51–3.76)</td>
<td>1.49 (0.87–2.93)</td>
</tr>
<tr>
<td>Si (%)</td>
<td>45.7 (43.5–59.6)</td>
<td>48.8 (44.2–60.8)</td>
</tr>
<tr>
<td>Al (%)</td>
<td>12.7 (12.6–16.3)</td>
<td>11.3 (10.8–14.4)</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>6.00 (5.34–6.34)</td>
<td>5.70 (3.76–6.59)</td>
</tr>
<tr>
<td>Mn (%)</td>
<td>0.15 (0.07–0.40)</td>
<td>0.14 (0.05–0.24)</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>0.80 (0.49–1.32)</td>
<td>1.46 (0.55–3.19)</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>20.7 (12.4–26.2)</td>
<td>7.95 (4.01–10.9)</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>72.7 (62.8–83.6)</td>
<td>71.0 (68.3–73.6)</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>6.63 (3.76–11.59)</td>
<td>21.1 (10.5–27.7)</td>
</tr>
</tbody>
</table>

The concentrations of the fractions of IP and their proportions in the individual samples are presented in Figure 2. The spatial distribution of the fractions varied considerably in the different reaches of the Xitiaoxi River, with a general increasing trend along the river course. Average concentrations of the different fractions in suspended sediments were found to be highest in the NaOH-P fraction (representing metal oxide-bound P), followed by similar levels for BD-P (reductant phosphorus) and HCl-P (calcium bound), while only low amounts of NH₄Cl-P (loosely adsorbed) were detected. There was little variation in this order between upstream and downstream or between suspended and surface sediments, though in upstream and midstream surface sediments HCl-P was higher than BD-P. More details about each fraction are discussed below.

The concentrations of NH₄Cl-P, representing the loosely adsorbed P, may include the dissolved P in pore water (Kaiserli et al. 2002). Measured concentrations ranged from 20.7 to 36.7 mg/kg, with an average of 27.3 mg/kg for suspended sediments. For surface sediments the average was even lower (18.7, range 13.3–25.0 mg/kg). Suspended sediments have smaller particles with stronger absorption ability, which may explain why the NH₄Cl-P concentration is higher here (Zhu et al. 2013). As is obvious from Figure 2, NH₄Cl-P was by far the smallest P fraction and represented less than 4% of IP in both the suspended and surface sediments.

BD-P represents the redox-sensitive P fraction, mainly including P bound to Fe hydroxides and Mn compounds (Kozerski & Kleeberg 1998). It is generally considered as a potentially mobile P fraction and may be released from anaerobic sediments (Kaiserli et al. 2002). The average concentration of BD-P was 276 mg/kg (28%) in suspended sediments and 200 mg/kg (26%) in surface sediments. A general increasing trend was observed from upstream to downstream, possibly as a result of variation in Fe and Mn presence due to human activities (Ballantine et al. 2008).

The NaOH-P fraction is indicative of phosphorus mainly bound to Fe and Al oxides. Others have reported that the biologically available phosphorus (BAP) extracted from TP mainly correlates with NaOH-P in heavily polluted sediments (Wang et al. 2010). Therefore, NaOH-P has been used to estimate both short-term and long-term available P for algal growth (Zhou et al. 2001). In the Xitiaoxi River, the overall trend of NaOH-P concentrations in sediments showed an ascending trend, which was consistent with the pattern of land use. The major land cover was woodland in the upstream, and more cropland or urban areas distributed in the midstream and downstream of the Xitiaoxi catchment. The concentration values ranged from 378 to 550 mg/kg, with an average of 466 mg/kg for suspended sediments and a slightly lower range (249 to 431 mg/kg, mean 323 mg/kg) for surface sediments. These represent 45–51% (mean 49%) of IP in suspended sediments, or 57–46% (41% mean) in surface sediments. These values are higher than the findings reported by others for sediments from Taihu Lake (21–57%, 33% mean) (Zhou et al. 2004), indicating that P in sediments from the Xitiaoxi River has a higher bio-availability.
HCl-P represents the P fraction sensitive to low pH and consists of apatite P (natural and detritus P), including P bound to carbonates and some hydrolysable organic P (Wang et al. 2006). This P fraction is stable in sediments and is generally not bio-available. In the Xitiaoxi River, the average concentration of HCl-P was 235 mg/kg, and constituted 31% of IP in surface sediments, which was considerably higher than in suspended sediments (200 mg/kg, mean 21%). The main reason is that surface sediments have more natural debris (coarse particles) that contains more carbonates or phosphate minerals. The proportion of HCl-P decreased from upstream to downstream in the Xitiaoxi River, suggesting that this natural debris decreased with increasing intensity of human activities.

The BAP is defined as the sum of NH₄Cl-P, BD-P and NaOH-P, and this value can be used to estimate potentially available P for plants or algae (Zhou et al. 2004; Liu et al. 2015). BAP values were higher in suspended than in surface sediments from the Xitiaoxi River. Mean concentrations of BAP as well as BAP/IP ratios were lowest in sediments from upstream locations, increasing with the direction of water flow. This indicates that BAP of sediments from arable and urban lands is higher than from forestlands in the Xitiaoxi catchment. In conclusion, the P fractions of sediment variability are mainly influenced by land use and pollution sources over the course of the river.

**Distributions and variations of phosphorus fractions in Dongtiaoxi sediments**

Similar analyses as presented in the previous section were performed for the samples originating from the Dongtiaoxi River (Figure 3). In contrast to the findings of the Xitiaoxi River, here the direction of water flow resulted in a decrease...
followed by an increase in overall levels, for both types of sediment. The distribution of the extractable fractions in suspended sediments was also different, in that HCl-P was more abundant than BD-P. In surface sediments, HCl-P was by far the largest fraction, followed by NaOH-P and BD-P, with minor amounts of NH4Cl-P.

The average concentration of NH4Cl-P was 27.6 mg/kg (range 17.1–42.1 mg/kg) for suspended sediments, with slightly lower values for surface sediments (21.9 mg/kg on average, range 12.3–26.5 mg/kg). The proportion of this fraction was overall similar for both rivers, but slightly lower than findings reported for sediments from shallow lakes in the middle and lower reaches of the Yangtze basin (Wang et al. 2006).

The average concentrations of BD-P were 208 mg/kg (20%) and 144 mg/kg (16%) for suspended and surface sediments, respectively, which are lower absolute and relative values than were obtained for the Xitiaoxi River. In accordance with the overall trend, the BD-P concentrations and proportions were lower in the midstream sediments of the Dongtiaoxi River than in the upstream and downstream sections. This trend is consistent with the domestic discharge of urban areas distributed in the upstream and downstream of the Dongtiaoxi catchment.

The absolute mean concentration of NaOH-P was higher in suspended than in surface sediments (462 mg/kg versus 318 mg/kg), while the range was wider for the latter (188–511 mg/kg compared to 358–562 mg/kg for suspended sediments). NaOH-P comprised a lesser fraction of total IP in suspended sediments of 41–50% (mean 45%) in the Dongtiaoxi river, compared to the mean value of 45–51% (mean 49%) in the Xitiaoxi River. The NaOH-P/IP ratios in surface sediments from the Dongtiaoxi River were close to the values from Taihu sediments (21–57%, mean 33%) reported by others (Zhou et al. 2004), but lower than our findings for Xitiaoxi sediments. Overall, the NaOH-P concentration and

Figure 3 | Concentrations (top) and proportions (bottom) of P fractions in sediments of Dongtiaoxi River, for (left) suspended sediments and (right) surface sediments.
proportion in sediments in the Dongtiaoxi River were lowest in the midstream sections and higher in upstream than in downstream samples, a trend similar to the BD-P distribution in this catchment, but not similar to samples in the Xitiaoxi River, probably as a result of the differences in the domestic discharge of urban activity distributed along the Dongtiaoxi River. There are some towns that release abundant P discharges from municipal sources in the upstream and downstream than in the midstream, which is mainly occupied by cropland and grassland in the Dongtiaoxi watershed. These differences affect the particle size, presence of OM, and metal (e.g., Fe, Al and Mn) compositions of sediments, resulting in obvious changes in NaOH-P.

The concentrations of HCl-P ranged from 257 mg/kg to 389 mg/kg, with an average of 319 mg/kg for suspended sediments. For surface sediments, these values were 345 to 524 mg/kg, an average of 435 mg/kg. It constituted 24–38% (mean 32%) of IP in suspended sediments, which was considerably lower than in surface sediments (34–58%, mean 48%). A comparison of the two catchments identified two major P fractions with different distributions: HCl-P > NaOH-P in surface sediments from the Dongtiaoxi River and NaOH-P > HCl-P in Xitiaoxi surface sediments. These differences are most likely consequences of inter-catchment variability in factors such as geology, topography, land use and pollution sources (Russell et al. 1998). It is reported that the area of limy soil is 209 km², occupying 4.5% of the total soil area, and mainly distributed in the Dongtiaoxi catchment (Li et al. 2013a). The limy soil has more calcite content than other soils; therefore, more HCl-P is formed in this catchment.

Although the TP and IP contents were higher in the sediments of the Dongtiaoxi River than in those of the Xitiaoxi River, the mean concentrations of BAP were lower, with 697 mg/kg in suspended sediments and 484 mg/kg in surface sediments (for Xitiaoxi sediments, 769 and 542 mg/kg respectively). This suggested a lower bio-availability of P in Dongtiaoxi sediments, which may be the result of fewer clay minerals and iron or manganese oxides being present, as these components exert a strong influence on P bio-availability (Ballantine et al. 2008).

### Effects of sediment properties on P fraction distributions

Phosphorus fraction distributions are often associated with sediment compositions and properties, and their relationships can not only reflect the sediment characteristics, but may also provide information about nutrient sources (Jarvie et al. 2002; Hu et al. 2009). A PCA was used to identify the factors influencing the observed distributions of P fractions. The obtained factor scores for the sediment data are presented in Table 2.

Four factors accounted for 88.5% of the variance in Xitiaoxi sediments. The first factor accounted for 34.9% of the total variance, producing positive scores for NH4Cl-P, BD-P, Mn and Fe, and negative scores for HCl-P, OM, Ca and sand content. This illustrates the important role of

<table>
<thead>
<tr>
<th>Variable</th>
<th>Xitiaoxi River</th>
<th>Dongtiaoxi River</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>F1</td>
<td>F2</td>
</tr>
<tr>
<td>NH4Cl-P</td>
<td>0.581</td>
<td>0.718</td>
</tr>
<tr>
<td>BD-P</td>
<td>0.524</td>
<td>0.774</td>
</tr>
<tr>
<td>NaOH-P</td>
<td></td>
<td>0.859</td>
</tr>
<tr>
<td>HCl-P</td>
<td>−0.749</td>
<td></td>
</tr>
<tr>
<td>OM</td>
<td>−0.846</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>0.647</td>
</tr>
<tr>
<td>Ca</td>
<td>−0.536</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.643</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.921</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td></td>
<td>0.610</td>
</tr>
<tr>
<td>Silt</td>
<td></td>
<td>0.501</td>
</tr>
<tr>
<td>Sand</td>
<td>−0.748</td>
<td></td>
</tr>
<tr>
<td>Variance (%)</td>
<td>34.9</td>
<td>23.5</td>
</tr>
</tbody>
</table>
iron and manganese compounds in regulating the loosely bound P and redox-sensitive P fractions of Xitiaoxi sediments. Other studies have shown that NH₄Cl-P or BD-P in sediments can be used as an effective indicator for eutrophic lakes or rivers, and were associated with Fe and Mn compounds (Sun et al. 2009; Wang et al. 2010; Liu et al. 2015). The second factor identified accounted for 23.5% of the variance and primarily correlated with NH₄Cl-P, BD-P, NaOH-P, clay and silt. This factor suggests that the BAP fraction in Xitiaoxi sediments may be influenced by fine sized sediments. In other studies, fine sediments (silt and clay) also correlated with higher concentrations of BAP (Kaiserli et al. 2002; Han et al. 2011). It seems contradictory that NaOH-P (mainly bound to the metal oxides of Fe and Al) correlated with clay and silt but did not correlate with Fe and Al amounts in this study. Fe, Al and Mn oxyhydrates commonly bind to fine size sediment surfaces via ligand exchange, thereby producing an indirect association between P and the clay mineral component of sediments (Cooper et al. 2015). Nevertheless, no significant relationship was observed between Fe and Al contents and P sorption capacity (Violintzis et al. 2009). Because these metal elements have different geochemical properties and contain both highly reactive (amorphous) and less reactive (crystalline) oxyhydroxide constituents, and active Fe and Al (e.g., Fe, Al oxyhydrates) are the main components to bound P in NaOH-P fraction (Haygarth 2005), then these active constituents only occupy some portion of total Fe, Al and Mn content. Therefore, NaOH-P is correlating with clay/silt fraction but not correlate with the total metal content in this study. The different constituents of the elements can affect their binding and release capacity for P fractions, which can be observed in Xiaoxi watershed.

The third factor that was identified strongly correlated with Al, clay and silt, and showed that higher aluminum contents correlated with fine sediments of the Xitiaoxi River. Lastly, a fourth factor primarily positively correlated with HCl-P, OM, Ca and sand content. HCl-P is generally a stable P fraction in sediments, and is mainly formed through co-precipitation or direct precipitation between calcite and P. It exists as Ca₅(PO₄)₃OH, Ca₅HPO₄(OH)₂, CaHPO₄·2H₂O and Ca₃(HCO₃)₂PO₄ (Cassagne et al. 2000; Berg et al. 2004). In addition, OM can present a very important constituent of sediments, especially in large grain-size materials (Han et al. 2011); such coarse sediments are often coated by OM and exhibit a higher concentration of HCl-P (Liu et al. 2015). These findings are in agreement with our observations that OM was an important factor affecting variation in P fractions, and was positively correlated with HCl-P, but negatively with NH₄Cl-P, BD-P, and NaOH-P, similar to findings reported for the sediments from the Haihe River (Han et al. 2011).

Based on the presented analyses, the BAP fractions in Xitiaoxi sediments are to some extent affected by OM, Mn and Fe, which is associated with anthropogenic activities (Ballantine et al. 2008). The sediment particle size influences the sediment composition. The finer particles (e.g., clay, silt) have higher specific surface area, more P-retention components (e.g., Al/Fe oxides or hydroxides) and corresponding stronger adsorption ability than coarser particles (sand), and exert a strong influence on particular bio-available fractions. The sediment particle size is also correlated with geological background and land use (Su et al. 2014). Besides, the P fraction distribution is also related with natural materials, because some elements (e.g., Al, Si, Ca) are lithogenic (Violintzis et al. 2009). In conclusion, the P fractions are considerably influenced by natural materials, and to some extent affected by anthropogenic activities in the Xitiaoxi catchment.

As can be seen from Table 2, different findings were obtained with Dongtiaoxi sediments, where three factors accounted for 85.3% of the total variance. The first factor, accounting for 54.3% of the variance, was positively correlated with BD-P, NaOH-P, Al, Mn, clay and silt, while it negatively correlated with HCl-P, OM, Ca and Fe. This factor can be interpreted to represent major processes influencing the main P fractions (BD-P, NaOH-P and HCl-P), including adsorption of BD-P and NaOH-P by fine sediment, and the P fraction combining with Al, Mn and organic complexes (Axt & Walbridge 1999), which result from the municipal input in the Dongtiaoxi catchment. The second factor, accounting for 21.3% of the variance, was positively correlated with NH₄Cl-P and sand, and negatively with Al. This factor may represent the coarse sediments that had a significant effect on the loosely adsorbed P fraction, and the allogetic origins of NH₄Cl-P that were due to erosion soils and sediments distributed by shipping. The third factor (9.7% of the variance) was primarily correlated with Mn and clay or silt. This shows that sediments are mainly influenced by runoff from municipal activities and surface soils in the Dongtiaoxi catchment.

CONCLUSIONS

We identified obvious differences in chemical compositions and nutrient concentrations in the suspended and surface sediments of the Xiaoxi watershed. Relative to surface sediments, suspended sediments have observably higher
concentrations of Al, Fe, Mn, OM, TN and TP, and lower concentrations of Si and Ca. Related to this, the concentration of BAP (NH₄Cl-P, BD-P and NaOH-P) is higher, while the stable phosphorus fraction (HCl-P) is lower in suspended sediments.

Compared to Xitiaoxi sediments, the concentrations of TP, IP and stable phosphorus (HCl-P) are higher, but the BAP concentration is lower in Dongtiaoxi sediments. In general, these contrasts reflect the spatial differences between the two sub-catchments in terms of environmental characteristics, such as geology, land use and the municipal source.

The distribution of the P fractions along a river reach displays obvious differences in sediment characteristics under different land use types. Usually, the BAP concentration in sediments from agricultural and urban lands is higher than in those from forestlands, but the HCl-P concentration shows an opposite trend. From the obtained data it is apparent that the P fractions of sediments are greatly influenced by land use and pollution sources along the catchment.

The sediment properties have an important influence on the different phosphorus fraction distributions in Xitiaoxi and Dongtiaoxi sediments. Fine sediments exhibit a significant correlation with BAP in Xitiaoxi sediments, while coarse sediments show a significant effect on the loosely adsorbed phosphorus fraction in Dongtiaoxi sediments. The phosphorus fractions in the latter are closely related to urban activity, whereas those in Xitiaoxi sediments are more influenced by natural factors. Therefore, the distributions of phosphorus fractions in sediments are dominated by both geological backgrounds and landscapes.

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