



# Seasonal variation characteristics and release potential of phosphorus in sediments: a case study of the Qiuxi River, a typical diffuse source pollution river in southwestern China

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## Abstract

**Purpose** To better control and manage phosphorus (P) in the aquatic environment of the Qiuxi River, a typical river severely influenced by anthropogenic activities in southwest China, the morphological characteristics and the release potential of P in sediments during different water seasons were determined.

**Materials and methods** The overlying water and sediment samples were collected from the Qiuxi River in the normal-water season (NWS), low-water season (LWS), and high-water season (HWS), and physicochemical properties were quantified. Total phosphorus (TP) in sediment and the inorganic phosphorus ( $P_i$ ) fraction were analyzed using the standard measures technology (SMT) procedure, and organic phosphorus ( $P_o$ ) was further determined to be labile  $P_o$  (LOP), moderately labile  $P_o$  (MLOP), or non-labile  $P_o$  (NLOP). The release potential of P from the sediments was studied by experiments under simulated conditions.

**Results and discussion** The results showed that P pollution in the Qiuxi River was the most serious during the LWS, with mean TP concentrations in the sediment of  $854.6 \text{ mg kg}^{-1}$ , and the release risk of the sediment P was also highest during this water season. The variation in P concentration was significantly influenced by the discharge of domestic sewage, agricultural diffusion, flow rate, and OM. The concentrations of P fractions varied with water season, but  $P_i$  was constantly higher than  $P_o$ . HCl-extractable  $P_i$  (HCl- $P_i$ ) accounted for most of the P in the sediments, which was related to its characteristics and the geographical location of the Qiuxi River. The maximum P release ( $R_{\max}$ ) was  $25.9 \text{ mg kg}^{-1}$  in the LWS and  $15.3 \text{ mg kg}^{-1}$  in the HWS, which were positively correlated with the TP ( $r^2 = 0.848$ ,  $p < 0.01$ ) and OM ( $r^2 = 0.847$ ,  $p < 0.01$ ) concentrations in the sediments and explained why the release risk of the sediment P in the LWS was higher than that in the HWS.

**Conclusions** Phosphorus pollution and the P release potential in the sediments of the Qiuxi River were most severe in the LWS, so more effective measures to restrain the release of P should be taken during the LWS. Moreover, OM in sediments should be given more attention owing to its significantly positive correlation with the risk of P release.

**Keywords** Qiuxi River · Southwestern China · Water season · Inorganic phosphorus fractions · Organic phosphorus fractions · Phosphorus release

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## 1 Introduction

Phosphorus (P) is an essential element in the biogeochemical cycle and has important nutritional value in surface water (Wang et al. 2006b; Zhang and Shan 2008; Yang et al. 2019). However, anthropogenic activities, including over fertilization, pesticide application, fossil fuel consumption, and wastewater discharge, in catchments input a large amount of P into surface water and are responsible for eutrophication (Withers and Jarvie 2008; Zafar et al. 2016; Ye et al. 2017; Yuan et al. 2018; Yang et al. 2019). Currently, agricultural diffusion P accounts for approximately 50% of the total amount of P emissions in Germany and many other

European countries (Umweltbundesamt 2014). Since the 2000s, the intensive development of agriculture has increased the P load of fertilizer and livestock breeding in agricultural areas. Nevertheless, only 10–15% of this P can be absorbed by the soil, and the rest is lost to surface or underground runoff (McDowell et al. 2001; Zhang and Shan 2008; Bortoluzzi et al. 2013; Zafar et al. 2016), demonstrating that agricultural pollution is an environmental problem that cannot be ignored. Sediment is a reservoir for pollutants from overlying water, and the continual release of sediment P under certain environmental conditions is one of the major sources of P in overlying water (Søndergaard et al. 1999; Wang et al. 2006b, 2009; Shilla et al. 2009).

The release of P from sediment to overlying water is considerably influenced by sediment and overlying water properties such as P concentration, temperature, pH, oxidation-reduction potential (ORP), organic matter (OM), and hydraulic conditions (Kim et al. 2003; Wang et al. 2006a; McDowell and Hill 2015; Zafar et al. 2016). The previous study demonstrated that the physicochemical properties of overlying water and sediment, stream discharge, and coverage of hydrophytes change with water season (Bryan et al. 2007; Zafar et al. 2016; Yang et al. 2019). Correspondingly, the fraction and release of P in sediment will vary with water season due to the influence of river properties, which causes different levels of P pollution in rivers during different water seasons (Zafar et al. 2016). Therefore, it is necessary to research the release characteristics of P in sediment according to different water seasons. The maximum P release ( $R_{\max}$ ) is an effective parameter used to evaluate the release risk and characteristics of P from sediment to overlying water. The release kinetics experiment simulates the release process of sediment, and  $R_{\max}$  is obtained by fitting the first-order kinetics equation (Pettersson 2001; Wang et al. 2009).

However, not all of the P fractions are released from sediment (Ruban et al. 2001; Wang et al. 2006b; Ni et al. 2019a). The concentration of various P fractions can indicate internal pollution status as well as the risk of sediment in a more effective way than total phosphorus (TP) concentration in sediment (Wang et al. 2006b; Ni et al. 2019a). Understanding the concentrations of different P fractions will help to identify the sources of P and explain the release characteristics of P in sediment (Ni et al. 2019a, b). Phosphorus exists in the form of complex salts with calcium, iron, or aluminum and OM in sediment and can also be adsorbed onto the mineral surface (Ruttenberg 1992; Ruban et al. 2001). The inorganic phosphorus ( $P_i$ ) fraction is usually loosely sorbed, potentially labile P (reductant-soluble P and ferrous-bound phosphorus), non-labile P (mostly calcium-bound phosphorus (Ca-P)), and occluded P (Ruttenberg 1992; Ruban et al. 2001; Ni et al. 2019a). Organic phosphorus ( $P_o$ ) compounds such as saccharide phosphates, nucleotides, hemic acid, and fulvic acid are usually treated as residues or refractory parts of the P cycle (Ruttenberg 1992; Ni et al. 2019b). However,  $P_o$  can

be converted into  $P_i$  by phosphate hydrolysis, bacterial degradation, non-biological hydrolysis, and photolysis (Ahlgren et al. 2006; Ni et al. 2019b). Thus, the role of  $P_o$  in the sediment-overlying water P cycle should not be ignored. In recent years, the  $P_o$  sequential fractionation scheme has been widely used, with the fractions determined to be labile  $P_o$  (LOP) ( $\text{NaHCO}_3\text{-}P_o$ ), moderately labile  $P_o$  (MLOP) ( $\text{HCl-}P_o$  and fulvic acid- $P_o$ ), and non-labile  $P_o$  (NLOP) (hemic acid- $P_o$  and residual- $P_o$ ) (Ivanoff et al. 1998; Ni et al. 2019a). Different fractions of  $P_o$  have different chemical characteristics and release risks (Wang et al. 2006b; He et al. 2015; Ni et al. 2019a). It is rare for NLOP to be absorbed biologically, while LOP can be easily converted into  $P_i$  by microorganisms and released into water (Hund et al. 2013).

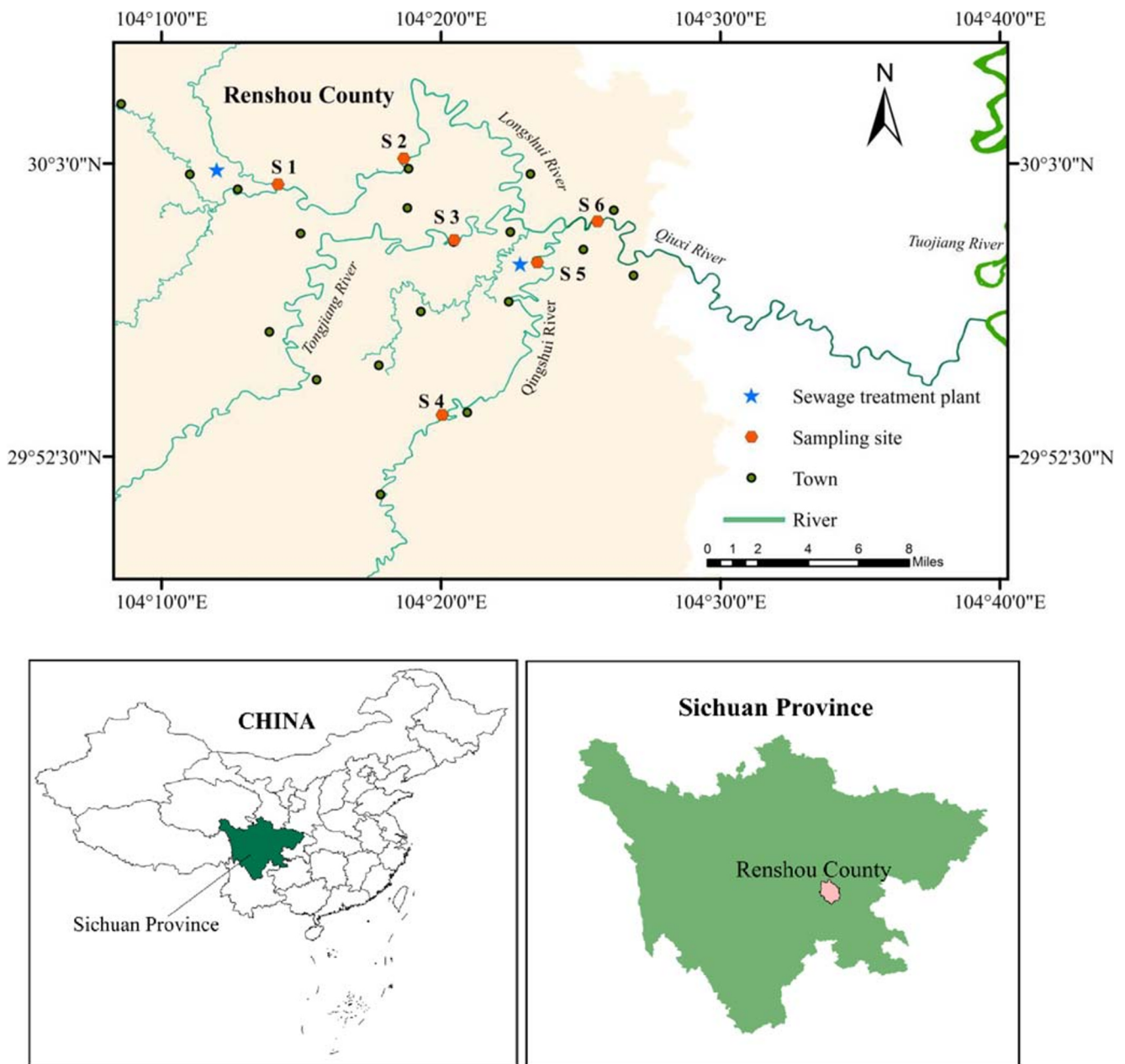
There are a large number of catchments severely polluted by agriculture and urban sewage in southwestern China due to the lack of domestic sewage collection systems and agricultural diffusion source pollution management, and the Qiuxi River is one of these catchments. To date, only a few studies have been conducted on P in sediments in typical diffusion-polluted regions. Our study is one of the first to research the variation in P pollution and release risk in different water seasons of these types of rivers. The main objectives of our research were to (1) evaluate seasonal characteristics of P pollution in sediments and overlying waters of the Qiuxi River; (2) determine the morphological characteristics of P in sediments and different fractions of P influenced by factors such as OM, ORP, particle size, temperature, pH, and hydraulic conditions in different water seasons; and (3) conduct simulation experiments to study the release characteristics of P in different water seasons.

## 2 Materials and methods

### 2.1 Study area

The study area is located in the Qiuxi River, Sichuan Province, southwest China. As the first-level tributary of the Tuojiang River, the Qiuxi River is the most important source of drinking water for the surrounding area, with a population of nearly 1.8 million. This river is a typical watershed in southwest China, most of which are secondary tributaries of the upper reaches of the Yangtze River, which is the largest river in China. There are 63 towns around the Qiuxi River, where the population is approximately 3.7 million. Phosphorus pollution in the Qiuxi River was most affected by domestic, farm, and agricultural factors, and the pollutants came mainly from three tributaries, including the Longshui River, Tongjiang River, and Qingshui River (Figs. 1 and 2) (Sichuan Provincial Department of Environmental Protection (SPDEP) 2017).

The concentration of TP in the overlying water was monitored in the national control section from 2011 to 2016, which is located in the confluence section of the



**Fig. 1** Study area and sampling sites. Tongjiang River, Qingshui River, and Longshui River are tributaries; sampling sites include S1, S2, S3, S4, and S5. Qiuqi River is the mainstream. Sampling sites include S6

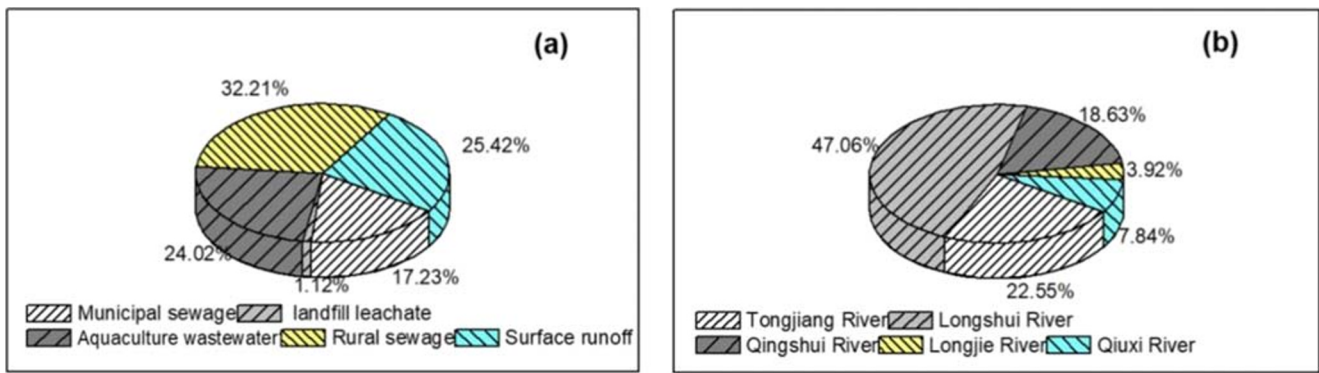
Qiuqi River and Tuojiang River (Table 1). The TP concentration in the overlying water of the Qiuqi River was higher than the standard of grade V of  $0.2 \text{ mg L}^{-1}$  and even reached  $0.42 \text{ mg L}^{-1}$  in 2016 (Standard of Surface Water Environment Quality of China (GB 3838–2002) 2002). After 2016, the growth rate of industrial development in the Qiuqi River basin was approximately 8.5%, and the population growth rate was approximately 2.6%, which increased P emissions.

The rainfall is unevenly distributed during different seasons, and precipitation is highest in summer, followed by autumn, and lowest in spring and winter (SPDEP 2017).

According to the water level and flow rate, the Qiuqi River is divided into three water seasons: the normal-water season (NWS), low-water season (LWS), and high-water season (HWS) (Sichuan Provincial Government 2017; Table 2).

### 2.2 Sample collection

According to the hydrogeological characteristics of the Qiuqi River and the amount of pollutant input, we selected six representative sampling sites (Table 3, Fig. 1). They are distributed on the main stream and in three tributaries of the Qiuqi River (SPDEP 2017). A total of eighteen surface sediment (0–10 cm)



**Fig. 2** The proportion of P pollutants discharged into rivers from different pollution sources (a), the proportion of total P pollutants in different tributaries (b). The total amount of P emissions from the five pollution sources was 693.50 t/year (SPDEP 2017)

**Table 1** Monitoring results of TP in overlying water in the section of Qiuxi River estuary from 2011 to 2016

Detection of the year	2011	2012	2013	2014	2015	2016
TP ( $\text{mg L}^{-1}$ )	0.24	0.18	0.17	0.22	0.23	0.42
Water quality classification	IV	III	III	IV	IV	Inferior V

Water quality classification reference *Standard of Surface Water Environment Quality of China (GB 3838-2002)*

**Table 2** The water level and water flow rate in different water seasons in Qiuxi River from 2014 to 2015

Water season	Month	Average water level (m)		Average flow rate ( $\text{m}^3 \text{s}^{-1}$ )	
		2014	2015	2014	2015
NWS	May and November	8.0 (7.5~8.5)	7.8 (7.5~8.4)	25.8 (5.1~52.5)	21.2 (5.8~56.9)
LWS	December to April	7.6 (7.4~8.2)	7.6 (7.5~8.2)	8.1 (1.9~34.7)	10.0 (5.2~34.7)
HWS	June to October	8.3 (7.3~14.9)	8.2 (7.5~11.0)	51.3 (1.6~916.0)	31.6 (5.2~303.0)

The data of water level and flow rate reference Sichuan Provincial Department of Environmental Protection (SPDEP) (2017). Values represent mean and the range in the brackets ( $n = 30$  for NWS, and  $n = 75$  for LWS and HWS)

**Table 3** List of sampling sites in Qiuxi River

Site	GPS	Location	
S1	Dongfeng Bridge	30° 2' 38" N, 104° 10' 19" E	Upper reaches of the Longshui River
S2	Qujiang Town	30° 2' 43" N, 104° 18' 51" E	Lower reaches of the Longshui River
S3	Xiean Village	30° 0' 20" N, 104° 20' 35" E	Lower reaches of the Tongjiang River
S4	Longnao Bridge	29° 59' 17" N, 104° 24' 3" E	Lower reaches of the Qingshui River
S5	Beidou Town	30° 1' 6" N, 104° 25' 54" E	Three River confluences
S6	Nongwang Town	29° 54' 1" N, 104° 19' 53" E	Middle reaches of the Qingshui River

samples and eighteen water samples were collected during the NWS (November 2017), LWS (March 2018), and HWS (September 2018). Each site was located with a global position system (GPS) unit, and the coordinates are provided in Fig. 1. In order to ensure that the sediment sample is representative, 500 g sediment sample and 800 mL water sample are composed of a mixture of samples collected at three sites. Prior to analysis, the sediment samples were immediately stored in sealable plastic bags at a temperature of 2–5 °C. The sediment samples were dried at 105 °C and then sieved with a 2-mm sieve before the experiment to ensure homogeneity prior to analysis. The water samples were stored in polyethylene bottles and placed at 4 °C. The concentration of TP in the water samples was determined within 3 days.

## 2.3 Analytical methods

### 2.3.1 Physicochemical properties of sediment and TP in overlying water

The temperature, pH, and ORP of the sediment at every sampling site were monitored in situ by portable parameter water quality meter. The organic matter was measured as loss on ignition (550 °C for 2 h) (Jensen et al. 1992). The sediment grain size distribution was measured with a laser particle size analyzer (Microtrac S2000) and was classified into three categories: clay (<0.002 mm), silt (0.002–0.02 mm), and sand (0.02–2 mm) (Day 1965).

### 2.3.2 TP determination and $P_i$ and $P_o$ fractionation scheme in sediment

The TP concentration and P fractions of sediments were analyzed using the standard measures technology (SMT) procedure (Ruban et al. 2001) (Fig. 3). Sediment P was separated into  $P_o$ ,  $P_i$ , NaOH- $P_i$ , and HCl- $P_i$ . NaOH- $P_i$  is NaOH-extractable P including P bound to Al, Fe, Mn oxides, or hydroxides. HCl- $P_i$  is HCl-extractable P including Ca-bound P. Organic P extraction method used in this study was from Ivanoff et al. (1998) (Fig. 3). Three  $P_o$  fractions, including LOP (NaHCO<sub>3</sub>- $P_o$ ), MLOP (HCl- $P_o$  and fulvic acid- $P_o$ ), and NLOP (hemic acid- $P_o$  and residual- $P_o$ ), were obtained using the sequential extraction procedure. Due to the difficulty of sampling S1, S3, and S4 in the NWS, a small number of sediment samples were collected, and only  $P_o$  fractions in the NWS were determined.

### 2.3.3 Sediment P release kinetics experiment

The dry sediments (0.25 g) were put into centrifuge tubes and mixed with 25 mL of KCl solution (0.02 mol L<sup>-1</sup>). These centrifuge tubes were shaken at 200 r min<sup>-1</sup> at 25 °C in a shaker. Samples were collected after 0.5, 1, 2, 4, 8, 12, 24,

and 36 h and centrifuged at 5000 r min<sup>-1</sup> for 10 min. The soluble reactive P concentration of the supernatant was measured, and sediment P release was calculated using the following Formula (1) (Tang et al. 2014):

$$R = \frac{(C_e - C_0)V}{W} \quad (1)$$

where  $R$  represents the amount of P (mg kg<sup>-1</sup>) released from sediment under experimental conditions,  $C_e$  is the concentration (mg L<sup>-1</sup>) of P in the solution and  $C_0$  is the initial concentrations of P in the solution, which is 0 mg L<sup>-1</sup>,  $V$  is the volume (mL) of added water, and  $W$  is the quality (g) of the dried sediment.

Phosphorus release kinetics is fitted with a first-order kinetic equation (Hansen and Strawn 2003) (Eq. (2)).

$$R_t = R_{\max} (1 - e^{-kt}) \quad (2)$$

where  $R_t$  is the amount of P released at time  $t$  (mg kg<sup>-1</sup>),  $R_{\max}$  is the maximum release of P (mg kg<sup>-1</sup>),  $k$  is the release rate constant of P, and  $t$  is the release time (h).

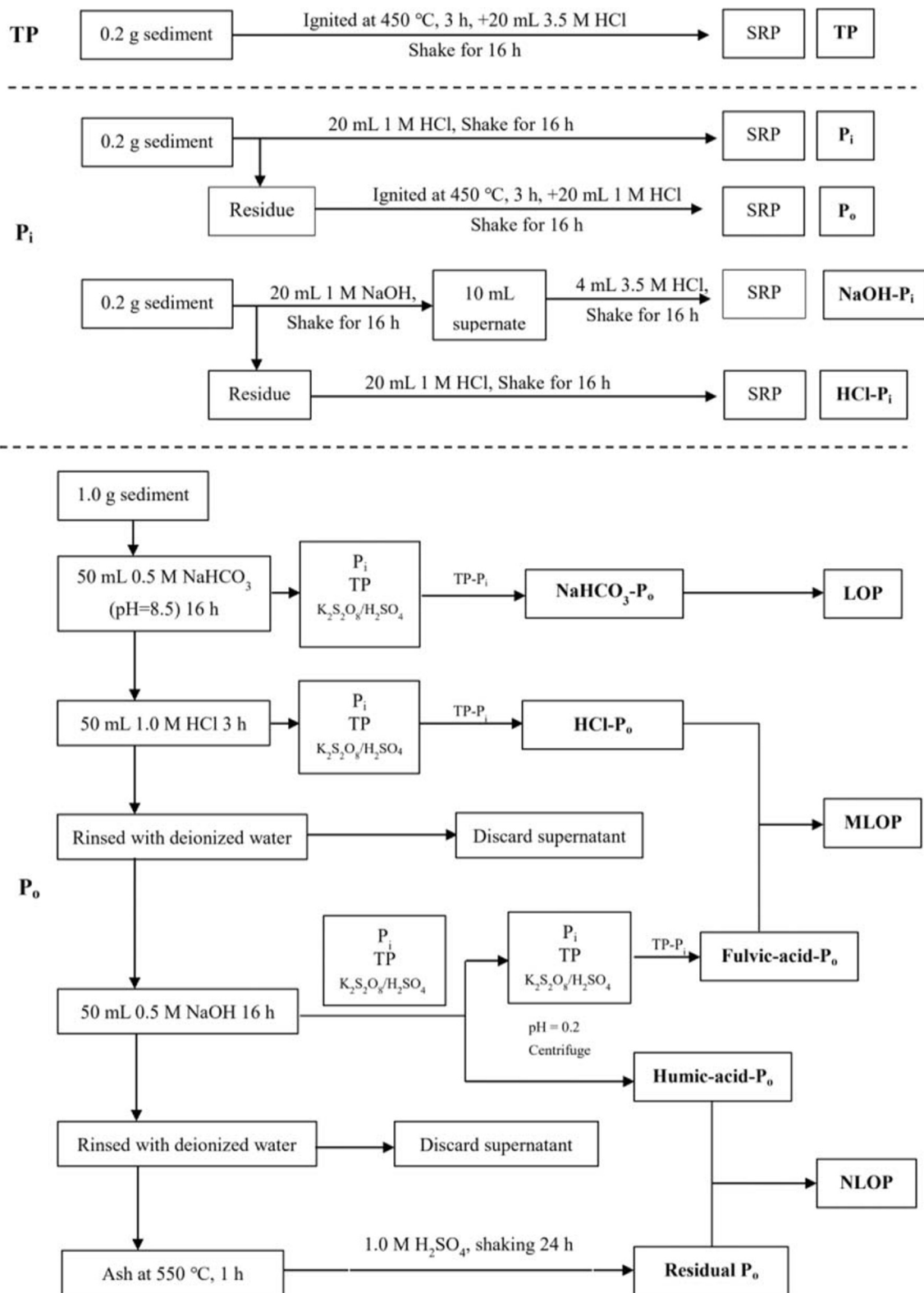
## 2.4 Data analysis and quality control

Pearson correlation analysis was carried out to identify the relationships among the various forms of P in the studied sediments, physicochemical characteristics of sediment, and  $R_{\max}$ . Data were subjected to ANOVA tests to evaluate the data of different water seasons and sampling site. Significant differences were reported at the  $p < 0.05$  level. All statistical analyses were conducted using the SPSS 22.0 (IBM, USA) software package. Figures were created using the Origin 8.0 (OriginLab, USA) software package. Measurements in triplicate of each sample were conducted, and their arithmetic mean values were reported.

## 3 Results

### 3.1 Physicochemical characteristics of sediment

The physicochemical characteristics of the sediments in the Qiuxi River had seasonal differences because of the significant differences in climate characteristics (Table 4). In general, OM concentration in sediments was the largest in the HWS, which was similar to that in the LWS, and the smallest concentration was observed in the NWS. This indicated that the input or sedimentation of OM in the HWS was the largest, and OM may accumulate gradually from the NWS to the HWS. In the NWS and HWS, the sediments were in a state of oxidation, while there were reduction conditions in the LWS, with an average ORP of –211.0 mV. The sand fraction (0.02–2 mm) dominated in the studied sediments, with



**Fig. 3** TP determination method and sequential extraction scheme of the  $P_i$  (Ruban et al. 2001) and  $P_o$  (Ivanoff et al. 1998) fractions in sediments. SRP soluble reactive phosphorus, TP total phosphorus,  $P_i$  inorganic phosphorus,  $P_o$  organic phosphorus, HCl- $P_i$  HCl-extractable inorganic

phosphorus, NaOH- $P_i$  NaOH-extractable inorganic phosphorus, LOP labile organic phosphorus, MLOP moderately labile organic phosphorus, NLOP non-labile organic phosphorus

**Table 4** Concentration and variation of selected physicochemical characteristics of sediment

	Normal-water season (NWS)	Low-water season (LWS)	High-water season (HWS)
OM (%)	7.5 (5.4–9.9)a	8.5 (5.7–12.2)b	8.66 (3.9–10.6)c
ORP(mV)	7.5 (–154.0–178.0)b	–211.0 (–290.0–135.0)a	51.0 (17.0–77.0)b
Clay (%)	4.0 (3.1–4.6)b	1.8 (0.4–3.0)a	1.9 (0.9–4.1)a
Silt (%)	24.3 (20.9–27.7)b	13.1 (6.2–20.2)a	13.9 (5.8–27.5)a
Sand (%)	72.2 (67.6–78.5)a	85.1 (76.7–93.4)b	84.1 (68.5–93.3)b
T (°C)	10.2 (4.9–11.9)a	21.0 (19.5–22.1)b	24.5 (25.5–23.9)c
pH	9.1 (8.2–9.5)b	8.3 (8.0–8.5)a	8.9 (9.1–8.6)b

Clay (< 2 μm), silt (2–20 μm), and sand (> 20 μm). OM organic matter, ORP oxidation-reduction potential, T temperature. Values represent mean and the range in the brackets (n = 6)

averages of 72.2%, 85.1%, and 84.1% in the NWS, LWS, and HWS, respectively. The results of Ye et al. (2017) showed that the contents of clay, silt, and sand in the Tiaoxi River watershed were 5.4–20.7%, 68.5–75.7%, and 6.6–26.1%, respectively. The temperature gradually increased owing to the sampling times in NWS, LWS, and HWS being in winter (November), spring (March), and summer (September), respectively. The pH in the sediment increased from the LWS to HWS.

### 3.2 Seasonal variation of TP in overlying water and sediment

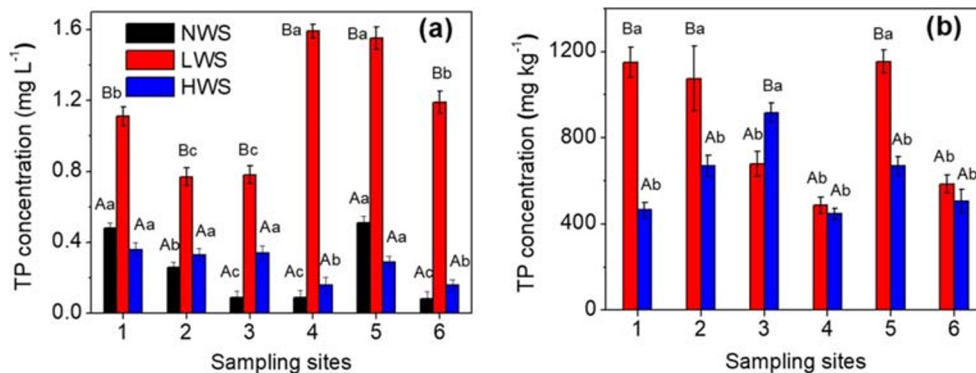
In general, P pollution in sediments and overlying water was the most severe in the LWS, followed by the NWS and HWS, and it was correspondingly suggested that P pollution is addressed during the LWS. The average TP concentrations of the overlying water was higher in the LWS (1.2 mg L<sup>-1</sup>) than that in the HWS (0.3 mg L<sup>-1</sup>) and NWS (0.2 mg L<sup>-1</sup>) (Fig. 4a), which was attributed to the low water volume in the LWS. The overlying water TP concentrations had no significant trend in the upper and lower reaches of the river in the NWS and HWS, while the mainstream TP concentrations of the Qiuxi River were higher than those of the other reaches in the LWS. The

seasonal distribution of the concentration of TP in the sediment varied considerably, and the average concentration of TP (854.6 mg kg<sup>-1</sup>) in the LWS was higher than that in the HWS (612.2 mg kg<sup>-1</sup>) (Fig. 4b). The concentration of TP in sediments at all sampling sites did not exceed sediment quality guidelines for the “severe effect level” of 2000 mg kg<sup>-1</sup> set by the Canadian Province of Ontario (Persaud et al. 1993; Owens and Walling 2002). However, according to Chinese environmental dredging common standards, when TP > 500 mg kg<sup>-1</sup>, the sediment is considered to be polluted and should be dredged (Liu et al. 1999). The TP concentration of sediments from five sampling sites of the LWS reached this limit, and four sampling sites reached this limit in the HWS. Therefore, effective measures need to be taken to control the source of P pollution and remove contaminated sediment.

### 3.3 P fraction seasonal variation in sediment

#### 3.3.1 P<sub>i</sub> fraction seasonal variation

The seasonal distribution of the P fractions varied considerably in the Qiuxi River, and P<sub>i</sub> was always the primary constituent of P. Due to the difficulty of sampling in the NWS, a small number of sediment samples were collected, and the P<sub>i</sub> fraction in the



**Fig. 4** TP concentrations in the overlying water (a) and sediments (b) in different water seasons. Different uppercase letters indicate that the concentration of TP in same site has significant differences (*p* < 0.05) among different water seasons. Different lowercase letters indicate that

the concentration of TP in same water season has significant differences (*p* < 0.05) among different sampling sites. Due to the difficulty of sampling and TP in NWS was not determined

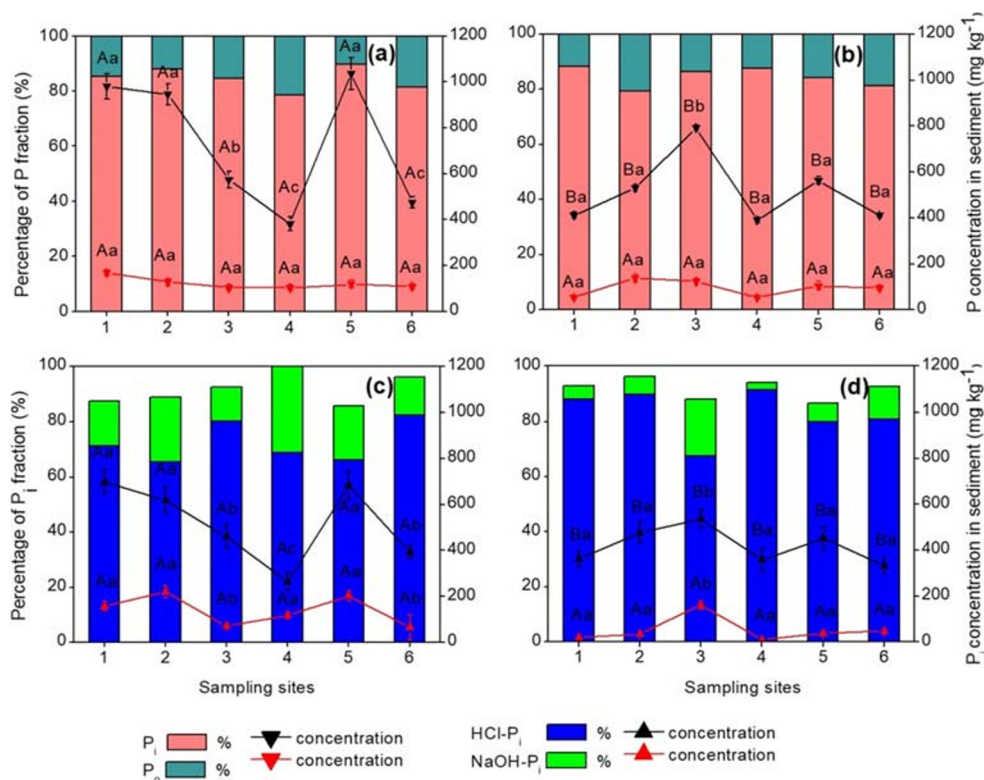
NWS was not determined. The average inorganic P fraction accounted for 84.6% of the TP in the sediments during the LWS and HWS (Fig. 5). The average concentrations of  $P_i$  in the LWS and HWS were  $732.6 \text{ mg kg}^{-1}$  and  $517.0 \text{ mg kg}^{-1}$ , accounting for 85.7% and 84.6% of the TP, respectively. The average  $P_o$  concentrations in the sediments were  $122.0 \text{ mg kg}^{-1}$  and  $95.2 \text{ mg kg}^{-1}$ , accounting for 14.28% and 15.4% of the TP in the LWS and HWS, respectively. With waster season transfer from the LWS to the HWS, the concentrations of sediment  $P_i$  and  $P_o$  decreased, but the proportions of TP maintained stability, indicating that both  $P_i$  and  $P_o$  were released to the overlying water. From Fig. 5, HCl- $P_i$  was the main fraction of  $P_i$  accounting for an average of 77.6% of the  $P_i$  fraction. The average concentrations of HCl- $P_i$  were  $519.9 \text{ mg kg}^{-1}$  and  $419.3 \text{ mg kg}^{-1}$  and accounted for 72.4% and 82.9% of  $P_i$  in the LWS and HWS, respectively. The high HCl- $P_i$  concentration was attributed to the calcareous terrain of the recharge area and land utilization (Wang et al. 2006b; Ni et al. 2019a). Although HCl- $P_i$  concentrations in sediments decreased from the LWS to the HWS, its proportion in  $P_i$  increased, suggesting that NaOH- $P_i$  has a weaker potential to be released than that of other forms of P. The average concentration of NaOH- $P_i$  was  $138.9 \text{ mg kg}^{-1}$ , accounting for 19.0% of the  $P_i$  fraction in the LWS, and decreased to  $51.7 \text{ mg kg}^{-1}$  (only 8.7% of the  $P_i$  fraction) in the HWS, which indicated that NaOH- $P_i$  was released from the LWS to the HWS.

### 3.3.2 $P_o$ fraction seasonal variation

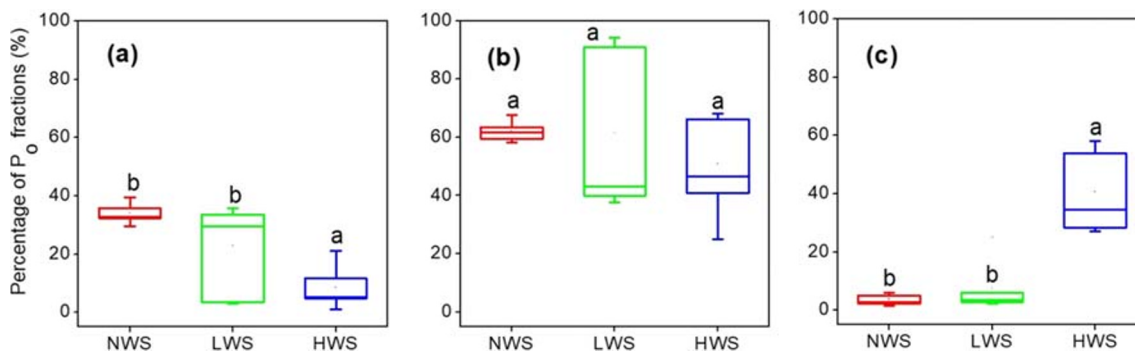
For the  $P_o$  fractions, the ratios of LOP to MLOP to NLOP were 34.1:62.2:3.7, 30.8:61.7:7.5, and 9.2:50.9:40.6 in the NWS, LWS, and HWS, respectively (Fig. 6). The main component of  $P_o$  fractions of sediments was MLOP and LOP in the NWS and LWS and NLOP in the HWS. These suggested that the MLOP and LOP of the main component of sediment  $P_o$  in the Qiuxi River was consistent with the results in Lakes Meiliang (47.8%), Yuantouzhu (47.3%), and Gonghu (47.3%) (Zhang et al. 2008). Furthermore, LOP was high in the NWS and LWS, with an average value of 34.1% and 30.8%, respectively. Overall, from the NWS to the HWS, the proportions of LOP (30.8 to 9.2%) and MLOP (61.7 to 50.9%) of the  $P_o$  fraction decreased, and that of NLOP (3.7 to 40.6%) increased. Compared with LOP and MLOP, the main source of plant-available P, NLOP had weaker bioavailability (Turner et al. 2005).

According to the fraction method of Ivanoff et al. (1998), LOP represented  $\text{NaHCO}_3\text{-}P_o$ , MLOP included HCl- $P_o$  and fulvic acid- $P_o$ , and NLOP denoted hemic acid- $P_o$  and residual- $P_o$ . We observed the following results in the NWS and LWS: HCl- $P_o$  >  $\text{NaHCO}_3\text{-}P_o$  > fulvic acid- $P_o$  > hemic acid- $P_o$  > residual- $P_o$ ; the average HCl- $P_o$  to  $\text{NaHCO}_3\text{-}P_o$  to fulvic acid- $P_o$  to hemic acid- $P_o$  to residual- $P_o$  ratio was 35.8:22.3:4.9:1.4:0.9 in the NWS and 47.6:30.8:14.0:4.6:3.0 in the LWS (Fig. 7). However, the pattern was HCl- $P_o$  > residual- $P_o$  > fulvic acid- $P_o$ .

**Fig. 5** Concentrations and percentages of different  $P_i$  fractions in the sediments in the LWS (a, b) and HWS (c, d).  $P_i$  inorganic phosphorus,  $P_o$  organic phosphorus, HCl- $P_i$  HCl-extractable inorganic phosphorus, NaOH- $P_i$  NaOH-extractable inorganic phosphorus. Different uppercase letters indicate that the concentration of same P fraction has significant differences ( $p < 0.05$ ) among different water seasons. Different lowercase letters indicate that the concentration of same P fraction has significant differences ( $p < 0.05$ ) among different sampling sites. Due to the difficulty of sampling in NWS, a small amount of sediment samples were collected, and  $P_i$  fractions in NWS was not determined







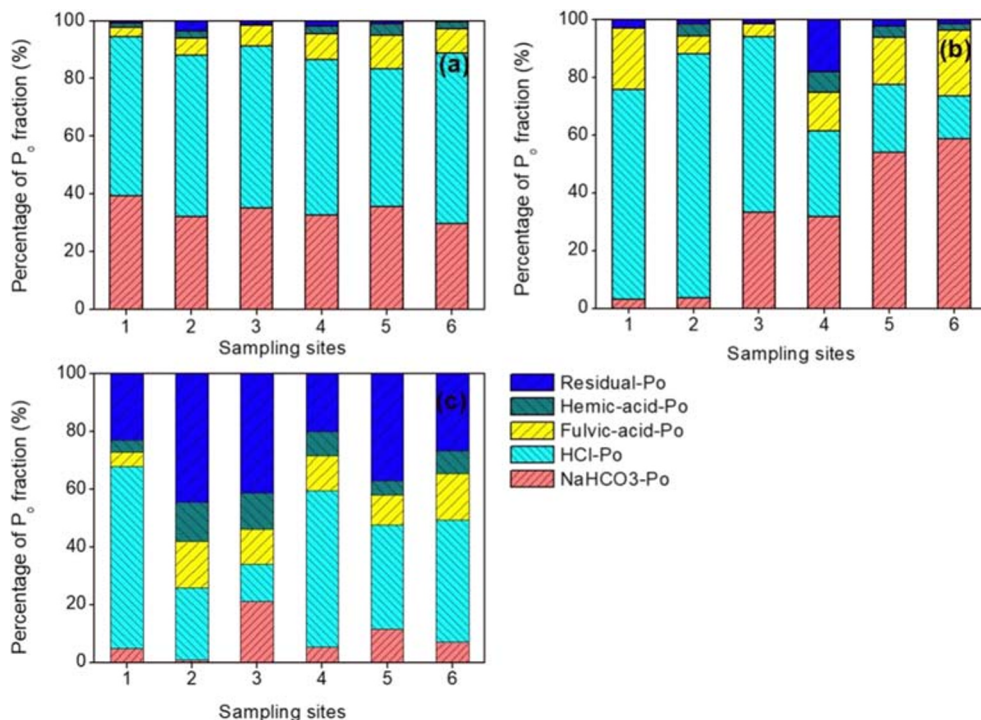
**Fig. 6** Seasonal distribution of the  $P_o$  fractions, including labile organic phosphorus (LOP) (a), moderately labile organic phosphorus (MLOP) (b), and non-labile organic phosphorus (NLOP) (c). Values represent

mean  $\pm$  SD; different letters indicate significant differences among different water seasons ( $p < 0.05$ )

> hemic acid- $P_o$  >  $NaHCO_3$ - $P_o$  in the HWS, and the average HCl- $P_o$  to  $NaHCO_3$ - $P_o$  to fulvic acid- $P_o$  to hemic acid- $P_o$  to residual- $P_o$  ratio was 38.9:32.0:12.0:8.8:8.5 (Fig. 7). The concentration of HCl- $P_o$  in the sediments of the Qiuxi River was the highest compared to that of other fractions of  $P_o$  in general and ranged from 12.9 to 84.7%, with the highest average value of 47.6% in the LWS. The HCl- $P_o$  is in the fraction of biomacromolecules and is labile to be decomposed, hydrolyzed, and mineralized and has potential biological effectiveness (Zhang et al. 2008). This suggested that there was a high possibility of release of  $P_o$  from the sediments of the Qiuxi River. The dissolved  $P_o$  compounds in overlying water are bioavailable, which could lead to a high risk of eutrophication, especially during the LWS (Wetzel 2001). The proportion of  $NaHCO_3$ - $P_o$  (LOP) was second only to HCl- $P_o$  in the NWS (accounting for 22.3% of  $P_o$ ) and LWS (30.8%) and gradually

decreased to the least prevalent component in the HWS (8.5%) because  $NaHCO_3$ - $P_o$  mainly consisted of phospholipids, nucleic acids, and phosphosaccharides and was easy to mineralize and decompose (Zhu et al. 2013). The  $NaHCO_3$ - $P_o$  (LOP) concentration was positively correlated with the nutritional loading of sediments, which suggests that the proportion of LOP is high in sediments with high nutrient loading (Zhang et al. 2008). Fulvic acid- $P_o$  belongs to the MLOP fraction, which accounted for 3.1–11.6% of  $P_o$  in the NWS, 4.5–22.9% in the LWS, and 4.9–16.2% in the HWS. The proportion of hemic acid- $P_o$ , which consists of inositol five-phosphate and inositol hexa-phosphate (phytic acid), was 0.2–4.0% in the NWS, 0.02–7.1% in the LWS, and 4.1–13.8% in the HWS (Ni et al. 2019a). The concentration of residual- $P_o$ , which consists of phytic acid-bound P and provides resistance to

**Fig. 7**  $P_o$  fraction in sediments in NWS (a), LWS (b), and HWS (c)



**Table 5** Pearson correlation for the relationship between P and its geochemical fractions of sediments from Qiuxi River in LWS and HWS ( $n = 6$ )

OM		LWS								
-.454	<b>Finer particle</b>									
-.388	-.454	<b>T</b>								
.831*	-.343	-.787	<b>pH</b>							
.840*	-.292	-.244	.652	<b>TP</b>						
.799	-.252	-.300	.665	.982**	<b>HCl-P<sub>i</sub></b>					
.843*	-.313	-.109	.586	.814*	.698	<b>NaOH-P<sub>i</sub></b>				
-.026	.711	.338	-.044	-.039	.054	-.238	<b>LOP</b>			
.824*	-.770	-.764	.859*	.647	.629	.608	-.432	<b>MLOP</b>		
.904*	-.405	-.353	.772	.586	.496	.833*	-.116	.744	<b>NLOP</b>	
OM		HWS								
.593	<b>Finer particle</b>									
-.399	-.375	<b>T</b>								
-.571	-.492	-.233	<b>pH</b>							
.092	-.023	-.162	.536	<b>TP</b>						
.028	.016	.039	.498	.951**	<b>HCl-P<sub>i</sub></b>					
.064	.028	-.320	.430	0.880*	.718	<b>NaOH-P<sub>i</sub></b>				
-.027	.167	-.520	.522	.772	.608	.934**	<b>LOP</b>			
-.402	.066	.219	-.381	-.865*	-.822*	-.633	-.466	<b>MLOP</b>		
.099	.043	.198	.192	.881*	.879*	.804	.610	-.687	<b>NLOP</b>	

Red color represents significance at the 0.01 level; blue color represents significance at the 0.05 level

OM organic matter, *Finer particle* including clay and silt, *T* temperature, *TP* total phosphorus in sediment, *HCl-P<sub>i</sub>* HCl-extractable inorganic phosphorus, *NaOH-P<sub>i</sub>* NaOH-extractable inorganic phosphorus, *LOP* labile organic phosphorus, *MLOP* moderately labile organic phosphorus, *NLOP* non-labile organic phosphorus

biodegradation, was 0.4–3.7% in the NWS, 1.4–18.0% in the LWS, and 19.9–44.4% in the HWS (Bowman and Cole 1978).

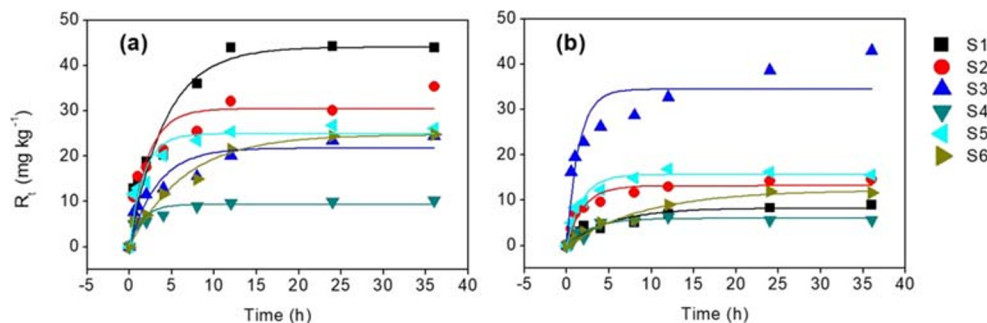
The relationship between geochemical fractions of P and physicochemical properties was analyzed using the Pearson correlation (Table 5). The TP in sediment was significantly positively correlated with P<sub>i</sub> during the HWS ( $r^2 = 0.990$ ,  $p < 0.01$ ) and LWS ( $r^2 = 0.998$ ,  $p < 0.01$ ) since P<sub>i</sub> was always the primary fraction of P in the Qiuxi River sediments. HCl-P<sub>i</sub> was the main fraction of P<sub>i</sub>; therefore, the correlation between HCl-P<sub>i</sub> and TP ( $r^2 = 0.982$  and  $0.951$ ,  $p < 0.01$ ) was also the most significant. Comparatively, P<sub>o</sub> and TP showed a certain correlation only in the HWS, in which MLOP ( $r^2 = -0.865$ ,  $p < 0.05$ ) and NLOP ( $r^2 = 0.881$ ,  $p < 0.05$ ) were correlated

with TP. There was also a correlation between P<sub>i</sub> and P<sub>o</sub>; in the LWS, only NaOH-P<sub>i</sub> and NLOP were positively correlated ( $r^2 = 0.833$ ,  $p < 0.05$ ). In addition, HCl-P<sub>i</sub> was positively correlated with NLOP ( $r^2 = 0.879$ ,  $p < 0.05$ ) in the HWS, and NaOH-P<sub>i</sub> was significantly positively correlated with LOP ( $r^2 = 0.934$ ,  $p < 0.01$ ). This may be because both HCl-P<sub>i</sub> and NLOP were stable P forms, and NaOH-P<sub>i</sub> and LOP were easily released P forms.

### 3.4 P release characteristics in different water seasons

Phosphorus release from sediments to overlying water is a complex kinetic process, including fast and slow-reaction

**Fig. 8** First-order kinetic equation fitting of P in sediment release kinetics in LWS (a) and HWS (b).  $R_t$  is the amount of P released at time  $t$ . Due to the difficulty of sampling and sediments, P release kinetics experiment in NWS was not determined



stages (Fig. 8) (Hansen and Strawn 2003; Wang et al. 2009). In our study, P release was a fast-reaction stage for the first 8 h, with an average release rate of  $2.0 \text{ mg (kg h)}^{-1}$  in LWS and  $1.7 \text{ mg (kg h)}^{-1}$  in HWS. After that, P release stabilized in a slow-reaction stage and tended to reach a dynamic balance, with an average release rate of  $0.08 \text{ mg (kg h)}^{-1}$  in the LWS and  $0.04 \text{ mg (kg h)}^{-1}$  in the HWS. The results revealed that the release rate in the fast-reaction stage was much higher than that in the slow-reaction stage. To further characterize the risk of P release in sediment, the initial release rate  $v_0$  of sediment was introduced and defined as the P release amount per unit mass of sediment within 0.5 h from the start of the reaction (Wang et al. 2006b). The  $v_0$  was  $10.1\text{--}25.9 \text{ mg (kg h)}^{-1}$ , with an average of  $18.0 \text{ mg (kg h)}^{-1}$  in the LWS and  $0.8\text{--}32.5 \text{ mg (kg h)}^{-1}$ , with an average of  $9.4 \text{ mg (kg h)}^{-1}$  in the HWS (Table 6). The whole P release process in the sediments of the Qiuxi River was fitted with the first-order kinetic equation ( $p < 0.05$ ). The  $R_{\text{max}}$  evaluates the release potential and risk of sediment in this study condition (He et al. 2015). The  $R_{\text{max}}$  of sediments in our study was  $9.4\text{--}44.0 \text{ mg kg}^{-1}$ , with an average value of  $25.9 \text{ mg kg}^{-1}$  in the LWS, and  $6.0\text{--}36.7 \text{ mg kg}^{-1}$ , with an average value of  $15.3 \text{ mg kg}^{-1}$  in the HWS (Table 6).

Comparing the  $R_{\text{max}}$  and  $v_0$  of the Qiuxi River in the LWS and HWS, the results show that the release risk of P in the LWS was greater than that in the HWS, except for S3, which might be attributed to the TP concentration in the LWS sediments being higher than that in the HWS sediments.

## 4 Discussion

### 4.1 Correlation between P fractions and sediment properties

Generally, P in sediments is transported to the overlying water and organisms through interstitial water under the influence of environmental factors such as temperature, pH, OM, ORP, sediment particle size, and aquatic plants (Zhang et al. 2008; Wu et al. 2014; McDowell and Hill 2015; Yang et al. 2019). Moreover, physicochemical properties and sediment compositions directly affect P fraction distributions, and their relationships can reflect the transformation of different P in sediment (Yang et al. 2019). According to the correlation analysis (Table 5), OM was the most significant correlation with the

**Table 6** Dynamic parameters of sediments release in the Qiuxi River

Site	LWS						HWS					
	$R_{\text{max}}$ ( $\text{mg kg}^{-1}$ )	$k$	$R^2$	$v_1$	$v_2$	$v_0$	$R_{\text{max}}$ ( $\text{mg kg}^{-1}$ )	$k$	$R^2$	$v_1$	$v_2$	$v_0$
				( $\text{mg (kg h)}^{-1}$ )						( $\text{mg (kg h)}^{-1}$ )		
S1	44.0	0.24	0.917	4.5	0.0	25.9	8.2	0.19	0.842	0.6	0.1	3.5
S2	30.4	0.48	0.882	3.2	0.1	21.9	13.2	0.52	0.930	1.4	0.1	7.4
S3	21.8	0.31	0.842	1.9	0.2	15.3	36.7	0.36	0.903	4.1	0.1	32.5
S4	9.4	0.66	0.850	1.1	0.03	10.1	6.0	0.36	0.902	0.7	-0.03	0.8
S5	25.0	0.60	0.906	0.6	0.03	23.2	15.7	0.56	0.957	3.0	-0.05	10.1
S6	24.7	0.15	0.953	0.6	0.1	11.4	12.2	0.11	0.972	0.5	0.1	2.2
Average	25.9	-	-	2.0	0.1	25.9	15.3	-	-	1.7	0.04	3.5

$R_{\text{max}}$  the maximum release amount of P at the release equilibrium,  $k$  the release rate constant of P,  $R^2$  correlation coefficient of first-order kinetic equation fitting,  $v_1$  represents the release rate of P of sediments in stages of fast reaction,  $v_2$  represents the release rate of P of sediments in stages of slow reaction,  $v_0$  represents the initial release rate of P of sediments

fraction distribution of P among all sediment property parameters in the LWS. The concentration of OM was positively correlated with the concentrations of TP, NaOH-P<sub>i</sub>, MLOP, and NLOP ( $r^2 = 0.840, 0.843, 0.824, \text{ and } 0.904, p < 0.05$ ) in the LWS; therefore, much more attention should be paid to the effect of OM on sediment P during the LWS in the Qiuxi River than during other seasons. In general, the sources of OM in sediments mainly include (1) bacteria, phytoplankton, and plants in nature (Otero et al. 2000) and (2) anthropogenic activities such as agriculture, urban runoff, and industry (Watanabe and Kuwae 2015; Ni et al. 2019a). There were a large number of farmland and residential buildings in the Qiuxi River Basin. Non-point agricultural sources and untreated domestic sewage were responsible for the increase in the concentration of OM in sediments. Organic matter can change the function of sediments as “source” and “sink” by changing the adsorption process and mode of various fractions of P<sub>o</sub> (Wang et al. 2012; Yang et al. 2019). In addition, microorganisms in sediment can consume OM combined with P<sub>o</sub>, convert P<sub>o</sub> into P<sub>i</sub>, and then release it into overlying water (Wang et al. 2008). Moreover, OM exhibited a correlation with P<sub>i</sub> by interfering with metal cation binding to P. Specifically, Ca<sup>2+</sup> can form a binary complex with OM (OM-Ca<sup>2+</sup>), which can form a poorly soluble P-Ca-OM (part of HCl-P<sub>i</sub>) complex (Lei et al. 2018). Furthermore, OM can inhibit P adsorption on iron oxides by forming negatively charged surface sites. However, in this study, there was a poor correlation between HCl-P<sub>i</sub> and OM, which was inconsistent with other studies (Lei et al. 2018; Ma et al. 2019). The possible reason for this might be that HCl-P<sub>i</sub> is usually closely related to inorganic apatite and carbonates from rock debris and soils (Ni et al. 2019a). In addition, we regard HCl-P<sub>i</sub> as Ca-P, but HCl can also extract the P combined with other metals in addition to Ca-P.

The pH also affected the distribution of P, and MLOP had a positive correlation with pH in the LWS ( $r^2 = 0.859, p < 0.05$ ). Acid and alkaline conditions are favorable for the release of P, and the amount of P release was lowest under neutral conditions (Liang et al. 2015). The sediments (the average pH

values in the NWS, LWS, and HWS were 9.1, 8.3, and 8.9, respectively) were under alkaline conditions in the Qiuxi River, thereby accelerating the release of P<sub>i</sub> and P<sub>o</sub>. For P<sub>o</sub>, acidic conditions are favorable for HCl-P<sub>o</sub> (MLOP) release, while alkaline conditions accelerate hemic acid-P<sub>o</sub> (MLOP) and fulvic acid-P<sub>o</sub> (NLOP) release (Wu et al. 2014; Liang et al. 2015). Comparatively, P<sub>i</sub> is mainly released by ion exchange, which is impacted by the pH affecting the combination of P and metal ions, as OH<sup>-</sup> competes with phosphate anions and weakens Fe and Al fixation of P, leading to an increase in P release (Beutel et al. 2008; Liang et al. 2015; Ma et al. 2019). The effect of pH on P release is reflected in the morphogenesis of sediments, and different sediments have different fraction conditions of P, so the effect of pH on P release in sediments is also different (Wang et al. 2006b; Liang et al. 2015).

The TP concentration of the sediments in the LWS was significantly higher than that in the HWS, which was similar to the Lower Changjiang River, China (Duan et al. 2008; Table 7). However, some previous studies had opposite results (Table 7). This result suggested that the TP concentrations of sediments in different catchments show different rules with the variation in the water season. On the one hand, in the HWS, runoff would bring shoreside pollutants into the catchment, leading to an increase in the concentration of P in the river (Duan et al. 2008; Varol 2012; Zafar et al. 2016). On the other hand, during the HWS, a large amount of river water had a dilution effect on the pollutants in the catchment (Lei and Keming 2011). The dilution effect of runoff on the pollutants was dominant. The dilution capacity of the overlying water was different due to the variation in the flow rate of the river (the average values were 10.0 m<sup>3</sup> s<sup>-1</sup> in the LWS and 31.6 m<sup>3</sup> s<sup>-1</sup> in the HWS), resulting in the concentrations of TP in the overlying water decreasing from 1.2 mg L<sup>-1</sup> in the LWS to 0.3 mg L<sup>-1</sup> HWS (SPDEP 2017). In addition, we analyzed the other reasons why P pollution was worst in the LWS compared to that in the HWS in the Qiuxi River and considered the following: (1) the release of P from the sediment to the overlying water increased because the activities of microorganisms and enzymes

**Table 7** Concentrations of TP in sediments of the Qiuxi River and other selected rivers from the literature

Water area	TP concentration in sediments (mg kg <sup>-1</sup> )		Reference
	LWS	HWS	
Qiuxi River, China	855	612	-
Lower Changjiang River, China	700	470	Duan et al. 2008
Tropical estuary, Southwest India	1164	1504	Renjith et al. 2011
Ditch system in Sanjiang plain, China	540	592	Lei and Keming 2011
Tigris River, Turkey	680	902	Varol 2012
Guaporé catchment, Southern Brazil	1489	1503	Zafar et al. 2016
Beibu Gulf, Southern China	1004	1248	Yang et al. 2019

**Table 8** Pearson correlation coefficients for the relationship between the P release parameters and selected sediment properties ( $n = 12$ )

	ORP	OM	Clay	Silt	Sand	TP	$P_i$	$P_o$	HCl- $P_i$	NaOH- $P_i$	LOP	MLOP	NLOP
$R_{\max}$	-0.704*	0.847**	-0.313	-0.247	0.257	0.848**	0.826**	0.781**	0.808**	0.731**	0.256	0.537	-0.064
$v_0$	-0.440	0.702*	-0.135	-0.081	0.088	0.868**	0.858**	0.702*	0.787**	0.850**	0.296	0.402	0.044

\*Correlation is significant at the 0.05 level (two-tailed). \*\*Correlation is significant at the 0.01 level (two-tailed).  $R_{\max}$  the maximum release amount of P at the release equilibrium,  $v_0$  represents the initial release rate of P of sediments, *ORP* oxidation-reduction potential, *OM* organic matter, *TP* total phosphorus,  $P_i$  inorganic phosphorus,  $P_o$  organic phosphorus, *HCl- $P_i$*  HCl-extractable inorganic phosphorus, *NaOH- $P_i$*  NaOH-extractable inorganic phosphorus, *LOP* labile organic phosphorus, *MLOP* moderately labile organic phosphorus, *NLOP* non-labile organic phosphorus

increased as the temperature increased from 21.0 to 24.5 °C (Table 4) (Søndergaard et al. 1999; Bryan et al. 2007; Liu et al. 2018), and (2) the exposed sediments were submerged, leading to the sediment-water interface changing from an oxidation to a reduction state; therefore,  $Fe^{3+}$  would be reduced to  $Fe^{2+}$ , resulting in the release of  $Fe^{3+}$ -P (Jensen et al. 1992; Wang et al. 2006b; Pellegrini et al. 2010). However, different from the overall trend, the concentration of TP in the sediment at S3 increased from the LWS to the HWS since there were a large number of submerged plants in the sediments at this sampling site in the LWS, which mitigated the resuspension of sediments and release of P, resulting in the accumulation of P in sediments, while a large number of dead tape grass in the HWS caused P fixed in the tape grass to be released to the sediment and overlying water (Wang et al. 2018). The release of P from sediments was influenced by many environmental factors and needs to be further studied through simulation experiments (Table 8).

## 4.2 Influence of anthropogenic activities on P fractions in sediment

The anthropogenic activities in the Qiuxi River, including diffuse pollution of agriculture and discharge of sewage, especially wastewater, also affect the P concentration (Zafar et al. 2016; SPDEP 2017; Ni et al. 2019a, b). There are approximately 0.4 million urban and 1.3 million rural residents around this area, making this area a representative catchment severely influenced by anthropogenic activities in southwest China. In the Qiuxi River, the P pollutants discharged from domestic sewage accounted for 49% of the total pollution sources, and agricultural pollution sources accounted for 24% the total pollution sources (Fig. 2). There were three sampling sites mainly polluted by domestic sewage, including S1, S2, and S5, which were located downstream of the town. For the concentration of sediment TP in these three sampling sites, the average was 1125.9 mg kg<sup>-1</sup> in the LWS and 601.5 mg kg<sup>-1</sup> in the HWS. In comparison, S3, S4, and S6 are located in an agricultural area mainly affected by agricultural activities (SPDEP 2017). The concentration of sediment TP in these three sampling sites (the average was 583.4 mg kg<sup>-1</sup> in the LWS and 622.9 mg kg<sup>-1</sup> in the HWS)

was similar to the mean value of the Bronx River sediments (580 mg kg<sup>-1</sup> in 2006 and 793 mg kg<sup>-1</sup> in 2007) with agricultural pollution, while it was higher than the mean value of sediment TP in Illinois streams (360 mg kg<sup>-1</sup>) (McDaniel and David 2009; Wang and Hari 2011).

The previous study demonstrated that urban untreated discharges may be a single major P source if not wisely managed, proving a major threat to water quality (Zafar et al. 2016; Ni et al. 2019a). Sampling site S5 was located downstream of Beidou Town with a permanent population of approximately 50,000; therefore, it was the most severely influenced by domestic sewage among all sampling sites. A large amount of domestic sewage was discharged into the stream in this area due to the lack of a sewage pipeline system in the households along the riparian. Previous studies found that domestic sewage usually contains NaOH- $P_i$ , and the concentration of NaOH- $P_i$  in sediments can be used as an effective index of P load in industrial and domestic sewage (Ni et al. 2019a). It can also be observed from correlation analysis that there was a positive correlation between TP in sediment and NaOH- $P_i$  ( $r^2 = 0.814$ ,  $p < 0.05$ ). It is worth noting that previous studies have shown that domestic sewage contains a large amount of Fe/Al-P. However, due to the limitations of the method, the extracted P cannot be accurately classified as a certain type of metal-bound P, which may become the focus of our future research. In this study, NaOH- $P_i$  is regarded as Fe/Al-P, but NaOH may extract P combined with other metals. NaOH- $P_i$  was once used for the estimation of available P in the sediments and was an indicator of algal available P (Wang et al. 2006b; Ye et al. 2017). Therefore, the NaOH- $P_i$  from domestic sewage would increase the risk of eutrophication.

Furthermore, agricultural activities also significantly increase the concentration of  $P_i$  in sediments (Ni et al. 2019a). The main reason for this increase is P emission from fertilizer and livestock farming, as the farmland soil can only absorb 10–15% of the P, and the rest is lost to the river through surface runoff or soil erosion, leading to a large increase in P such as phytate P in the river (Zhang and Shan 2008; McDaniel and David 2009). Phytate P, belonging to the NLOP, includes hemic acid- $P_o$  and residual- $P_o$  and comes mainly from the indigestible P components of crops (such as legumes, triticeae, cereals) (Waldrup et al.

2005; Ni et al. 2019a). In the HWS, the correlation between NLOP and TP in sediment was positive ( $r^2 = 0.881$ ,  $p < 0.05$ ) and was an important component of  $P_o$ , accounting for 40.6% of  $P_o$  on average in the Qiuxi River. Non-labile  $P_o$  is difficult to release in sediments, but it can be hydrolyzed by phytase hydrolyzation (Zhu et al. 2013). Nevertheless, agricultural development has increased the concentration of phytase hydrolyzation in soil, which induces an increase in NLOP release in sediments when P migrates to rivers (Suzumura and Kamatani 1995; Cheng and Lim 2006).

In addition, a previous study illustrated that the concentration of HCl- $P_i$  in sediments of agricultural lakes or rivers was relatively high (accounting for 70% of TP) because P fertilizer usually contains a large amount of calcium (Dittrich et al. 2013), and the average proportion of HCl- $P_i$  in our research was 77.6% in the Qiuxi River. Moreover, the background value of Ca concentration in the soil will also affect the concentration of HCl- $P_i$  in sediments. In southwest China, a large amount of carbonate apatite exists in the soil, and calcareous soil accounted for the majority of carbonate apatite in the soil. The soil area with calcium carbonate concentrations  $\geq 1\%$  accounted for 64.1% of the total cultivated land area (Wang et al. 2006b; Ni et al. 2019a). HCl- $P_i$  is stable in sediments and is generally not bioavailable (Wang et al. 2006b; Ye et al. 2017). A large amount of input and release difficulty is the reason for the increase in HCl- $P_i$  in the sediment. All of the above results illustrated that the P pollution of agricultural pollution sources and domestic sewage pollution sources cannot be ignored.

### 4.3 Influence of sediment properties on P release in sediment

Sediment release is a complex kinetic process affected by many factors, such as OM, ORP, and sediment particle size; therefore, investigating the kinetic characteristics of sediment release could be useful to evaluate the P release risk (Kim et al. 2003; Wang et al. 2006a, 2009; Zafar et al. 2016). In our study, OM was positively correlated with  $R_{\max}$  and  $v_0$  ( $r^2 = 0.847$ ,  $p < 0.01$ ;  $r^2 = 0.702$ ,  $p < 0.05$ ), which implied that P release was greatly affected by OM. The results from He et al. (2015) and Wang et al. (2017) also demonstrated that the river carbon cycle had a significant impact on the migration and transformation of P in sediments. Moreover, a study revealed that there is a positive correlation between OM and alkaline phosphatase activity, thereby indicating that the higher the OM concentration is, the higher the alkaline phosphatase activity; therefore, more  $P_o$  is released (Wang et al. 2006a, 2012; Yang et al. 2019). According to the results of correlation analysis,  $R_{\max}$  had a negative correlation with ORP ( $r^2 = -0.704$ ,  $p < 0.05$ ) demonstrating that the risk of P release from sediment increases when sediment is in a reduced state since iron is labile and will combine with P to increase the migration of P and, and the reduction of  $Fe^{3+}$  and sulfate

promotes the mobilization of P under reducing conditions (Dieter et al. 2015). Furthermore, fine particles (e.g., clay, silt) usually have higher specific surface area, more P-retention components (e.g., Al/Fe oxides or hydroxides), and correspondingly stronger adsorption abilities than coarser particles (sand) (Zafar et al. 2016; Ye et al. 2017; Yang et al. 2019). However, sediment particle size had no correlation with  $R_{\max}$  and  $v_0$  ( $p > 0.05$ ).

A significantly positive correlation between  $R_{\max}$  and TP ( $r^2 = 0.848$ ,  $p < 0.01$ ) illustrated that the higher the TP concentration in sediments was, the greater the  $R_{\max}$ . Similarly, a previous study also showed that the magnitude of the P released is different among the different concentrations of P sediments, and a high P concentration has a high risk for P release (Gloor et al. 2005; Wang et al. 2006b, 2009). This explained why the  $R_{\max}$  in the Qiuxi River during the LWS was greater than that in the HWS (the average concentration of sediment TP was 854.6 mg  $kg^{-1}$  and 612.2 mg  $kg^{-1}$ , and the average  $R_{\max}$  was 25.9 mg  $kg^{-1}$  and 15.3 mg  $kg^{-1}$  in the LWS and HWS, respectively) (Fig. 4b; Table 6). However, the  $R_{\max}$  of P in S3 sediment was higher in HWS (36.7 mg  $kg^{-1}$ ) than in LWS (21.8 mg  $kg^{-1}$ ) might be because the concentration of sediment TP in the HWS (916.5 mg  $kg^{-1}$ ) was higher than that in the LWS (679.0 mg  $kg^{-1}$ ).

In addition, the difference in P forms and the different bonding interactions between different P forms and sediments have an impact on the release risk of P in sediments (Wang et al. 2006b, 2009). Inorganic P was the main P fraction in the sediments of the Qiuxi River, and  $R_{\max}$  was significantly positively correlated with HCl- $P_i$  and NaOH- $P_i$  ( $r^2 = 0.808$  and  $0.731$ ,  $p < 0.01$ ). The proportion of NaOH- $P_i$  in  $P_i$  was not high (14.0%), while it was a potentially active P that was labile for release to the overlying water (Kaiserli et al. 2002; Wang et al. 2006b). The average concentration of NaOH- $P_i$  decreased 62.8% from the LWS to HWS (Fig. 5). Wang et al. (2006b) studied P release from lake sediments in the middle and lower reaches of the Yangtze River areas and found that over 50% of P released was from NaOH- $P_i$ , and approximately 10% was from HCl- $P_i$ . The most NaOH- $P_i$  is only temporarily immobilized in sediments and is very sensitive to changes in environmental factors such as pH and temperature. As sediment is suspended or other river biochemical reactions are processed, temporarily bound NaOH- $P_i$  is readily released into the overlying water again (Jensen et al. 1992; Ruttenberg 1992). Generally, the condition of higher temperature and slight acid or alkaline is beneficial to the release of NaOH- $P_i$  from the sediment (Table 4 and Fig. 4) (Wang et al. 2006a; Zafar et al. 2016). The result shows that pH (from 8.3 to 8.9) and temperature (from 21.0 to 24.5 °C) increased from LWS to HWS, and the NaOH- $P_i$  decreased (from 138.9 to 51.7 mg  $kg^{-1}$ ). Comparatively, HCl- $P_i$  was unlikely to be released or utilized in sediments, but it accounted for a high proportion of TP (77.6%), and a small amount of release

would affect  $R_{\max}$ . The total  $P_o$  concentration was also significantly positively correlated with  $R_{\max}$  ( $r^2 = 0.781$ ,  $p < 0.01$ ). The  $P_o$  compounds can be hydrolyzed by alkaline phosphatase into various orthophosphate, which is then released into the overlying water (Ni et al. 2019b).

## 5 Conclusions

This study is one of the first studies to research the seasonal variation of the pollution status, fractions, and release characteristics of P in a typical river catchment that is severely polluted by agriculture and urban sewage in southwestern China. We found that P concentration and the risk of P release in sediments had similar seasonal variation trends in the Qiuxi River, both of which were highest in the LWS owing to the influence of the discharge of domestic sewage, agricultural diffusion, flow rate, and OM. It is necessary to take appropriate measures to inhibit the release of sediment P during the LWS. In particular, OM was significantly correlated with P fractions and  $R_{\max}$ ; therefore, the seasonal influence of OM on P migration and transformation in sediments is worthy of further investigation. Inorganic phosphorus (accounting for 84.6% of TP) was the main component of P, in which the  $HCl-P_i$  average accounted for 77.6%. Comparatively, MLOP was the main component of  $P_o$ , and  $HCl-P_o$  constituted most of the MLOP. Moreover, as the water season changed from the LWS to HWS, the average  $P_o$  concentrations in sediments decreased by  $26.8 \text{ mg kg}^{-1}$ , indicating that the contribution of the release of sediment  $P_o$  to P pollution in the aquatic environment cannot be ignored. We also observed that there was a significantly positive correlation between  $R_{\max}$  and TP in sediments ( $r^2 = 0.848$ ,  $p < 0.01$ ), which demonstrated the necessity of decreasing the P concentration in sediment to control P pollution in the overlying water. This paper explores the migration and transformation of P in sediments of the Qiuxi River, which provides information for sustainable development of local agriculture and data support to the study of sediments from typical agricultural polluted rivers. Moreover, the research results show that the P concentration and release risk in the sediment during the LWS was higher than that during the HWS. Therefore, taking measures to control river P pollution during the LWS should be recommended.

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