

Phosphorus Fractions and Its Summer's Release Flux From Sediment in the China's Three Gorges Reservoir

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ABSTRACT. The amounts and forms of phosphorus (P) in sediments, orthophosphate (Pi) concentrations as well as Pi release fluxes across the sediment-water interface were investigated from five sampling sites in the Three-Gorges Reservoir (TGR). The Total P (TP) contents of surface sediments (0-2 cm) ranged from 415.5 to 1047.9 mg/kg, and the predominant fraction was HCl-P (Ca-bound P). The main rank order of P-fractions was HCl-P > Res-P (Residual-P) > NaOH-P (Al-adsorbed P) > BD-P (Redox sensitive P) > NH₄Cl-P (Labile P), and ranged from 164.5 to 687.2 mg/kg, 96.0 to 140.8 mg/kg, 75.8 to 111.5 mg/kg, 34.0 to 104.8 mg/kg, and 5.9 to 15.9 mg/kg, respectively. The pH values ranged from 6.4 to 8.2 across sediment-water interface and sediment pH values were lower than those of the corresponding overlying water. The average Pi concentrations of pore water were higher than those of the open water and overlying water. Based on calculations using the Fick's first law, sediment in Xiangxi River (XX03) functioned as a P sink, with Pi flux of -0.003 mg/m²/d, while sediments from Modaoxi03 (MDX03), Daning02 (DN02), Caotanghe (CTH) and Changjiang Badong (CJBD), had Pi fluxes of 0.013 mg/m²/d, 0.009 mg/m²/d, 0.004 mg/m²/d and 0.007 mg/m²/d, respectively, and served as an internal P source in summer.

Keywords: phosphorus fractions, sequential extraction, sediment, release fluxes, orthophosphate, pH, Three-Gorges Reservoir

1. Introduction

Phosphorus (P) has been identified as the "limiting nutrient" to phytoplankton development (Jin et al., 2006a; Khan and Ansari, 2005) and orthophosphate (Pi) is the only form of P that can be assimilated by bacteria, algae, and plants. Excessive concentration of P is the most common cause of eutrophication in freshwater lakes, reservoirs, streams, and head waters of estuarine systems (Correll, 1998). Therefore, controlling P has been well accepted as the best approach for reducing eutrophication (Dahl et al., 1993). To improve water quality, it will be necessary to further reduce the P sources including sediment release, especially when external pollution is reduced (Abrams and Jarrell, 1995; Sun et al., 2009; Xie et al., 2003). The factors affecting P release processes from sediments have been extensively studied over the past years (Boström, 1988; Jensen and Andersen, 1992). Most of the previous studies focused on the relevant environmental

factors e.g. temperature, pH, redox potential and hydrological conditions (Andersen, 1974; Kim et al., 2003; Ramin and Bates, 1979). However, the release of P from surface sediments depends not only on the environmental factors, but also on the concentration of mobile P and transport processes, primarily diffusion (Rydin, 2000). Thus, it is of importance to probe P release, physical and chemical properties of sediments, especially the factors as well as processes affecting P release.

The Three-Gorges Project (TGP), regarded as the biggest water-control project in the world, has been operated at full capacity since the end of 2008 (Fu et al., 2010). The Three-Gorges Reservoir Area (TGRA), from Jiangjin District of Chongqing to Yichang City of Hubei, covers 20 county-level administrative regions with an area of 58,000 km² in total and the reservoir surface water area is over 1,080 km² at a water level of 175 m with storage capacity of 39.3 billion m³ (Huang, 2001; Wu et al., 2003; Fu et al., 2010). The annual runoff flow at the Three Gorges Dam (TGD) is 451 billion m³ with the annual sediment discharge of 5.30 × 10⁸ t. However, some environmental problems and challenges have to be faced for the TGP, especially the decrease of water quality of reservoir bays and backwater areas of its main tributaries (Fu

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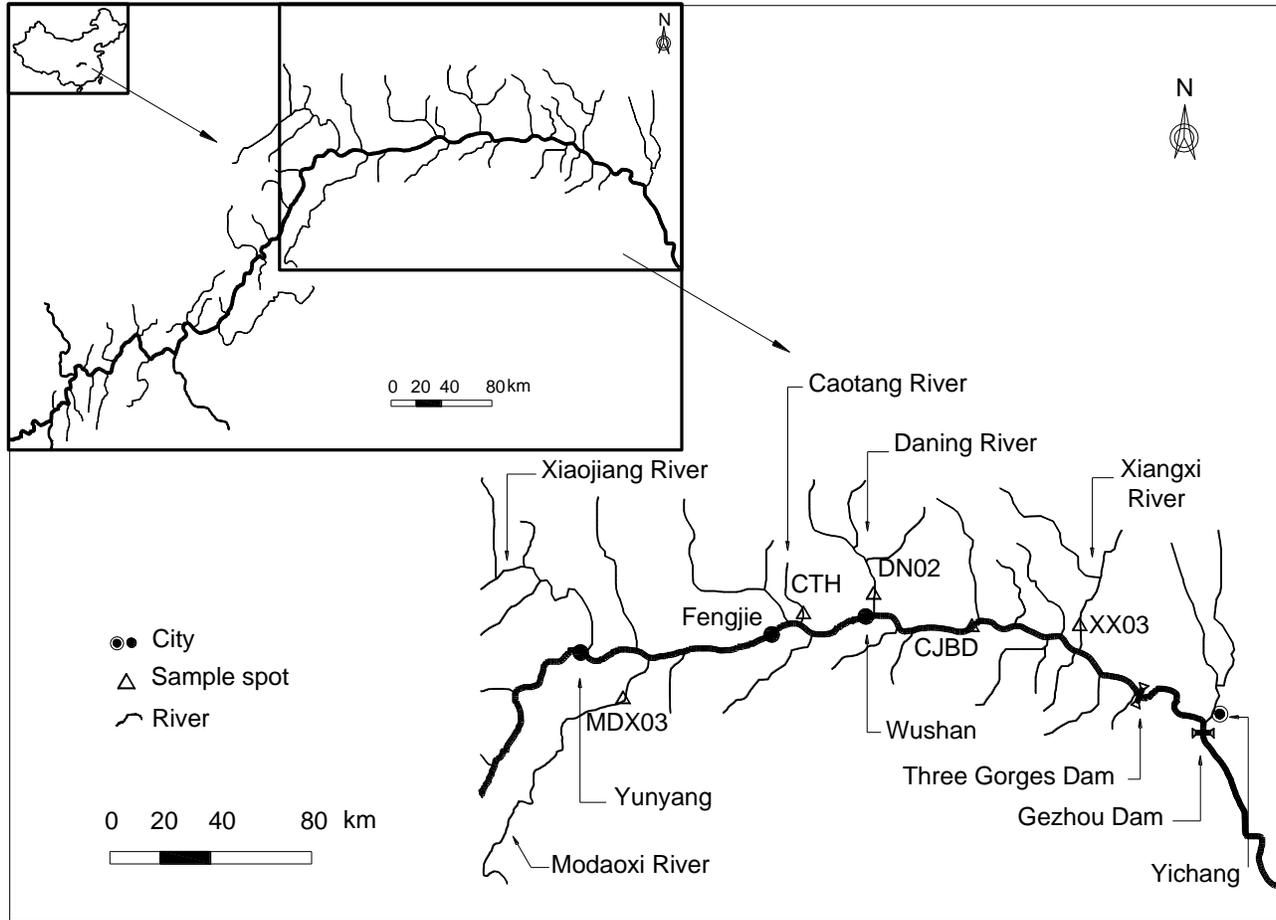


Figure 1. The geographic location of the sampling sites in the Three Gorges Reservoir.

Table 1. Geographic and Morphometric Features of the Related Rivers

River	Position	Drainage area	Sampling site depth	Average annual runoff	Annual average flow	Annual nutrient input amount of nutrient		References
		km ²	m	10 ⁸ m ³	m ³ /s	10 ³ kg TN	10 ³ kg TP	
Xiangxi River	31°5'21"N 110°45'5"E	3,099	48	19.56	62.5	1,623.49	331.85	Li et al., 2008; Zheng et al., 2008
Daning River	31°08'36"N 109°53'58"E	4,181	56	33.43	106	2,008.84	34.06	Zhang et al., 2007; Hua et al., 2009
Modaoxi River	30°51'55"N 108°52'40"E	3,167	33	17.6	55.8	-	-	
Caotang River	31°02'55"N 109°34'37"E	210	54	2.369	7.51	-	-	Chen et al., 2004
Badong	31°02'49"N 110°23'10"E	-	88	-	-	-	-	

et al., 2010). Since 2004, algal blooms caused mainly by dinoflagellates have occurred in the 22 tributaries including the Xiangxi, Tongzhuang, and Daning Rivers each February (Fu et al., 2010). The occurrence of algal blooms is directly linked to slow tributary flow caused by the impoundment (Deng and Gong, 2007; Li et al., 2007a; Yang et al., 2010),

and changed water chemistry (Ye et al., 2006). The slow flow can weaken the water exchange in vertical direction, and protract the residence time of water which leads to the deposition of nutrient and particulates (Li et al., 2007a; Zheng et al., 2008). In some tributaries, the flow velocities were even below 0.05 m/s (Deng and Gong, 2007; Li et al., 2007a; Li et

al., 2007b; Yang et al., 2010). Increased fertilizer use and decreased fertilizer use efficiency are implicated as another major causal factors for increased riverine nutrient transport (Liu et al., 2006). The application of chemical fertilizer from 1996 to 2007 in the TGRA increased by 23% (Fu et al., 2010). Other sources are from agricultural and industrial waste, sanitary waste discharge, the release of the sediments and so on. Therefore, rational regulation of the water and sediment to mitigate the negative ecological and environmental impacts is challenging on the Yangtze River.

The objective of this study was to analyze the orthophosphate (Pi) concentrations in water body and to estimate the amounts and forms of total phosphorus (TP) and P fractionations of sediments in the whole profiles. Fick's First Law was used to evaluate summer's release fluxes of the studied sediments, and the factors affecting P release were also discussed.

2. Materials and Methods

2.1. Study Area

The sampling sites were located at the mainstream and tributaries of the TGRA (Figure 1). Xiangxi03 (XX03), Daning02 (DN02) and Modaoxi03 (MDX 03) were situated at the midstream of Modaoxi, Daning and Xiangxi River, Caotanghe (CTH) was located at the estuary of Caotang River and Changjiang Badong (CJBD) was taken from the mainstream of the Yangtze River near the Badong County. Detailed locations and morphometric features of the five sampling sites were shown in Table 1.

2.2. Sampling

Undisturbed samples were collected from the five sampling sites along the Yangtze River during 31st, July to 4th, August 2011. Open water samples were separately obtained from the surface, middle and bottom water of each sampling profile (0.5 m underneath water level, 0.6 and 0.8 times the depth of water depth, respectively) with card cover type water harvesting device, and stored in 200 mL polyvinyl chloride (PVC) bottles. The water temperature of the hypolimnion was measured using water thermometer. The corresponding overlying water (near the sediment-water interface) and sediment samples were collected using a gravity corer (Wang et al., 1998) with Plexiglas sampling tubes (diameter 6.5 cm and length 60 cm). The subsampling of overlying water and sediments as well as the determination of pH values was carried out in situ. The pH values were measured using a glass electrode and overlying water samples collected by the gravity corer had a length of 18, 12, 8, 10, and 10 cm in XX03, DN02, MDX03, CTH and CJBD, respectively. Stratified overlying water was injected into PVC bottles at an interval of 2 cm. The sediment cores obtained from the top 10 cm layer, were continuously sub-sampled into sections of 2 cm length, were fully packed in polyethylene centrifuge tubes and sealed to avoid sediment oxidation in the subsampling process. All samples were collected in triplicates, taken in air-sealed plastic bags and kept at 4 °C prior to analysis (within 12 h).

2.3. Analysis

2.3.1. Water Chemistry

Open water samples, overlying water and pore water (extracted from sediment samples by centrifugation at 4000 rpm for 30 minutes) samples from the five sampling sites were immediately filtered through 0.45 µm Whatman GF/C filters (Bakri and Chowdhury, 2006). The filtered water samples were analyzed immediately to determine the concentrations of orthophosphate (Pi), with the molybdenum blue method (Wei et al., 2002). All samples were analyzed in triplicates and the data were reported as their average.

2.3.2. Sediment Analysis and Phosphorus Fractions

Part of sediments were used to calculate the water content and porosity, which were measured based on weight loss after drying of the sediments at 105 °C (Egemoose et al., 2009; Kaiserli et al., 2002). The other sediment samples after centrifuged were freeze-dried, homogenized, passed through a 200 mesh sieve and stored in the dryer. Sieved sediment sample (0.50 g), used for sediment TP determination, was put into 50 ml tube, and digested with K₂S₂O₈ and H₂SO₄ (30% v/v) at 110 °C for 15 min (Gächter et al., 1992), thereafter deionized water was added into each tube to obtain a solid/water ratio at 1:100 (W/W). Then P was determined with the acidic molybdate ascorbic acid method (Murphy and Riley, 1962; Zhou et al., 2001). All samples were analyzed in triplicates and the data were reported as their average.

Phosphorus fractionations were determined using the sequential extraction scheme given by Christophoridis and Fytianos (2006) (Table 2). 0.30 g sediment sample was used and the extracts with a solid/water ratio of 1:100 (W/W) were centrifuged at 4,000 r/min for 30 min. The supernatants were filtered through a 0.45 µm GF/C filter membrane. The soluble reactive P (SRP) in each sample was determined according to the molybdenum blue method (Wei et al., 2002). This extraction procedure divided P fractions into loosely sorbed P (NH₄Cl-P), redox-sensitive P (BD-P), metal oxide bound P (NaOH-P), calcium bound P (HCl-P) and residual P (Res-P). Res-P was calculated as TP minus total extracted P. Table 2 provided a summary of the fractions determined according to the selected scheme (Christophoridis and Fytianos, 2006). For each fraction, three replicates were performed and all the data were expressed as the average.

2.4. Flux Estimation Methods

Theoretical release flux rates were estimated from the gradients of Pi concentration present at the interface of water and sediment according to Fick's First Law (Berner, 1980):

$$J = -\phi D_s (\partial C / \partial x)_{x=0}, \quad (1)$$

where J is the release flux (mg/m²/d); ϕ is the porosity in the upper part (0 ~ 4 cm) of the sediment; and $(\partial C / \partial x)_{x=0}$ is the concentration gradient of orthophosphate across the sediment-

Table 2. Phosphorus Fractions in the Sediment and Their Descriptions (Christophoridis and Fytianos, 2006)

Fraction	Description	Description
NH ₄ Cl-P	Labile P	P loosely adsorbed to surface, immediately available
BD-P	Redox sensitive P	Redox-sensitive P, bound to the surface of Fe and Mn oxides and hydroxides; released by reductive Fe dissolution
NaOH-P	P bound to metal oxide, mainly of Fe and Al	P sorbed on the surface of Al oxides and the interior of Fe oxides; released at high pH due to ligand exchange reactions in which hydroxide ions replace orthophosphate
HCl-P		P fixated in Ca and Mg minerals (carbonates and apatite); relatively stable under alkaline conditions
Residual P		Organic and refractory P of the Si crystal lattice

water interface (Mortimer et al., 1998). D_s is the effective diffusion coefficient; and D_0 is the molar diffusion coefficient of the sediment, which is dependent on porosity and temperature (Chowdhury and Bakri, 2006). The parameter D_s is approximately related to D_0 by the relation (Ullman and Aller, 1982; Ullman and Sandstrom, 1987):

$$D_s = \phi D_0 \phi \leq 0.7 \tag{2}$$

$$D_s = \phi^2 D_0 \phi \geq 0.7 \tag{3}$$

The porosity (ϕ) of sediments at each sampling site was assumed to be more than 0.7 and the corresponding $D_s = \phi^2 D_0$. The water temperature of the hypolimnion had little difference and the average value was 18 °C, so calculated D_0 ($H_2PO_4^-$) = $7.15 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Krom and Berner, 1980).

3. Results and Discussion

3.1. pH

The pH values of vertical profiles decreased with depth across sediment-water interface and sediment pH values were lower than that of respective overlying water (Figure 2). The cause of this phenomenon maybe the gradual enhance of organic evolution and degradation with increasing depth (Xiao et al., 2011). The pH values at sediment-water interface were medium weak alkaline and ranged from 6.4 to 8.2 except for the sediment pH values of MDX03 and XX03, which were lower than 7.0. The vertical changes between CJBD and CTH were not significant, mainly correlated with the relatively similar environment conditions. Previous studies indicate that the pH value of the overlying water and sediment was a dominating factor (Ramin and Bates, 1979), while P release from the sediments occurred in neutral condition was less favorable than in both acidic and alkaline conditions (Jin et al., 2006b). So the currently pH values of sediments in the TGR would not significantly promote the P release.

3.2. Pi Concentrations of Water Body

Pi concentrations of water samples at different sites in the TGR varied greatly (Figure 3). For each sampling site, the average Pi concentration of open water was expressed as the average values of the surface, middle and bottom water of the

vertical profiles. The result shows that average Pi concentration of water body was in the order of surface pore water (0.052 mg/L) > overlying water (0.035 mg/L) > open water (0.018 mg/L). The export of P from surface sediments may act as a P source in the TGR. Because the sediment contains large quantities of dissolved substances, and the pore water as the medium of dissolved substances in the transportation from sediment to overlying water (Wu et al., 1996), has relatively higher Pi concentration than the corresponding overlying water and open water.

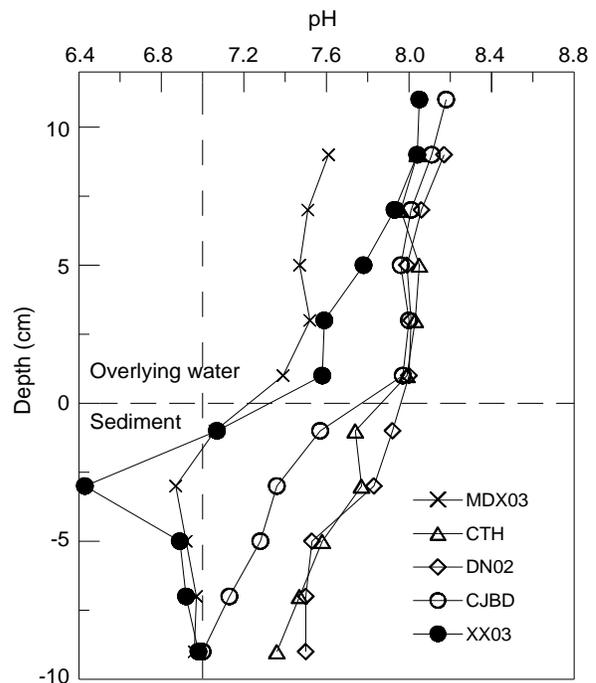


Figure 2. Vertical distributions of pH values at the sediment-water interface of different sampling locations.

The maximum and minimum of Pi concentrations occurred at MDX03 and DN02, which were appropriate for the three kinds of water body. There are several small hydropower stations in the Modaoxi River (Sun et al., 2011), such as Fotang, Ganhang and Changtan power station, probably due to the dam foundation, the deposition of external and internal organic matters resulted in the accumulation of phosphorous in the reservoir sediment (Liu et al., 2009) and then Modaoxi River had the highest Pi concentration among the sampling

sites. In contrast, Daning River appeared a better ecology and environment, owing to its relatively less population and high vegetation coverage (Ji et al., 2010; Yang et al., 2010). In the whole profile, Pi concentrations exhibited a steep increase at the surface sediment of MDX03, CTH and XX03, this and phenomenon was pervasively observed both in laboratory experiments (Bartoli et al., 2009; Jensen et al., 1995; Moore et al., 1998) and in field (Clavero et al., 2000; Jensen and Thamdrup, 1993; Kleeberg et al., 2010; Søndergaard, 2007; Selig and Schlunbaum, 2003). The Xiangxi River had a high and relatively fluctuant Pi concentration distribution across the sediment-water interface (Figure 4). Two reasons may be responsible to it. One is the high soil background value of phosphorus in the Xiangxi River basin, which was mainly caused by the drainages of phosphorus diggings and factory discharges (Li et al., 2007b), the other reason is the occurrence of the density currents in distributaries bay, and the latter is probably the main cause. Density currents are mainly resulted from the water temperature difference between the mainstream of the Yangtze River and tributaries bay (Ji et al., 2010; Yang et al., 2010). The upstream water of distributaries mainly flow down the slope and out of the bay driven by a bottom density current, meanwhile, the mainstream water of the Yangtze River enters into these backwater bays in reverse density currents. Thus Pi concentrations of the open water or at the sediment-water interface in the distributaries bay were fluctuated, which was influenced by continuous and complex water exchanging between these backwater bays and the mainstream of the Yangtze River.

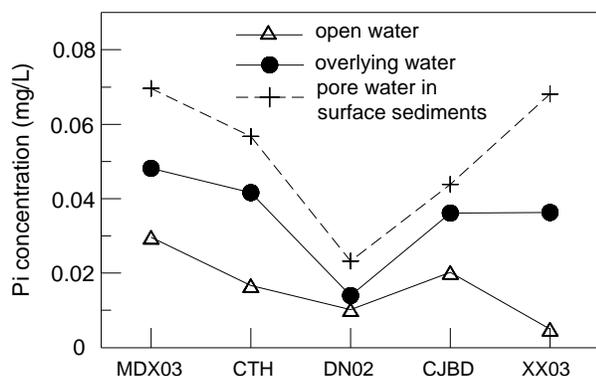


Figure 3. The average Pi concentrations of the open water, overlying water, and pore water (0 ~ 4 cm).

3.3. TP Contents and Phosphorus Fractions Composition

The amounts of TP in surface sediments (0 ~ 2 cm) of the five sampling sites with the mean value of 636.4 mg/kg, ranged at 415.5 ~ 1,047.9 mg/kg, which is similar to Han River, Korea (580 ~ 1,450 mg/kg) (Kim et al., 2004), and lower than that of Haihe River, China (968 ~ 2,017 mg/kg) (Sun et al., 2009). The sediment TP contents of five sampling sites were in the order of XX03 (1,047.9 mg/kg) > CJBD (666.2 mg/kg) > CTH (624.1 mg/kg) > DN02 (428.5 mg/kg). It im-

plies that the P load in the TGR sediments was not significant and Xiangxi River has relatively higher P load. The contents of different P fractions in surface sediments ranged greatly (Figure 5). For all sampling sites, surface P-fractions was in the order: HCl-P > Res-P > NaOH-P > BD-P > NH₄Cl-P, except XX03 with sequence of HCl-P > BD-P > Res-P > NaOH-P > NH₄Cl-P. The predominant fraction was HCl-P, and this distribution pattern was in accordance with that of the previous studies (Wang et al., 2008).

The HCl-P represents the P fraction sensitive to low pH and is fixated in Ca and Mg minerals (carbonates and apatite) (Christophoridis and Fytianos, 2006). HCl-P is a relatively stable fraction of sedimentary P and contributes to a permanent burial of P in the sediments (Hupfer et al., 1995). The HCl-P contents in surface sediments varied from 164.5 to 687.2 mg/kg, and the relative contribution ranged at 38.4 ~ 65.6%. Xiangxi River had the highest HCl-P contents and percentage among the sampling sites. Previous studies reported that the relatively higher HCl-P content can be attributed to the calcareous terrain of the recharge area (Jin et al., 2006b; Sun et al., 2009).

The NH₄Cl-P represents the loosely sorbed P in the sediments and is readily soluble under all conditions (Christophoridis and Fytianos, 2006). In the sampling sites of the TGR, the mean NH₄Cl-P amounts in surface sediments were the lowest among the five P fractions. The highest NH₄Cl-P amount was observed in XX03 (15.9 mg/kg), which was almost three times than that in MDX03 (5.9 mg/kg). The percentage of NH₄Cl-P contributing to TP was in the range of 1.4 ~ 2.2%. These results indicated that the NH₄Cl-P contributed little to TP in surface sediments.

The BD-P represents the redox-sensitive P forms, mainly bound to the surface of Fe (III) and Mn oxides and hydroxides (Christophoridis and Fytianos, 2006). This fraction is considered as potentially mobile pool of P (Kaiserli et al., 2002; Rydin, 2000), released by reductive Fe dissolution from anaerobic sediments (Christophoridis and Fytianos, 2006) and acted as an internal P source to the overlying water (Kleeberg and Kozerski, 1998). The BD-P amounts in the surface sediments ranged from 34.0 mg/kg (DN02) to 104.8 mg/kg (XX03), which contributed 7.9 ~ 11.2% to the TP and the percentage in different sites showed little difference. DO depletion, high pH level or bacterial activity that might enhance P-release from BD-P fraction, while high organic content in sediments might inhibit binding of P by Fe, by competition from binding sites (Kleeberg and Kozerski, 1998).

NaOH-P is the P fraction sorbed on the surface of aluminum hydroxides and the interior of ferric oxides of the sediment particles (Christophoridis and Fytianos, 2006), which is stored relatively as stable forms (Zhang et al., 2011). A 10.1 ~ 18.8% sedimentary TP in the studied samples was NaOH-P, which ranged from 75.8 to 111.5 mg/kg (Figure 5). Residual P consists mainly of refractory organic P as well as the inert inorganic P fraction (Rydin, 2000), ranged from 96.0 (CTH) to 140.8 mg/kg (DN02) at the five sites. The percentages of

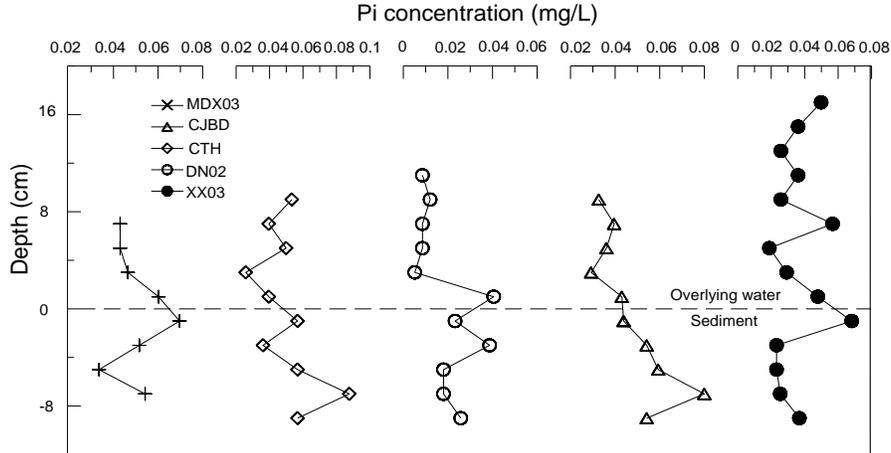


Figure 4. Pi concentrations of pore water and the corresponding overlying water.

Res-P in DN02 and MDX03 were even above 25%. This P fraction is considered to be “permanently bound” in comparison with other extract P forms (Rydin, 2000).

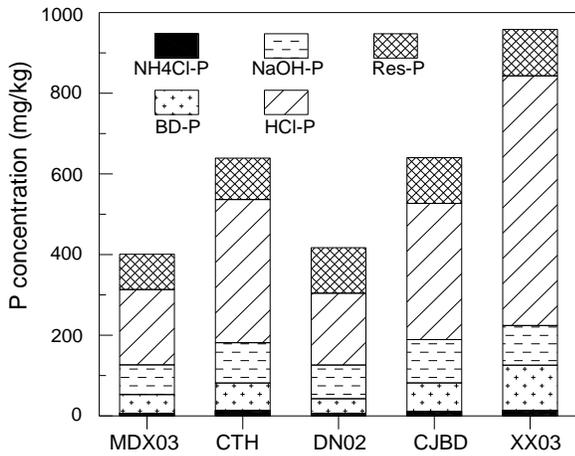


Figure 5. Concentrations of different P forms in surface sediments (0-2 cm) at the five sampling sites in the TGR.

Profile concentrations of various P forms in the sediments from five sampling sites are shown in Figure 6. The concentrations of $\text{NH}_4\text{Cl-P}$ and BD-P , acted as mobile P (Gächter et al., 1992), ranged from 35.6 to 157.4 mg/kg and contributed 8.4 ~ 15.8 % to the TP. Both $\text{NH}_4\text{Cl-P}$ and BD-P were stable throughout the sediment profile (except for XX03). XX03 had higher mean concentration (125.7 mg/kg) and mean percentage (13.2 %) of mobile P than other sampling sites, which was consistent with the results that Xiangxi River has relatively higher P load (Li et al., 2007b). The contents of HCl-P declined at 0 ~ 4 cm depth, over this depth interval there was an increase in the sampling sites. The increase of HCl-P in the sediment profile could have been due to the formation of refractory inorganic P forms during “aging” of the sediment (Rydin, 2000), where occlusion of P was one

possibility (Froelich, 1988). In different sites the concentrations of NaOH-P and Res-P varied greatly in the sediment profiles. The sampling sites of CJBD, DN02 and MDX03 in the whole profile followed the same order as surface sediments, which was $\text{HCl-P} > \text{Res-P} > \text{NaOH-P} > \text{BD-P} > \text{NH}_4\text{Cl-P}$. At site CTH, the rank order was $\text{HCl-P} > \text{NaOH-P}$, $\text{Res-P} > \text{BD-P} > \text{NH}_4\text{Cl-P}$. And the rank order was $\text{HCl-P} > \text{BD-P}$, Res-P , $\text{NaOH-P} > \text{NH}_4\text{Cl-P}$ at XX03. The trend of profile concentrations of various P forms between CTH and CJBD was similar, which reveals that the sampling site of CTH, located in estuary, was intensely influenced by the main stream.

3.4. Estimated Pi Release Fluxes

Release fluxes of orthophosphate (Pi) between water and sediments were summarized in Table 3, which ranged from $-0.003 \text{ mg/m}^2/\text{d}$ (XX03) to $0.013 \text{ mg/m}^2/\text{d}$ (MDX03) at the five sites. Negative values indicates Pi flux from water column into sediment (Moore et al., 1998). The result shows that the sediment in Xiangxi River might be a sink for phosphorus (negative flux), while the sediments at other sampling sites acted as P sources (positive fluxes) (Ullman and Sandstrom, 1987). The reasons might lie that the sediments in the TGR were newly and quickly deposited (Liu et al., 2012) and high Pi content of runoff (Luo et al., 2007) might reduce the P releasing rate from the sediments.

Compared with other studies, the Pi fluxes of the five sampling sediments in the TGR was relatively lower than that of Lake Dudinghausen (Chowdhury and Bakri, 2006) and Suma Park Reservoir (Chowdhury and Bakri, 2006). The minimum Pi flux for Xiangxi River (XX03) was even $-0.003 \text{ mg/m}^2/\text{d}$. Due to the sample was obtained in flood period, high Pi content of runoff and environmental conditions prompted XX03 as a sink of P. However, there are several factors influencing the P-release on the sediment-water interface, such as advection, bioturbation, irrigation, physical wave activity and current effects (Selig and Schlungbaum,

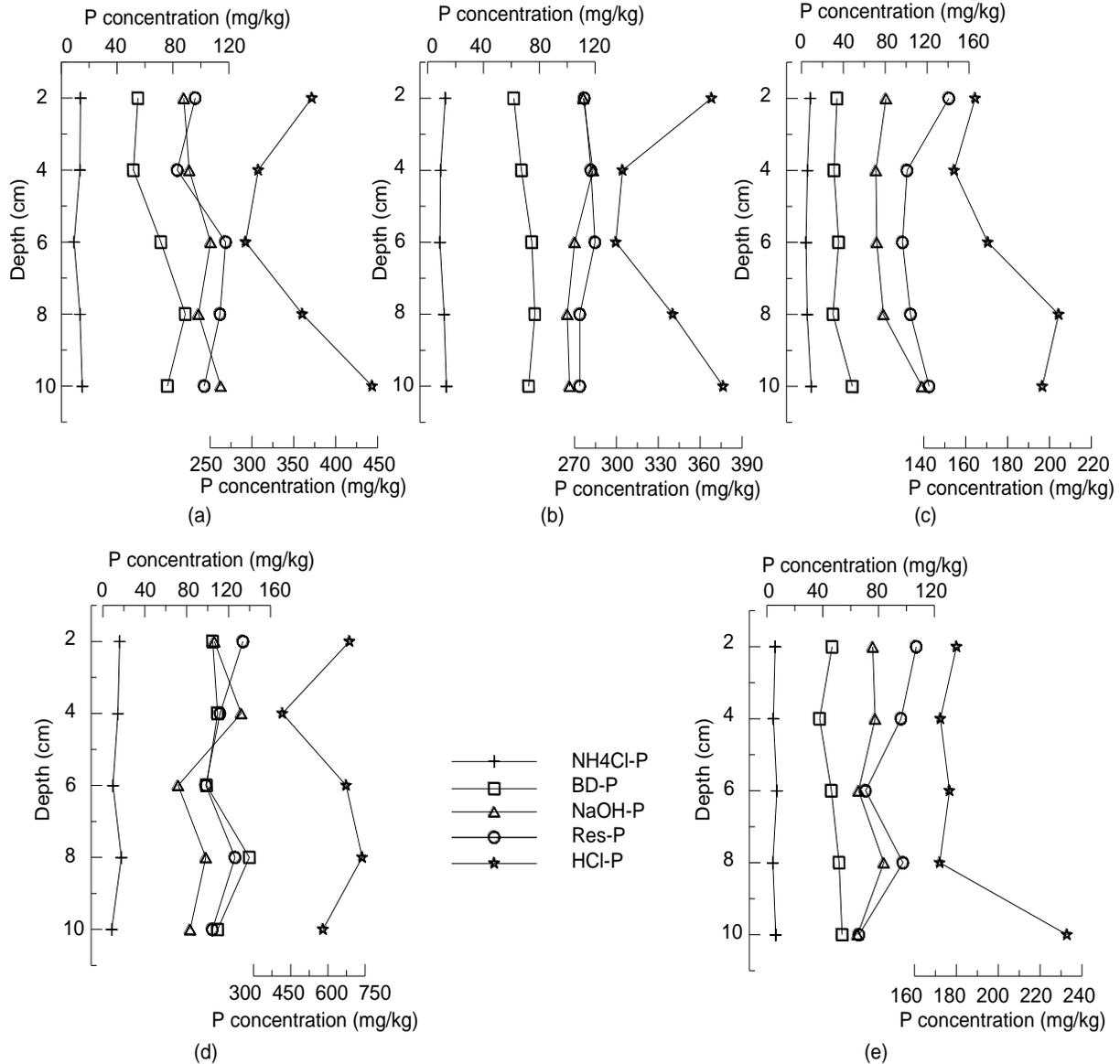


Figure 6. P forms in the sediment profiles from five sampling sites of the TGR, (a) at CTH; (b) at CJBD; (c) at DN02; (d) at XX03; (e) at MDX03.

Table 3. Comparison of P_i Fluxes among the Five Sampling Sites and Other Areas

Site	P_i fluxes ($mg/m^2/d$)	Reference
Three Gorges Reservoir, China	-0.003-0.013	This study
Lake Dudinghausen, Germany	0.041-0.567	Selig and Schlungbaum, 2003
Lake Tiefer, Germany	0.060-0.151	Selig and Schlungbaum, 2003
Suma Park Reservoir, Australia	0.05-0.22	Chowdhury and Bakri, 2006
Chaffey Reservoir, Australia	0.03-0.91	Sherman et al., 2001

2003). In addition, P_i flux from sediments is very sensitive to changes in O_2 status of the overlying water, with anaerobic conditions promoting large P fluxes (Moore et al., 1998). In conclusion, the sediments of the TGR acted both as a source and a sink for phosphorus, with relatively low P_i fluxes across

the sediment-water interface in summer. But due to the slower water flow, TP concentrations were decreased according to particulate deposition. However, the P load in sediments would release back to water under specific conditions (Yang et al., 2010). The density current was the main form of the

water exchange between mainstream and tributaries of the TGR (Yang et al., 2010), and the main stream reverse effect could aggravate the eutrophication of TGR water (Luo et al., 2007). The plunging depth and length of the density current were varied with seasonal variation of physico-chemical properties of water, the upstream inflow, water level in TGR and water level daily fluctuations (Ji et al., 2010), which might be an important determinant of mixing depth in Xiangxi River (Liu et al., 2012). In addition, TP concentration of surface water in the main stream of the Yangtze River was higher than tributaries bay (Yang et al., 2010). The main form of P was dissolved phosphorus in Spring (May) and Winter (February) while particle phosphorus was the main forms of P in summer (August) (Zeng et al., 2012). So, the values and changing features of Pi fluxes in other seasons of the TGR should be taken further research.

4. Conclusions

This study evaluated sediment characteristics, P forms and orthophosphate (Pi) concentrations as well as Pi release fluxes across the sediment-water interface in five sampling sites of the Three Gorges Reservoir (TGR). The TP contents of surface sediments (0 ~ 2 cm) ranged from 415.5 to 1,047.9 mg/kg, with the mean value of 636.4 mg/kg, where the mean values of NH₄Cl-P, BD-P, NaOH-P, HCl-P, and Res-P contents were 11.3, 60.4, 92.4, 354.3 and 118.0 mg/kg, respectively. The main rank order of P-fractions was: HCl-P > Res-P > NaOH-P > BD-P > NH₄Cl-P, and the predominant fraction was HCl-P, which is a relatively stable fraction of sedimentary P. TP contents and main P fraction (HCl-P) indicates that the P load in the TGR sediments was not significant.

Sediment pH values decreased with depth at all sites and was lower than that of respective overlying water. The average Pi concentration of water body was in the order of surface pore water (0.018 mg/L) > overlying water (0.035 mg/L) > open water (0.052 mg/L), which indicated that the export of P from surface sediments might act as a P source in the TGR. The release fluxes of orthophosphate (Pi) across sediment-water interface ranged from -0.003 mg/m²/d (XX-03) to 0.013 mg/m²/d (MDX03) at the five sites. In summer, the sediment of Xiangxi River might be a sink for phosphorus, while the sediments of other sampling sites acted as P sources.

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References

Abrams, M.M., and Jarrell, W.M. (1995). Soil phosphorus as a potential nonpoint source for elevated stream phosphorus levels. *J.*

- Environ. Qual.*, 24(1), 132-138. <http://dx.doi.org/10.2134/jeq1995.00472425002400010019x>
- Andersen, J.M. (1974). Nitrogen and phosphorus budgets and the role of sediments in six shallow Danish lakes. *Arch. Hydrobiol.*, 74(4), 528-550.
- Bakri, D.A., and Chowdhury, M. (2006). Internal nutrient flux in an inland water supply reservoir, New South Wales, Australia. *Lakes Reserv.: Res. Manage.*, 11(1), 39-45. <http://dx.doi.org/10.1111/j.1440-1770.2006.00286.x>.
- Bartoli, M., Longhi, D., Nizzoli, D., Como, S., Magni, P., and Viaroli, P. (2009). Short term effects of hypoxia and bioturbation on solute fluxes, denitrification and buffering capacity in a shallow dystrophic pond. *J. Exp. Mar. Biol. Ecol.*, 381(2), 105-113. <http://dx.doi.org/10.1016/j.jembe.2009.09.018>.
- Berner, R.A. (1980). Early diagenesis: A theoretical approach. Princeton University Press.
- Boström, B. (1988). Relations between chemistry, microbial biomass and activity in sediments of a sewage-polluted vs. a nonpolluted eutrophic lake. *Internationale Vereinigung fuer Theoretische und Angewandte Limnologie Verhandlungen IVTLAP*, 23(1), 451-459.
- Chen, K.F., Yang, D.Y., Jiang, H.T., Zhou, B., Xu, Y.H., Liu, Q.Y., and Dong, J. (2004). The geochemistry characteristic of weathering crust in the Three Gorge Areas-The example of CaoTang River drainage area in the Three Gorge Areas. *J. East China Inst. Technol.*, 27(2), 141-146.
- Chowdhury, M., and Bakri, D.A. (2006). Diffusive nutrient flux at the sediment-water interface in Suma Park Reservoir, Australia. *Hydro. Sci. J.*, 51(1), 144-156. <http://dx.doi.org/10.1623/hysj.51.1.144>.
- Christophoridis, C., and Fytianos, K. (2006). Conditions affecting the release of phosphorus from surface lake sediments. *J. Environ. Qual.*, 35(4), 1181-1192. <http://dx.doi.org/10.2134/jeq2005.0213>.
- Clavero, V., Izquierdo, J.J., Fernandez, J.A., and Niell, F.X. (2000). Seasonal fluxes of phosphate and ammonium across the sediment-water interface in a shallow small estuary (Palmones River, southern Spain). *Mar. Ecol. Prog. Ser.*, 198, 51-60.
- Correll, D.L. (1998). The role of phosphorus in the eutrophication of receiving waters: A review. *J. Environ. Qual.*, 27(2), 261-266. <http://dx.doi.org/10.2134/jeq1998.00472425002700020004x>
- Dahl, M., Dunning, C.P., and Green, T. (1993). Convective transport of chemicals across a sediment-water interface. *Water Sci. Technol.*, 28(8-9), 209-213.
- Deng, C.G., and Gong, L. (2007). The Study on the Trend of Eutrophication in the Three Gorges Reservoir. *J. Agro-Environ. Sci.*, 26, 279-282. doi:10.3321/j.issn:1672-2043.2007.z1.064.
- Egemose, S., Wauer, G., and Kleeberg, A. (2009). Resuspension behaviour of aluminium treated lake sediments: effects of ageing and pH. *Hydrobiologia*, 636(1), 203-217. <http://dx.doi.org/10.1007/s10750-009-9949-8>.
- Froelich, P.N. (1988). Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnol. Oceanogr.* 33(4), 649-668.
- Fu, B.J., Wu, B.F., Lü, Y.H., Xu, Z.H., Cao, J.H., Niu, D., Yang, G.S., and Zhou, Y.M. (2010). Three Gorges Project: Efforts and challenges for the environment. *Prog. Phys. Geog.*, 34(6), 741-754. <http://dx.doi.org/10.1177/0309133310370286>.
- Gächter, R., Tessier, A., Szabo, E., and Carignan, R. (1992). Measurement of total dissolved phosphorus in small volumes of iron rich interstitial water. *Aquat. Sci.*, 54(1), 1-9. <http://dx.doi.org/10.1007/BF00877261>.
- Hua, L.Z., He, X.B., Yan, C.Z., Wei, J., and Nan, H.W. (2009). Assessment of sediment delivery Ratio in Daning River Watershed based on AnnAGNPS Model. *Bull. Soil Water Conserv.*, 29(3), 154-158.

- Huang, Z.L. (2001). Biodiversity conservation for the Three Gorges project. *Chin. Biodivers.*, 9(4), 472-481. <http://dx.doi.org/10.3321/j.issn:1005-0094.2001.04.021>.
- Hupfer, M., Gächter, R., and Giovanoli, R. (1995). Transformation of phosphorus species in settling seston and during early sediment diagenesis. *Aquat. Sci.*, 57(4), 305-324. <http://dx.doi.org/10.1007/BF00878395>.
- Jensen, H.S., and Andersen, F.Ø. (1992). Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow, eutrophic lakes. *Limnol. Oceanogr.*, 37(3), 577-589.
- Jensen, H.S., Mortensen, P.B., Andersen, F.Ø., Rasmussen, E., and Jensen, A. (1995). Phosphorus cycling in a coastal marine sediment, Aarhusbay, Denmark. *Limnol. Oceanogr.*, 40(5), 908-917.
- Jensen, H.S., and Thamdrup, B. (1993). Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. *Hydrobiologia*, 253(1-3), 47-59. <http://dx.doi.org/10.1007/bf00050721>.
- Ji, D.B., Liu, D.F., Yang, Z.J., and Xiao, S.B. (2010). Hydrodynamic characteristics of Xiangxi Bay in Three Gorges Reservoir. *Sci. Sin. Phys., Mech. Astron.*, 40(1), 101-112.
- Jin, X.C., Wang, S.R., Bu, Q.Y., and Wu, F.C. (2006a). Laboratory experiments on phosphorous release from the sediments of 9 lakes in the middle and lower reaches of Yangtze River region, China. *Water Air Soil Pollut.*, 176(1-4), 233-251. <http://dx.doi.org/10.1007/s11270-006-9165-3>.
- Jin, X.C., Wang, S.R., Pang, Y., and Wu, F.C. (2006b). Phosphorus fractions and the effect of pH on the phosphorus release of the sediments from different trophic areas in Taihu Lake, China. *Environ. Pollut.*, 139(2), 288-295. <http://dx.doi.org/10.1016/j.envpol.2005.05.010>.
- Kaiserli, A., Voutsas, D., and Samara, C. (2002). Phosphorus fractionation in lake sediments-Lakes Volvi and Koronia, N. Greece. *Chemosphere*, 46(8), 1147-1155. [http://dx.doi.org/10.1016/S0045-6535\(01\)00242-9](http://dx.doi.org/10.1016/S0045-6535(01)00242-9).
- Khan, F.A., and Ansari, A.A. (2005). Eutrophication: an ecological vision. *Bot. Rev.*, 71(4), 449-482. [http://dx.doi.org/10.1663/0006-8101\(2005\)071\[0449:EAENV\]2.0.CO;2](http://dx.doi.org/10.1663/0006-8101(2005)071[0449:EAENV]2.0.CO;2).
- Kim, L.H., Choi, E., Gil, K.I., and Stenstrom, M.K. (2004). Phosphorus release rates from sediments and pollutant characteristics in Han River, Seoul, Korea. *Sci. Total. Environ.*, 321(1-3), 115-125. <http://dx.doi.org/10.1016/j.scitotenv.2003.08.018>.
- Kim, L.H., Choi, E., and Stenstrom, M.K. (2003). Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. *Chemosphere*, 50(1), 53-61. [http://dx.doi.org/10.1016/S0045-6535\(02\)00310-7](http://dx.doi.org/10.1016/S0045-6535(02)00310-7).
- Kleeberg, A., Herzog, C., Jordan, S., and Hupfer, M. (2010). What drives the evolution of the sedimentary phosphorus cycle? *Limnologia*, 40(2), 102-113. <http://dx.doi.org/10.1016/j.limno.2009.11.001>.
- Kleeberg, A., and Kozerski, H.P. (1998). Phosphorus release in Lake Großer Müggelsee and its implications for lake restoration. *Hydrobiologia*, 342/343, 9-26. <http://dx.doi.org/10.1023/A:1017079029053>.
- Krom, M.D., and Berner, R.A. (1980). The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments. *Limnol. Oceanogr.*, 25(2), 327-337.
- Li, C.M., Huang, Z.L., Zhang, S., and Chang, J.B. (2007a). Risk forecast of algal bloom in the Three Gorges Reservoir. *Resour. Environ. Yangtze Basin*, 16(1), 1-6.
- Li, F.Q., Ye, L., Liu, R.Q., Cao, M., and Cai, Q.H. (2007b). Investigation on aquatic environmental factors in Xiangxi River watershed. *Ecol. Sci.*, 26(3), 199-207.
- Li, F.Q., Ye, L., Liu, R.Q., Cao, M., and Cai, Q.H. (2008). Dynamics of main nutrient input to Xiangxi Bay of the Three-Gorges Reservoir. *Acta Ecol. Sin.*, 28(5), 2073-2079. [http://dx.doi.org/10.1016/S1872-2032\(08\)60044-X](http://dx.doi.org/10.1016/S1872-2032(08)60044-X).
- Liu, C., Wang, Q.X., and Watanabe, M. (2006). Nitrogen transported to three Gorges Dam from agro-ecosystems during 1980-2000. *Biogeochemistry*, 81(3), 291-312. <http://dx.doi.org/10.1007/s10533-006-9042-6>.
- Liu, C.Q., Wang, F.S., Wang, Y.C., and Wang, B.L. (2009). Responses of aquatic environment to river damming-from the geochemical view. *Resour. Environ. Yangtze Basin*, 18(4), 384-396.
- Liu, L., Liu, D.F., Johnson, D.M., Yi, Z.Q., and Huang, Y.L. (2012). Effects of vertical mixing on phytoplankton blooms in Xiangxi Bay of Three Gorges Reservoir: Implications for management. *Water Res.*, 46, 2121-2130. <http://dx.doi.org/10.1016/j.watres.2012.01.029>.
- Luo, Z.X., Zhu, B., Zheng, B.H., and Zhang, Y. (2007). Nitrogen and phosphorus loadings in branch backwater reaches and the reverse effects in the main stream in Three Gorges Reservoir. *China Environ. Sci.*, 27(2), 208-212.
- Moore, P.A., Reddy, K.R., and Fisher, M.M. (1998). Phosphorus flux between sediment and overlying water in Lake Okeechobee, Florida: spatial and temporal variations. *J. Environ. Qual.*, 27(6), 1428-1439. <http://dx.doi.org/10.2134/jeq1998.00472425002700060020x>
- Mortimer, R.J.G., Krom, M.D., Watson, P.G., Frickers, P.E., Davey, J.T., and Clifton, R.J. (1998). Sediment-water exchange of nutrients in the intertidal zone of the Humber Estuary, UK. *Mar. Pollut. Bull.*, 37(3-7), 261-279. [http://dx.doi.org/10.1016/S0025-326X\(99\)00053-3](http://dx.doi.org/10.1016/S0025-326X(99)00053-3).
- Murphy, J., and Riley, J.P. (1962). A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.*, 27, 31-36. [http://dx.doi.org/10.1016/S0003-2670\(00\)884445](http://dx.doi.org/10.1016/S0003-2670(00)884445).
- Ramin, N., and Bates, M.H. (1979). The effects of pH on the aluminum, iron and calcium phosphate fractions of lake sediments. *Water Res.*, 13, 813-815. [http://dx.doi.org/10.1016/0043-1354\(79\)90247-1](http://dx.doi.org/10.1016/0043-1354(79)90247-1).
- Rydyń, E. (2000). Potentially mobile phosphorus in Lake Erken sediment. *Water Res.*, 34(7), 2037-2042. [http://dx.doi.org/10.1016/S0043-1354\(99\)00375-9](http://dx.doi.org/10.1016/S0043-1354(99)00375-9).
- Søndergaard, M. (2007). Nutrient dynamics in lakes-with emphasis on phosphorus, sediment and lake restoration. Ph.D. dissertation, Freshwater Ecology, University of Aarhus, Denmark.
- Selig, U., and Schlungbaum, G. (2003). Characterisation and quantification of phosphorus release from profundal bottom sediments in two dimictic lakes during summer stratification. *J. Limnol.*, 62(2), 151-162.
- Sherman, B., Ford, P., Hatton, P., Whittington, J., Green, D., Baldwin, D., Oliver, R., Shiel, R., Berkel, J.v., Beckett, R., Grey, L., and Maher, B. (2001). The Chaffey Dam Story. Final report for CRCFE projects B.202 and B.203. Murray-Darling Freshwater Research Centre.
- Sun, R., Yuan, X.Z., Liu, H., and Li, X. (2011). Influence of cascaded exploitation of small hydropower on riparian plant communities in Modaoxi River. *Adv. Water Sci.*, 22(4), 561-567. <http://dx.doi.org/CNKI:32-1309-P-20110514-1449-019>.
- Sun, S.J., Huang, S.L., Sun, X.M., and Wen, W. (2009). Phosphorus fractions and its release in the sediments of Haihe River, China. *J. Environ. Sci.*, 21(3), 291-295. [http://dx.doi.org/10.1016/S1001-0742\(08\)62266-4](http://dx.doi.org/10.1016/S1001-0742(08)62266-4).
- Ullman, W.J., and Aller, R.C. (1982). Diffusion coefficients in nearshore marine sediments. *Limnol. Oceanogr.*, 27(3), 552-556.
- Ullman, W.J., and Sandstrom, M.W. (1987). Dissolved nutrient fluxes from the nearshore sediments of Bowling Green Bay, central Great Barrier Reef Lagoon (Australia). *Estuar. Coast. Shelf Sci.*, 24, 289-

303. [http://dx.doi.org/10.1016/0272-7714\(87\)90051-5](http://dx.doi.org/10.1016/0272-7714(87)90051-5).
- Wang, Y., Shen, Z.Y., Hu, L.J., and Niu, J.F. (2008). Adsorption and release of phosphorus from sediments from the main branches of the Three-Gorges Reservoir. *Acta Sci. Circumstant.*, 28(8), 1654-1661.
- Wang, Y.C., Huang, R.G., and Wan, G.J. (1998). A newly developed sampler for collecting samples near the lacustrine sediment-water interface. *Geol. Geochem.*, 1(1), 94-96.
- Wei, F.S., Qi, W.Q., and Hong, S.J. (2002). Water and wastewater monitoring and analysis method. 4th ed. Beijing: China Environmental Science Press.
- Wu, F.C., Wan, G.J., and Cai, Y.R. (1996). Biogeochemical processes at the sediment-water interface. *Adv. Earth Sci.*, 11(3), 191-197. <http://dx.doi.org/10.3321/j.issn:1001-8166.1996.02.013>
- Wu, J.G., Huang, J.H., Han, X.G., Xie, Z.Q., and Gao, X.M. (2003). Three-Gorges Dam-Experiment in habitat fragmentation? *Science*, 300(5623), 1239-1240. <http://dx.doi.org/10.1126/science.1083312>.
- Xiao, S.B., Liu, D.F., Wang, Y.C., Gao, B., Wang, L., and Duan, Y.J. (2011). Characteristics of heavy metal pollution in sediments at the Xiangxi Bay of Three Gorges Reservoir. *Resour. Environ. Yangtze Basin*, 20(8), 983-989.
- Xie, L.Q., Xie, P., and Tang, H.J. (2003). Enhancement of dissolved phosphorus release from sediment to lake water by Microcystis blooms-an enclosure experiment in a hyper-eutrophic, subtropical Chinese lake. *Environ. Pollut.*, 122, 391-399. [http://dx.doi.org/10.1016/S0269-7491\(02\)00305-6](http://dx.doi.org/10.1016/S0269-7491(02)00305-6).
- Yang, Z.J., Liu, D.F., Ji, D.B., and Xiao, S.B. (2010). Influence of the impounding process of the Three Gorges Reservoir up to water level 172.5 m on water eutrophication in the Xiangxi Bay. *Sci. China Tech. Sci.*, 40(4), 1114-1125. <http://dx.doi.org/10.1007/s11431-009-0387-7>.
- Ye, L., Xu, Y.Y., Han, X.Q., and Cai, Q.H. (2006). Daily dynamics of nutrients and chlorophyll a during a Spring phytoplankton bloom in Xiangxi Bay of the Three Gorges Reservoir. *J. Freshwater Ecol.*, 21(2), 315-321. <http://dx.doi.org/10.1080/02705060.2006.9665001>.
- Zeng, F.H., Zhang, S., Xiong, Q., Lv, P.L., and Lan, F. (2012). Seasonal variation of nitrogen and phosphorus in three-gorge reservoir. *China Environ. Sci.*, 28(5), 29-32.
- Zhang, S., Li, C.M., Zheng, B.H., Zhai, C.Z., Zheng, J., and Zhang, Q. (2007). Trophic states and nutrient output of tributaries bay in Three Gorges Reservoir after impoundment. *Environ. Sci.*, 28(3), 500-505. <http://dx.doi.org/10.3321/j.issn:0250-3301.2007.03.010>
- Zhang, Z.J., Wang, Z.D., Wang, Y.W., Chen, X.Y., Wang, H., Xu, X., Lin, X.Y., and Czapar, G.F. (2011). Properties of phosphorus retention in sediments under different hydrological regimes: A laboratory-scale simulation study. *J. Hydrol.*, 404(3-4), 109-116. <http://dx.doi.org/10.1016/j.jhydrol.2010.06.018>.
- Zheng, B.H., Cao, C.J., Qin, Y.W., and Huang, M.S. (2008). Analysis of nitrogen distribution characters and their sources of the major input rivers of Three Gorges Reservoir. *Environ. Sci.*, 29(1), 1-6. <http://dx.doi.org/10.3321/j.issn:0250-3301.2008.01.001>
- Zhou, Q.X., Gibson, C.E., and Zhu, Y.M. (2001). Evaluation of phosphorus bioavailability in sediments of three contrasting lakes in China and the UK. *Chemosphere*, 42(2), 221-225. [http://dx.doi.org/10.1016/S0045-6535\(00\)00129-6](http://dx.doi.org/10.1016/S0045-6535(00)00129-6).