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The fate of phosphorus in sediments after the full operation of the Three Gorges Reservoir, China^{\star}

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ABSTRACT

The hydro-dynamic conditions have been changed after the impoundment of Three Gorges Reservoir (TGR), which result in changes of phosphorus (P) distribution in sediments. To investigate the variation and storage of P in the surface sediments of the TGR, continuously and intermittently submerged sediment samples were collected from 14 sites in 2014, and P fractions were analyzed using a modified Hedley sequential extraction method. The results showed that the concentrations of total P (TP) (904 \pm 105 mg/kg) in the sediments did not exhibit an apparent spatial trend. A decreasing trend of bioavailable P (Bio-P) concentration in the continuously submerged sediment (177 \pm 29 mg/kg) was observed from Fuling to Zigui, while an opposite trend appeared in the intermittently submerged sediment (139 \pm 49 mg/kg) from Jiangjin to Zigui. The water depth and sediment grain size had important implications for the variation of the Bio-P in the sediments along the TGR. After the full operation of the TGR, the concentration of TP in the intermittently submerged sediment is a major P pool of the TGR with an annual Bio-P deposition flux of 2.14 \times 10⁴ t/a, of which 87% was retained in the reaches from Fuling to Zigui. Considering the slow release of P from the sediment (0.16 -2.75 t/a), the sediment has been a P "sink" since the full operation of the TGR in 2010.

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1. Introduction

Phosphorus (P) has been regarded as one of the limiting nutrients in freshwater ecosystems (Correll, 1999; Reddy et al., 1999). P bioavailability in the sediment is an important factor for eutrophication (Correll, 1998), which is one of the most serious problems in reservoirs, lakes and rivers. External inputs of P can be stored in sediment, and the internal P release from sediment could become a fundamental long-term P source to the overlying water after the external P load is controlled (Wang et al., 2009). Soluble P interacts strongly with sediment by the combined processes of sorption/ desorption and mineral precipitation/dissolution (House, 2003). As dams constructed, sediment deposition condition changed and impacted the adsorption and retention of P in reservoirs (Klaver et al., 2007; Withers and Jarvie, 2008; Kunz et al., 2011; Cunha et al., 2014).

The total P (TP) concentration in sediment is not always adequate to assess the P release risk associated with its presence in natural waters (Katsaounos et al., 2007). The stability and chemical fractions of P in sediment affect the level of dissolved P in the water column. The P fraction feature of sediment is commonly based on sequential chemical extractions, in which bioavailable P (Bio-P) is supposed to be selectively removed from different compounds in the sediment (Pettersson et al., 1988). Loosely bound inorganic/ organic P and P combined with metal oxides/hydroxides (such as Al/Fe/Mn combined P) is identified as Bio-P (Sondergaard et al., 2003). The Bio-P can be released from the sediment under certain conditions, such as a change in the water flow velocity, pH, dissolved oxygen (DO) or redox potential (Eh) (Christophoridis and Fytianos, 2006). Apart from aquatic environmental conditions, sediment properties (grain size, organic matter, metal oxides/hydroxides) are also important factors that influence the release of P







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from sediment (Boström et al., 1988).

The Three Gorges Dam (TGD), located on the main channel of the Yangtze River, is the biggest hydroelectric dam in the world. The Three Gorges Reservoir (TGR, 29°16' to 31°25' N, 106°20' to 111°50' E) covers the reach of Yangtze River between Jiangjin and Zigui with a total water surface area of 1.08×10^3 km² and a storage capacity of 39.3 billion m³ at a water level of 175 m (Bao et al., 2015). The TGR was impounded to the elevations of 135 m. 156 m, and 175 m above the sea level in 2003, 2006, and 2010, respectively. Therefore, the TGR was fully operational in 2010 with water level fluctuating between 145 m (from April to September) and 175 m (from October to mid-April). The water-level fluctuation zone, with area of 349 km², was formed after the full operation of the TGR (areas with different slopes and altitudes see Table S1). The hydro-dynamic conditions and geochemical processes of P have changed since the impoundment of the TGR with a water level of 175 m.

After the first impoundment of the TGR in 2003, the water flow velocity decreased (Lan, 2005) and the spatial distribution of sediment changed (Hu et al., 2013). Approximately 70% of the annual sediment discharge from the upper reaches of the Yangtze River was trapped in the TGR (Yang et al., 2006). A downstream decrease in the concentration of suspended particles and TP in the water column was also observed (Ding et al., 2013; Huang et al., 2014). The operation of the TGR has a great impact on the sediment of the water-level fluctuation zone. The sediment undergoes periodic wet-dry cycles, which causes changes in sediment properties (Zhang et al., 2012; López et al., 2016). The variation of P in the sediment of the water-level fluctuation zone is associated with sediment properties, and the P exchange at the sediment-water interface is altered when the sediment is submerged again (Steinman et al., 2012; Ni et al., 2015).

Many studies investigated and modeled the transportation and release of P, and revealed the distribution of P in some reaches of the TGR before the water level was elevated to 175 m (Wang et al., 2009; Cao et al., 2011; Zhang et al., 2012; Huang et al., 2015; Wang et al., 2015). However, few studies have a look at the variations of P in sediment in the whole TGR due to the changes of hydrodynamics and geochemical processes after the water level rose to 175 m. The role that the sediment plays in the P cycling after the full impoundment of the TGR is still unclear.

Therefore, to understand the distribution of sediment P and its potential effects, total P and its fractions in the continuously and intermittently submerged sediment were investigated. The objectives of this work are: 1) to clarify the spatial and temporal variations in the status of sediment P and the controlling factors after the water level reached 175 m; 2) to reveal the influences of the operation of the TGR on the variations of sediment P; and 3) to evaluate the Bio-P pool in the sediment and its potential influences on the water quality of the TGR.

2. Materials and methods

2.1. Study area

The TGR area, which is mainly controlled by the humid subtropical monsoon climate, has a mean annual temperature and precipitation of 16–19 °C and 1000–1200 mm respectively. The geomorphological characteristics of the TGR were reported by Bao et al. (2015). The fluctuant and permanent backwater zones were formed after the operation of the TGR. The terminal of backwater reaches Jiangjin (S1) when the water level rises to 175 m, and withdraws to Changshou (S3) after the water level falls to 145 m. Therefore, the fluctuant backwater zone (FBZ) is from Jiangjin (S1) to Changshou (S3), and the permanent backwater zone (PBZ) is from Changshou (S3) to Zigui (S14) (Fig. 1). The deposition of sediment in the TGR mainly appears in the PBZ with an elevation below 145 m, 75% of which is stored in the reaches from Fuling (S6) to Fengjie (S11) (Yuan et al., 2013; Li and Zhang, 2015). A little sediment is deposited in the water-level fluctuation zone, and the deposited sediment distributes in the width, lower sections of the zone with a slope of less than 25° (Bao et al., 2015).

Considering the distribution of deposited sediment in the TGR, 14 sites in the water-level fluctuation zone from Jiangjin (S1) to Zigui (S14) were selected to collect the intermittently submerged sediment (Fig. 1, Table S2). The coarse particles could not be sampled by a gravity sampler from the continuously submerged sediments in the FBZ from Jiangjin (S1) to Fuling (S5), therefore, only seven sites in the PBZ from Fuling (S6) to Zigui (S14) were selected to collect the continuously submerged sediment samples (Fig. 1).

2.2. Sample collection

The intermittently submerged sediment was collected at an elevation of 150 m at the 14 sites in July 2014. At each sampling site, three sediment profiles were hand-dug and sediment from 0 to 30 cm depth in each profile was collected and mixed for one sample. Three continuously submerged sediment cores were collected by a gravity sampler (100 cm long and 6 cm internal diameter) at the seven sites. The upper 30 cm of sediment in each core was used as one sample. The sediment samples were dried at 40 °C in the laboratory to a constant weight, and the dried samples were grounded to powder when needed before the analysis.

2.3. Chemical analysis

Original sediment sample (5 g) for the grain size analysis was placed in a beaker, which was rinsed beforehand. HCl (5% in volume) and H_2O_2 were added to remove carbonates and organic matter respectively, and then the sample was washed to neutral by deionized water. The residues were dispersed with an ultrasonic oscillator for 1 min after mixing with a dispersant solution ((Na₂PO₃)₆). The grain size was measured using a Mastersizer 2000 Laser Grain-size Meter (clay: <4 µm; silt: 4–64 µm; sand: >64 µm).

The organic matter (OM) content was measured using the method of loss on ignition (LOI), which consists of the burning of a 5 g sediment sample for 4 h at 550 °C in a muffle. The pH of the sediment was measured in a 1:2.5 sediment/water suspension using a glass electrode and a potentiometer (HACH Co., HQ30d, with the accuracy of 0.01 pH).

Amorphous Al, Fe, Mn (Fe_{ox}, Al_{ox}, Mn_{ox}) were extracted by oxalic acid and ammonium oxalate (pH = 3.5). The sediment used for the analysis of the TP, Ca, Mg concentrations was digested with HNO₃-HF-HClO₄. P, Al, Fe, Mn, Ca, and Mg in extracted suspensions were analyzed using an American Leeman Labs Profile Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, detection limit: 0.02 mg P/L, 0.01 mg Al/L, 0.002 mg Fe/L, 0.5 mg Mn/L). Standard solution SPEXTM from the USA was used as the standard. Quality control was assured by the analysis of duplicate samples, blanks, and reference materials (GSD-9 and GSD-11, Chinese geological reference materials). The precision was good with variability in the repeated analysis of samples and reference materials below 5%. Recovery was 90 \pm 6% (error expressed as a 95% confidence interval) for the reference materials.

The modified P sequential extraction method (Hedley et al., 1982) was used to separate the P fractions in the sediment of the TGR. Briefly, the fractionation procedure was performed as follows: the dried sediment (0.5 g) was transferred to 50 mL flasks and sequentially extracted with: 1) 20 mL deionized water and two

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