Phosphorus distribution and sorption-release characteristics of the soil from newly submerged areas in the Danjiangkou reservoir, China

Zhixin Song, Baoqing Shan, Wenzhong Tang, Hong Zhang, Chao Wang, Yu Zhao

A State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
b University of Chinese Academy of Science, Beijing 100049, China

A R T I C L E   I N F O
Article history:
Received 31 August 2016
Received in revised form 21 November 2016
Accepted 21 November 2016
Available online 27 November 2016

Keywords:
Newly submerged area
P
Distribution
Sorption-release

A B S T R A C T
The phosphorus (P) distribution and sorption-release characteristics of the surface soil in new submerged areas from the Danjiangkou Reservoir were investigated, and assessed the potential risk of P released from the soils. The results indicated that the TP (total phosphorus) contents in the soils varied from 161.01 mg/kg to 1150.94 mg/kg, and the mean content value of TP was the highest in arable land (732.91 mg/kg), especially distributed in arable land above 160 m elevation; Calcium bound phosphorus (HCl-P) was the major fraction of TP, the proportion was ranged from 60.77% to 83.38% for different land using types; the highest proportion of OP (organic phosphorus) was 32.07% in grass land soils. For all the samples, the rank order P-fractions was HCl-P > OP > NaOH-P (Phosphorus bound to Al and Fe oxides). Besides, the contents of TP correlated significantly with the HCl-P contents, (r = 0.936, P < 0.01), NaOH-P contents (r = 0.661, P < 0.01), OP contents (r = 0.762, P < 0.01), and IP contents (r = 0.970, P < 0.01), but OP contents was no significantly correlated with HCl-P. NaOH-P contents. The sorption capacity of soil ranged from 578.79 to 1457.44 mg/kg, and the amount of P released from the soils were ranged from 0.635 to 5.957 mg/kg; however, due to the concentration of P in the overlying water, about 80% of the newly submerged area would act as sink of P.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Since 2002, China has been implementing the Middle Route of the South-to-North Water Diversion Project transferring water from the Danjiangkou Reservoir to the Huabei (north China region) for irrigation, domestic and industrial usage (Jarvie et al., 2005). After completion of the Danjiangkou Reservoir dam heightening project, the storage level increased from 157 to 170 m, and large soil areas are submerged by water, which has potential ecological risk due to previous human activities in the newly submerged areas. The P accumulated in newly submerged area could be releasing into the water, and affecting the water quality (Ulen et al., 2007), causing eutrophication of reservoir (McDowell et al., 2002). However, there is very little known about the distribution characteristics and P release risk in newly submerged area.

P is a major contributor to the eutrophication of freshwater ecosystems, and in most freshwater systems it limits primary production (Edwards and Withers, 2007), its excess supply can lead to eutrophication (Schindler et al., 2008). When the external loading of P increased, the soils act as a sink can absorb it (Sattari et al., 2012). However, after the external loading is reduced, the soils as a source would release the adsorbed P back into water (Williams et al., 1970). The characteristics of soils, environmental factors, and concentration of P in the overlying water (Kronvang et al., 2005), will affect the transfer direction of phosphate on the interface of the soil–water (Carpenter, 2005). P in soils of newly submerged area of the Danjiangkou Reservoir would have physical, chemical and biological exchanges through overlying water (Williams et al., 1971). Therefore, under certain conditions, the soil may acts as a source or sink for P that can affect the trophic status of the Danjiangkou Reservoir (Eveborn et al., 2014). However, not all of the P fractions can be released from soils into the overlying water (Dong et al., 2011), the P behavior in soils for promoting reservoir eutrophication can be more efficiently evaluated based on the P fractions (Huo et al., 2011). The aims of this study were to investigate the characteristics of the phosphorus fractions (inorganic P (IP)), calcium-bound...
P extracted using hydrochloric acid (HCl-P), Al and Fe oxide- and oxihydroxide-bound P extracted using sodium hydroxide (NaOH-P), organic P (OP), OP, and TP according to the SMT protocol (Ruban et al., 1999; Ahlgren et al., 2011), and according to different land use types and elevation, describe isotherms of P sorption, to calculate the characteristics of the P sorption or release from the soils of the newly submerged area, and assessment risk of potential phosphorus release situation.

2. Experimental

2.1. Study area

The Danjiangkou Reservoir (32°36′–33°48′N, 110°59′–111°49′E) is located in the juncture of Hubei and Henan province, China (Fig. 1), built in 1970s, area of water surface is 745 km². It has a subtropical monsoon humid climate, with an average annual temperature is 15.8 °C, and an average annual precipitation is 804.3 mm, rainfall in the area is abundant but uneven, and mainly precipitation in July and September. The first phase of Danjiangkou Reservoir dam was completed in 1973 and the storage level is 157 m (water level above sea), after the 2nd phase completed in 2014, the storage level up to 170 m, the area of newly submerged land up to 307.7 km², covered 26 counties (cities) of Henan and Hubei province. The water periodic scheduling would take place from May 1 to June 21 every year. The water level would be gradually reduced from 170 m to 160 m in summer. On August 21, the reservoir allowed gradually began filling water up to 163.5 m. After October 1, the reservoir was filled to the normal storage level of 170 m. During this period (one year), the water level fluctuates between 160 m and 170 m, indicating a variation in water level of up to 10 m in the submerged land zone.

The study area was located at the main newly submerged area, in Xichuan, which are tributaries to Henan province. A map of the study area is shown in Fig. 1. Basic information of the sampling sites distribution and the number of sampling sites between in different elevation zones as shown in Table S1.

2.2. Sample collection and analysis

Based on the high–resolution remote-sensing images of the Danjiangkou Reservoir area, we divided the newly submerged area into several investigation units, as shown in Table S1. We designed the scheme according to the samples site uniformity, representativeness, feasibility principle, and percentage of different land using types of total the newly submerged area. Using GPS (Global Positioning System) positioning and sampling soils in each survey unit (Fig. 1), and 92 samples were collected. Sampling points were distributed evenly in the newly submerged area of Xichuan County; covered the different land using types and elevation (Table S1). In July 2014, the sample were collected surface to 10 cm depth soil samples (Peng et al., 2007), the samples sealed polyethylene bags, keep in 4 °C condition. Upon arrival in laboratory, the samples were freeze dried by using FD–1A–50 freeze drier, and then mixed thoroughly.

Organic matters (SOM) in sediment were determined by loss of ignition at 550 °C for 4 h. The grain-size distribution was determined by laser particle size analyzer (Mastersizer 2000, Malvern, USA) and classified into clay (<0.002 mm), silt (0.002–0.05 mm), and sand (0.05–2 mm) (Gee and Bauder, 1986). The contents of main elements in soil were measured by atomic absorption spectrometry.

2.3. Phosphorus fractions

The soil samples were sieved with a standard 100-mesh sieve, and sequential P fraction was carried out by using the SMT protocol (Zhu et al., 2013), as shown in Fig. S1. The SMT protocol, proposed by the Community Bureau of Reference, was applied to extract five P fractions: IP, HCl-P, NaOH-P, OP and TP (Zhang et al., 2012). P was separated into five fractions by this method. P bound to Al, Fe, and Mn oxides and oxihydroxides were extracted by NaOH. P bound to calcium was extracted using HCl and the residual P was treated at 450 °C to produce the OP fraction. The TP in the soils was determined by processing the sample at 450 °C, followed by HCl extraction. The P concentrations in the supernatant of the extractions were analyzed by using the molybdenum blue method (Jin et al., 2013).

2.4. Phosphate sorption kinetic experiments

Dried soil samples (0.5 g) were added in a series of 100 ml acid-washed screw-cap centrifuge tubes with 50 ml P solution (KH₂PO₄, containing 10 mg/L). Besides, two drops of chloroform were added to inhibit the bacterial activity. The centrifuge tubes were capped and incubated at 25 ± 1 °C in an orbital shaker at 200 rpm for different time intervals, varying within 64 h (0, 0.25, 0.5, 1, 2, 3, 5, 7, 9, 18, 27, 36, 48, and 64 h). The samples were immediately centrifuged at 4390 × g for 15 min, and filtered through 0.45 μm GF/C filter membrane, the results described in following sections are mean of three analyzing parallel samples (Pan et al., 2013).

2.5. Phosphate sorption isotherm experiments

We determined the dissolved phosphorus concentration at which there is no net adsorption or release of dissolved P from soils (equilibrium P concentration value, EPC₀). To determine EPC₀ for each soil samples, 0.5 g sample were put into the 100 ml screw cap centrifuge tubes and 50 ml P standard solutions (anhydrous KH₂PO₄) of various concentrations ranged from 0 mg/L to 20 mg/L (0, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 mg/L P). The conditions of the other experiments were the same as that of the adsorption kinetics experiments. After equilibration, the solutions were centrifuged at 4390 × g for 15 min and supernatants were removed for P analysis (Jin et al., 2013).

In order to evaluate whether the settled matter as sediment acted as a sink or source in the water system, modified Langmuir adsorption model was used to obtain the equilibrium P concentration value (EPC₀). The phosphate sorption capacity was fitted by Lopez et al. (Lopez et al., 1996)

\[ Q = \frac{Q_{\text{max}} \times C}{K_d + C} \]  

(1)

where C is the P sorption equilibrium concentration (mg/L), Q is the P sorption capacity (mg/kg dry weight) and is the absorbed P when the equilibrium is reached, Qmax is the maximum P sorption capacity (mg/kg dry weight), Kd is the half-saturation concentration (mg/L), i.e., the phosphate concentration that must be added to obtain an sorption equal to the half Qmax, and the slope of sorption isotherm is a measure of the P sorption efficiency of sediments (Zhang et al., 2012).

In order to judge whether the soil acts as a source or sink of P for the surface water (Pan et al., 2002), defined a criterion of \( \lambda = C/EPC₀ \), and Jarvie defined EPCₜₕₑₚₑ = ((EPC₀ – DIP)/EPC₀) × 100%, DIP (dissolved inorganic phosphate) (Jarvie et al., 2014). However, EPC₀ is in the denominator in both equations, both of the methods could easily enlarge the measurement error especially when EPC₀ is low. Here, we developed a new simple criterion δ. According to Eq. (1) adsorption isotherm, EPC₀ is the zero equilibrium concentration (mg/L), Ceq is the concentration of DIP in water samples. We define:

\[ \delta = C_{\text{eq}} - EPC₀ \]

(2)
Table 1

| Item               | Range       | Mean       | Median     | SD         |
|--------------------|-------------|------------|------------|------------|
| SOM (mg/kg)        | 7654.32–20827.67 | 12568.11   | 11432.21   | 6544.28    |
| TP (mg/kg)         | 161.01–1150.94 | 498.09     | 534.59     | 206.42     |
| Al (mg/kg)         | 45763.78–79762.23 | 62015.56   | 63211.47   | 9712.43    |
| Fe (mg/kg)         | 28926.82–44783.36 | 36344.44   | 34872.28   | 4463.81    |
| Mn (mg/kg)         | 457.89–723.46 | 572.88     | 560.43     | 134.93     |
| Ca (mg/kg)         | 5242.31–45327.94 | 16617.78   | 10538.92   | 11946.22   |
| Clay (%)           | 3.52–12.98   | 9.51       | 11.23      | 7.36       |
| Silt (%)           | 51.96–71.93  | 63.96      | 65.32      | 26.31      |
| Sand (%)           | 18.23–35.82  | 26.54      | 28.14      | 27.17      |

when $\delta < 0$ (desorption), sediment is a source of P; When $\delta > 0$ (adsorption), sediment is a sink for P.

2.6. Statistical analysis

Sample points distribution was generated using ArcGIS 9.3; the data was analyzed using SPSS 16.0. Origin Pro 8.5 software was used to plot the data. Two-sample t-tests ($p < 0.05$) were used to assess the differences between groups of data. All of the results used were averages of the results found from analyzing three parallel samples (samples are from each sampling site).

3. Results and discussion

3.1. Soil characteristics

The general physical and chemical component contents of the soils in the newly submerged area of the Danjiangkou Reservoir are presented in Table 1. The SOM accounting for 7654.32–20827.67 mg/kg of the total samples, and the standard deviation was 6544.28, the SOM contents could affect the P fractions in the soils, and since the SOM contents in grassland soils were very high. Silt was the major particle fraction (51.96%–71.93%) and the lowest values were found in sampling sites from bare land. Clay was the minor fraction, ranged from 2.69% to 12.98%. All the components were mainly affect P mobility from the soils to the water column (Mellander et al., 2013).

3.2. P distribution and fractions

We were firstly to analyze P and fractions in samples from different land use types, as shown in Fig. 2(a). The mean content values of TP in arable land soil was 732.91 mg/kg, higher than in other land use types, which may be due to the various different compositions of soluble soils caused by human activities such as agricultural production activities or domestic sewage discharged (Pionke et al., 2000). The content values of TP were the smallest in bare land (mean value 288.57 mg/kg). It was indicated that the arable land was affected by anthropogenic sources and enhanced P contents.

The mean content values of HCl-P were higher in arable land and other land (construction land and wasteland), were 546.92 and 365.93 mg/kg respectively, while grass land, woodland, and bare land were relatively lower. The mean content values of NaOH-P followed a decreasing sequence for arable land > grassland > woodland > other land > bare land.

The mean content values of OP in grassland were strongly affected by rich microbial and SOM sources, and higher than other land use types (Storkey et al., 2015), due to grass led to enhanced rates of P cycling, increasing P solubility (Borggaard et al., 2005). Grassland Soils had increased dissolved organic P, phosphatase enzyme activity, microbial diversity, and biomass P, compared with other land using types (Lazzarotto et al., 2005).

For all the soil samples, P-fractions were in rank order of HCl-P > OP > NaOH-P, except for O-L, as shown in Fig. 2(b). For the HCl-P, the highest proportion in other land was 83.38% (average), 60.77% was the lowest in Wasteland. For NaOH-P, the highest proportion was 10.8% in bare land, and 2.19% was for other land. In many studies, the IP is the sum of HCl-P and NaOH-P (IP = HCl-P + NaOH-P) (Jin et al., 2013). IP was the major phosphorus fraction in soils, which was an important source of bioavailable phosphorus in eutrophic
sediments (Ribeiro et al., 2008). For O-P, 32.07% for grassland was the highest proportion and the lowest was 7.55% in bare land. Based on the results of sequential extraction of P, lability and bioavailability was in decreasing rank order as follows: NaOH-P > OP > HCl-P. Therefore, the biogeochemical cycle of NaOH-P and OP might play an important role induced the eutrophic status of Danjiangkou Reservoir (Lin et al., 2009). According to the results, the arable land was main zone contributed significantly to P release during a water storage period, and 51.7% of the total newly submerged area in the Danjiangkou Reservoir was designated as arable land, thus it was important to explore the distribution characteristics of P in the arable land. Besides, it is unwise to establish grass buffer strips in the newly submerged area, because grass buffer strips may be increasing the susceptibility P move to adjoining water (Stutter et al., 2009).

3.3. Identifying the potential P release zone

One of purposes in this study was to identify which was the potential P release zone during a water storage period that should be given more attention, especially about the arable land. The results indicated that arable land was the main potential P release area, and the standard deviation values fluctuated considerably. Therefore, we were to consider the sampling sites at different elevation, and attempt to produce an accurate estimation of P distribution in arable land. The P fractions were analyzed in different elevation, as shown in Fig. 3. The TP and HCl-P contents increased with elevation, NaOH-P and OP contents were higher at arable land above 160 m elevation. For example, the mean content values of TP in arable land at “<160 m”, “160–165 m”, “165–170 m” and “>170 m” elevation were 549.0, 726.37, 748.01, and 740.79 mg/kg, respectively, the mean content values of HCl-P were 473.21, 513.15,
34. The sorption kinetics and isotherm of phosphate on soils

In order to judge whether the soils act as a source or sink of P for the water body during a water storage period, we set a groups of adsorption experiments. The soil samples came from arable land from 160 to 170 m elevation areas of the newly submerged area. The TP contents of samples were as follows: A: 1050.94 mg/kg, B: 816.95 mg/kg, C: 693.4 mg/kg, D: 534.69 mg/kg, F: 261.3 mg/kg, which represent a uniform distribution of different TP contents. The P sorption kinetic results are shown in Fig. 4(a). The P sorption rate was increased rapidly with time increasing within 2 h, slowed down gradually before 10 h. After 20 h, the sorption was reached to equilibrium. The sorption kinetics was similar among the other studied soils samples. The sorption rate was used to describe the P sorption capacity by the soils, which was the slope of the curve, from Fig. 4 we could saw the sorption rates of 0–0.5 h were the highest within 64 h, ranged from 49.91 to 86.3 mg/kg.h (shown in Table S2). The results indicated that a quick sorption process was mainly within 0.5 h. P sorption on soil was mainly depended on its physical and chemical properties. The similar results were also reported in shallow lakes in the middle and lower reaches of Yangtze River region in China (Zhang et al., 2012).

In the second set of adsorption experiments, according to sorption kinetics and ascertain equilibration time was 20 h, thus centrifuge tubes were capped for 20 h. The sorption isotherms of P on the soils were shown in Fig. 4(b). The adsorption isotherms crossed over the aqueous concentration axis. It was due to natural particles often containing NAP (the amount of total native adsorbed P) before they are used in experiment. Under temperature conditions of 25 °C, the experimental data fits well into Eq. (1).

In addition, the Qmax sorption capacity was varied from 578.79 to 1457.44 mg/kg, Kd ranged from 2.53 to 4.08 mg/L. When P adsorbed falls to zero, the equilibrium concentration of P in trial solution (C) is equal to EPC0: C = EPC0, and the system is already in equilibrium without net adsorption or desorption.

To confirm that P could be released from the soil back into the water when the water DIP concentration was lower than EPC0, it involved placing the soil samples into ultra-pure water. It was found that soil acted as a new pollutant source to release P into the overlying water. The amount of P released by the soils was ranged from 0.635 to 3.557 mg/kg. The proportion of the released P ranged from 0.143% to 0.568%. The amount of P released from the sediments had a positive relationship with the TP contents level (Siciliano et al., 2016). However, no correlation was found between the amount of P released from the soils and the HCl-P contents. It was implied that only some of the P fractions could be released from soils into the overlying water. The NaOH-P could easily be released from soils and was identified as the major fraction of soils influencing the P distribution in the overlying water (Pan et al., 2013). In many eutrophic reservoirs, oxygen penetration into the sediments is limited within a confined layer and the release of P was attributed to reduction of iron hydroxides and iron phosphate under anoxic conditions (Ahlgren et al., 2005). The major controlling factor of P released into reservoir may be mediated processes by Fe reduction due to oxygen depletion (Wilfert et al., 2015). Meanwhile, the reservoir with high value of pH, P would be liberated from the FeOOH-P

534.62, and 572.32 mg/kg, and the OP contents in arable land at “<160 m” elevation lower than in arable land at “>160 m” elevation. The mean content value of NaOH-P was similar in different elevation and the highest at “160–165 m” elevation. Overall, the results revealed that the arable land at above 160 m elevation was major risk area, and the content values of TP were low at below 160 m elevation of arable land. It was due to the periodic flooding reduces P of the surface soil (Aye et al., 2006), or because the local farmers worried about the crops would be flooded sometime and reduced input of investments such as fertilizer. The areas of 160–170 m elevation in the newly submerged area were swamped between October and May (the next year), the mean temperature was about 10.7 °C during the period, and microbial activity was low, which may reduce the potential risk of eutrophication to the water (Sondergaard et al., 2013).

The relationships between P fractions and soils compositions contents in the newly submerged area of Danjiangkou Reservoir were analyzed using the Pearson correlation coefficients (Tables 2 and 3). The TP contents correlated significantly with the HCl-P contents, (r = 0.936, P < 0.01), NaOH-P contents (r = 0.661, P < 0.01), OP contents (r = 0.762, P < 0.01), IP contents (r = 0.970, P < 0.01), HCl-P contributed substantially to the supply of IP in the soils, thus IP contents correlated significantly with HCl-P. NaOH-P and OP contents. OP contents were no significantly correlated with HCl-P, NaOH-P contents. There were no significant relation-
pool due to competition with OH⁻ ions (Pardo et al., 2004). The competition capacity can be excluded as a possible mechanism that contributes to NaOH-P from the overlying water. Therefore, NaOH-P fraction may contribute to P-released from soils by enhancing the reduction of both the P ion-competition and fixation capacity. Although the content of NaOH-P was low, the P behavior in soils could efficiently be evaluated based on the NaOH-P fraction.

The sorption capacity and efficiency were compared with some soil physical and chemical parameters. The correlation coefficients among soil compositions indicate that there was no significant correlation between soil compositions and the maximum phosphate sorption capacity, and phosphate sorption efficiency. However, some studies have shown that the maximum phosphate sorption capacity was significantly correlated with Fe, TOC, TN, TP, Ca, and IP contents (Baliarsingh et al., 2013), the ratio of NaOH-P and the P sorption efficiency were positively related to Fe content in the sediment of shallow lakes in the middle and lower reaches of Yangtze River region.

The calculated data of $Q_{\text{max}}$, $K_d$, EPC₀, $R^2$, and $\delta$ were listed in Table 4. The concentrations of P in the overlying water in the Danjiangkou Reservoir were ranged from 0.017 to 0.0468 mg/L, and mean values was 0.032 mg/L ($C_{\text{eq}}$). If $\delta < 0$, the net effect of sorption was the release of NAP from the natural soils (soils serves as source of P). On the other hand, if $\delta > 0$, the net effect of sorption was P uptake by soils (soils serves as sink of P). In this study, the EPC₀ of A, B and C values were higher than the mean concentration values of DIP in the Danjiangkou Reservoir water, $\delta < 0$, which indicated that only some sites of the soils act as source of P release into the overlying water. The higher contents of TP in soils, the greater release will be. The newly submerged area in the Danjiangkou Reservoir become a weak sink of P as the $\delta$ values become negative, the soils of D, E and F represent the sink of sites, as the TP level in the sample is relatively low. Therefore, about 20.33% of all samples can release P to water when submerged, and the newly submerged area soils mainly adsorbed P from the water, unless the level of P concentrations in water decreased.

### 4. Conclusions

The arable land was the highest TP content values in all land using types in the new submerged area of the Danjiangkou Reservoir, especially above the elevation of 160 m. The mean content values of P-fractions ranked order was: HCl-P > OP > NaOH-P. The P sorption on soils was mainly occurred within 20 h and then reached to dynamic equilibrium. The P sorption rates were obviously affected by the TP contents in soils. There was no significant correlation between soil compositions and the maximum phosphate sorption capacity. The P was not strongly enriched in the study area and the potential risk of P in soils was minimal in the newly submerged area of Danjiangkou Reservoir at present; besides, the risk would be varying according to the P concentrations of the overlying water, and it’s difficult to accurately determine which areas are source or sink when submerged. Thus more studies are urged in consideration that the reservoir will run for many years and has a far-reaching influence.

### Acknowledgments

This research was supported by the One-Three-Five Program of the Research Center for Eco-Environmental Sciences (No. YSW2013B02), the Youth Innovation Promotion Association CAS (Wenzhong Tang), and the National Environmental Protection Public Welfare Science and Technology Research Program of China (No. 201509027).

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecoleng.2016.11.072.
