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Original Research

Phosphorus Fractions and Phosphorus Adsorption Characteristics of Soils from the Water-Level Fluctuating Zone of Nansi Lake, China

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Abstract

Nansi Lake, a typical shallow and macrophyte-dominated lake in south Shandong Province, China, has a total surface area of 1,266 km^2 and is the largest and most important freshwater reservoir in northern China for the eastern route of the South-North Water Diversion (SNWD) project, in which the water in Yangtze River will be transported more than 1,100 km from Yangzhou to Tianjin and Beijing. A water-level fluctuating zone (WLFZ) near Nansi Lake will be formed when the SNWD project begins to transport water flowing through the lake. Phosphorus fractions and adsorption-release characterization for soil samples from four typical lands (reed, wood, maize, and soybean) were conducted to investigate soil phosphorus stability. In addition, a soil submerged experiment was performed to simulate phosphorus release under submerged conditions. Phosphorus adsorption-desorption equilibrium concentrations (C_{EPC}) of four lands were 0.006, 0.089, 0.110, and 0.287 mg L^{-1}, respectively, which means that maize, soybean, and woodland had higher potentials than reed land for phosphorus releasing to the overlaying water. Submerged experiment results showed that the quantities of phosphorus released from reed, wood, maize, and soybean soils were -0.14, 0.06, 0.12, and 0.97 mg kg^{-1}, respectively. Soils in the reed land adsorbed phosphorus from overlying water, but the other soils released phosphorus into the water. Thus, in order to decrease the phosphorus releasing quantity from the wood, soybean, and maize land under the conditions of submerged lands at water diversion time, the land uses of wood, soybean, and maize should be switched to land for planting reed.

Keywords: water-level fluctuating zone (WLFZ), soil, phosphorus release, phosphorus adsorption, Nansi Lake

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Introduction

A water-level fluctuating zone (WLFZ) is a special zone where the area of submerged soils changes seasonally with the seasonal water level fluctuation of a reservoir or lake. It is the most extraordinary and fragile zone in aquatic and land ecosystems [1-4]. Riis and Hawes reported that water level fluctuations influenced vegetation diversity [5]. Lawniczak et al. found that the reduction of water level resulted in a negative effect on biomass production and nutrient concentrations [6]. Fluctuating water levels increase the area of shoreline vegetation, and the diversity of vegetation types and plant species. Any stabilization of water levels would likely reduce marsh area, vegetation diversity, and plant species diversity [2,7-9]. Sasikala et al. reported that the water level fluctuation caused a considerable reduction in radial oxygen loss and root porosity, and produced a significant improvement in total nitrogen (TN) and NH_4^+-N removal [10]. Lawniczak et al. evaluated the changes in soil P speciation and availability with time following applications of grain-fed cattle manure or monoammonium phosphate. They found that fluctuations in total bioactive soil P were two to four times greater than aboveground biomass P, highlighting the importance of accounting for seasonal dynamics in assessing offsite P transport risks [11]. However, research on the phosphorus fraction releasing from soils in WLFZ is rare.

To solve the water resource shortage in northern China, the South-to-North Water Diversion (SNWD) project has been conducted to transfer the water in Yangtze River to the North China, and the conduit canals for the project have three routes (named West, Middle, and East). For the East route, water will be diverted from the Yangtze to Hebei and Shandong provinces during the autumn, winter, and spring seasons (summer excluded). After the project is completed, a 0.5 m high WLFZ will be formed at Nansi Lake. The soils around Nansi or situated in the WLFZ will be submerged during the period of water-diverting periods and then emerge above water level again in summer. According to the Chinese governmental regulation titled "Water Pollution Prevention Planning of the SNWD (East route) of Shandong Section," the phosphorus content of the overlying water in Nansi Lake should be controlled below 0.05 mg L^{-1} [12]. Currently, the potential WLFZ has been farmland for maize, soybean, and wheat production for a long time. During recent years, the dosage of phosphorus fertilizer to farmland keeps increasing in order to enhance the yield of crops, and often exceeds phosphorus uptake by crops. The phosphorus fractions and quantities in soils were inconstant in the different conditions [13-15]. Numerous studies support the idea that phosphorus-based fertilization had increased the potential for phosphorus release from soils [16-20]. The resin-extractable P and $NaHCO_3$-extractable inorganic P and NaOH-extractable organic P significantly increased under P fertilization in cultivated soils during two years [19]. However, Kai Y. et al. reported that N addition decreased soil inorganic P availability, microbial biomass P, and acid phosphatase activity in the larch plantation. Soil inorganic P availability decreased after N addition due to the changes in both microbial properties and plant uptake [21]. The P in the

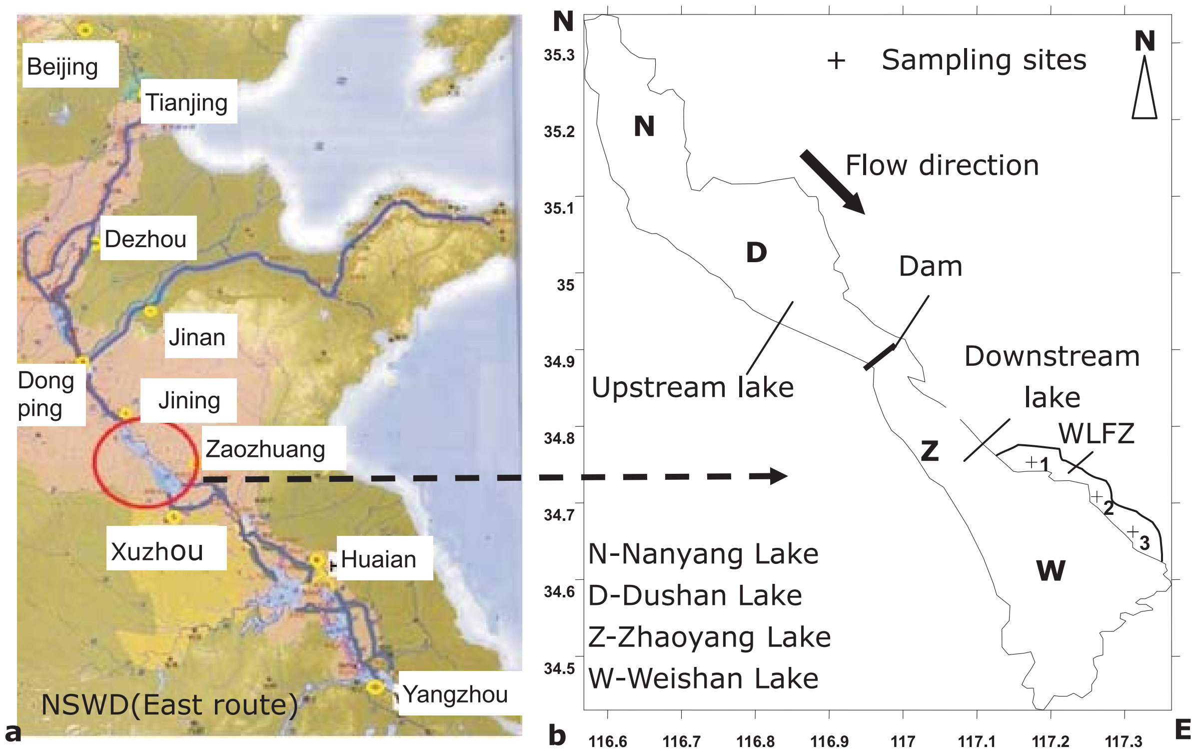

Fig. 1. Geographic map of the South-to-North Water Diversion (East route) project and sediment sampling sites at the water-level fluctuating zone (WLFZ) in Nansi Lake.

albic bleached luvisol meadow soil was mainly associated with Fe oxides and organic matter, and Fe-P supports the majority of available P [22]. Therefore, it is necessary to investigate the P fractions in WLFZ. When the soil in WLFZ is submerged, the phosphorus released from soil into the overlying water would represent greater potential for contamination of surface and subsurface waters [8, 23, 24].

Study on soil P fraction in WLFZ is an important aspect in probing the mechanisms of soil P accumulation in farmland and mitigating its losing risk to the environment. The objective of this research is to investigate phosphorus fractions and phosphorus release performance in WLFZ, and to evaluate the potential effect of various land usage on lake water quality in the future.

Materials and Methods

Lake Site and Soil Sampling

Nansi Lake (34°27′–35°20′N, 116°34′–117°21′E) is situated southwest of Shandong Province and consists of four consecutive lakes, i.e., Nanyang (N), Dushan (D), Zhaoyang (Z), and Weishan (W). The total surface area is 1,266 km^2 with an average depth of 1.46 m. It serves as a buffer lake of the East route (Fig. 1).

The soil samples were taken from three sites, i.e., site 1 (34°42′N, 117°11′E), site 2 (34°40′N, 117°16′E), and site 3 (34°37′N, 117°20′E) in the WLFZ (Fig. 1). The farm lands in WLFZ are generally used to cultivate maize, soybean, wood, and reed. A lot of fertilizers are needed for a high-yield maize. $(NH_4)_2HPO_4$ is used as a common fertilizer with a dosage of 750 kg ha^{-1} for maize and about 150 kg ha^{-1} for soybean growth. The organic fertilizer for wood land is limited, while no fertilizer is applied in reed land. Based on the difference in type and dosage of fertilizer for different plants, four different types of land, i.e., maize, soybean, wood, and reed land, were selected in this study.

Soil samples (about 1000 g for wet weight) were collected from surface soils (0-10 cm) separately at three sites for each type of land (reed, wood, maize, and soybean) in November 2013. Samples from the same type of land were homogenized prior to tests. At below soil analysis, all samples were analyzed in triplicate, and the results were expressed as mean and standard deviation.

Soil Analysis

All samples were collected in sealed plastic bags, frozen, and then transferred to the laboratory of Weishan Station, where soil samples were freeze-dried, ground in an agate mortar, and sieved with a standard 2 mm sieve for further studies. The grain size distribution of sediment samples was analyzed using a Mastersizer 2000 Laser Size Analyzer (Malvern Co., UK), and was classified into clay (0.02-4.0 μm), silt (4-63 μm), and sand fractions (63-2,000 μm) [25]. The total contents of major elements as Fe and Al were measured by ICP-AES PS-950 after digestion. Organic matter (OM) content was measured as weight loss after ignition at 550ºC for 6 h [26]. The soil pH value was measured in saturated paste using a glass electrode, and cation exchange capacity (CEC) using NaOAc method [27].

Phosphorus Fractions and Analysis

A harmonized scheme (SMT protocol) to determine the extractable phosphorus contents in freshwater sediments has been harmonized through interlaboratory studies in the frame of the Standards Measurements and Testing Program of the European Commission [28]. A homogeneous and stable sediment reference material was prepared based on this SMT protocol. The SMT protocol, together with the reference material, is a useful tool in the field of water management. It has been developed based on the comparison of existing schemes and inter-laboratory studies. This operationally defined scheme consists of five steps i.e., extraction of NaOH-extractable P (P bound to Al, Fe and Mn oxides and hydroxides), HCl-extractable P (P associated with Ca), organic P (OP), inorganic P (IP), and concentrated HCl-extractable P (total P, TP).

For the first step, 0.2 g soil was placed into a 50 mL acid-washed screw cap centrifuge tube and 20 mL 1 mol L^{-1} NaOH solution was added for NaOH-P extraction. In the second step the residue of the first step was then used for HCl-P extraction with 20 mL 1 mol L^{-1} HCl solution. The third step saw 0.2 g soil extracted with 20 mL 1 mol L^{-1} HCl solution for IP, and the residue of this step was extracted with 20 mL 1 mol L^{-1} HCl solution after ignition (450ºC) for OP (fourth step). In the fifth step 0.2 g soil was extracted with 20 mL 3.5 mol L^{-1} HCl solution after ignition (450ºC) for TP [28].

The extract solution was centrifuged at 5,000 rpm for 15 min and then filtered through a 1.2 μm GF/C filter membrane. The P concentration (as the form of phosphate) in solution was analyzed using the molybdenum-blue method [29]. The P concentration in each P fraction was calculated based on phosphate concentration, solution volume, and soil sample weight.

Phosphate Adsorption Isotherm Experiments

One-gram air-dried soil samples were weighed in an acid-washed conical flask (250 ml), and 200 ml phosphorus standard solutions (anhydrous KH_2PO_4) of various concentrations (0, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 mg L^{-1}) were added. Two drops of 0.1% chloroform were added to inhibit bacterial activities. The pH values of the solutions were adjusted to 7.0-8.0 by adding 0.01mol L^{-1} and 0.01mol L^{-1}, which were similar to the actual pH in the Lake. The flasks were capped and placed at 20±1°C in an orbital shaker at 250 rpm for 24 h to ensure equilibrium. After equilibrium and centrifuging (5,000 rpm for 15 min), the suspension was filtered through a 1.2 μm GF/C membrane filter and the phosphate concentration was measured by the molybdenum-blue method [29]. The phosphate adsorbed on the soil samples was calculated

Table 1. Physical and chemical characteristics of four soils.

Land uses	OM (%)	TP (mg kg^{-1})	TN (mg kg^{-1})	Al (mg kg^{-1})	Fe (mg g^{-1})	pH	CEC (mol kg^{-1})	Clay (%)	Slit (%)	Sand (%)
reed	8.33(±0.21)	442.8(±6.2)	1316(±21)	213.0(±9.2)	161.5(±10.2)	8.17	56.7(±4.2)	3.80(±3.2)	24.3(±5.5)	68.1(±8.5)
wood	10.44(±0.30)	584.2(±8.1)	1652(±15)	279.9(±7.3)	206.1(±22.2)	8.09	99.5(±6.5)	3.8(±3.5)	31.0(±5.8)	61.3(±8.2)
maize	11.49(±0.25)	1164.8(±9.2)	1988(±24)	330.0(±5.2)	221.7(±15.6)	8.04	87.3(±6.6)	4.8(±3.0)	32.1(±6.6)	58.3(±9.0)
soybean	8.22(±0.23)	856.7(±4.2)	1428(±18)	307.1(±9.1)	236.5(±14.8)	8.10	122.4(±7.3)	1.4(±2.2)	19.6(±6.4)	77.6(±7.8)

based on the difference between the initial and equilibrium phosphate concentrations.

The phosphate adsorption isotherm was fitted according to Eq. 1. [30]

$$Q = m\, C_{eq} - \omega_{NAP} \quad (1)$$

…where C_{eq} is the phosphate concentration in solution after a 24 h equilibration period (mg L^{-1}), Q is the amount of phosphate adsorbed by the solid phase (mg kg^{-1}), m is the slope (which is a measure of the phosphate sorption efficiency of the sediments), and ω_{NAP} is the content of native adsorbed phosphorus (NAP) (mg kg^{-1}).

Phosphorus adsorption-desorption equilibrium concentration or zero equilibrium phosphorus concentration (C_{EPC}) is an important parameter that provides useful information whether a given soil releases or adsorbs phosphate. If $C_{eq} < C_{EPC}$, NAP will be released from the soil to water. Conversely, if $C_{eq} > C_{EPC}$, phosphate in water will be adsorbed by soil. When $C_{eq} = C_{EPC}$, the adsorption and desorption reached an equilibrium state within the system [26, 30].

Soil Submerged Experiment

A soil submerged experiment was performed to determine the phosphorus adsorption/desorption potential for four different soil samples. Soil samples (200 g) were put into four glass pipes with a diameter of 9 cm and a length of 80 cm, and the bottom of the pipes were sealed with rubber stoppers. In each pipe, 2 L of water collected from Nansi Lake (0.038 mg PO_4^{3-}-P L^{-1}) was added by siphon. Subsequently, overlying water samples (100 ml) were collected from each pipe at 1, 3, 7, 15, and 28 d, filtered through a 1.2 µm GF/C filter membrane, and then used for phosphate analysis.

Results and Discussion

Soil Characteristics

The physical and chemical characteristics of the soils are shown in Table 1. The sequence of TP contents in the soil samples from different lands are maize > soybean > wood > reed, while TN contents are maize > wood > soybean > reed.

The contents of TP and TN in the soils from maize land were 1,164.8 mg kg^{-1} and 2016 mg kg^{-1}, respectively, which were the highest among all samples. The contents from reed land were the lowest, at 442.8 mg TP kg^{-1} and 1316 mg TN kg^{-1}, respectively. This indicated that the contamination levels of the soils were determined by the types of dosage of fertilizers applied. The highest levels were the samples from maize due to excessive fertilizer accumulated in the soils. In addition, the phosphorus concentration in soils with phosphorus fertilizers increased with cultivation time [19, 20, 31]. Shi Y. et al. suggested that total P declined under the corn-soybean rotation, and the combined no-tillage and P fertilization enhanced soil Pi fractions, thereby improving soil P supplying capacity and P balance [32]. Less fertilizer is applied in soybean land, and a small quantity of organic fertilizer is applied in woodland. Therefore, TP and TN contents in these two soils were lower than the one in maize land separately. As the soil phosphorus is continuously removed by the harvest of reed, which uptakes phosphorus from the soil, the phosphorus in reed land decreases gradually.

The grain size distribution of the soil particles of the samples was classified into clay, silt, and sand fractions (Table 1). Sand was the major fraction of all soils, accounting for 58.3-77.6% of the total particles. Clay was the minor fraction, accounting for 1.4-4.8% of the total. Our observation is different from what was previously reported by An and Li about sediment samples of Nansi Lake silt fraction being the major fraction [30]. The proportions of clay and silt grains of the soils from WLFZ were smaller than those in the sediments in Nansi

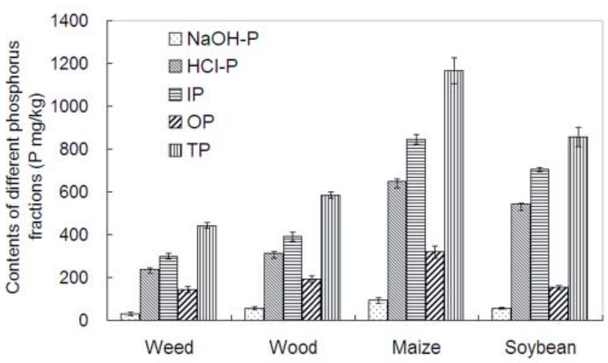

Fig. 2. Distribution of soil phosphorus fractions in the Nansi Lake WLFZ.

Table 2. The proportions of P fractions to TP.

Land uses	NaOH-P %	HCl-P %	IP %	OP %
reed	6.77	53.68	67.74	32.26
wood	9.63	53.48	66.90	33.10
maize	7.95	55.78	72.56	27.44
soybean	6.80	63.57	82.15	17.85

Lake. Due to the differences in specific surface areas, the adsorption and ion-exchange capability for phosphate was different, and the finer grains have greater adsorption capacity because of the higher specific surface area. The soils in WLFZ with lower portion of clay and silt grains have less capacity to adsorb phosphorus. Therefore, phosphorus would be released easily from soils in WLFZ than the sediments in Nansi Lake.

The CEC values in the soil samples were different. The reed land soil had the lowest CEC values of 56.7 mol kg^{-1}, and soybean land soil had the highest CEC value of 122.4 mol kg^{-1} (Table 1). The CEC values did not show correlation with phosphorus content. The pH values of the samples indicate that these soils are slightly alkaline, varying from 8.04 to 8.17. The contents of Al and Fe showed slight differences in the different soils. The reed land samples contained less Fe and Al than the other samples (Table 1).

Phosphorus Fractions

The contents of different phosphorus fractions in the soils from four types of land are shown in Fig. 2. The contents of TP and phosphorus fractions varied greatly. TP contents in the soils ranged from 442.8 to 1,164.8 mg kg^{-1} and the average content was 762.1 mg kg^{-1}. IP contents in all the soils varied from 299.9 to 845.2 mg kg^{-1}, accounting for more than 65% of TP, and the OP contents ranged from 142.9 to 319.6 mg kg^{-1}. HCl-P contents ranged from 237.7 to 649.7 mg kg^{-1}, accounting for more than 50% of TP, and NaOH-P from 29.9 to 92.6 mg kg^{-1}, lower than 10% of TP.

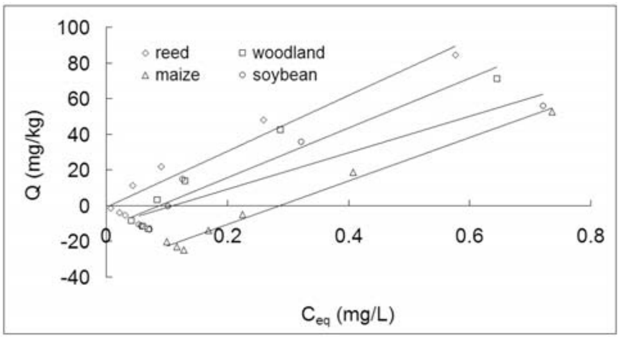

Fig. 3. Phosphate adsorption isotherms of the soils. (Reed, wood, maize, and soybean represent land with different types of land use, respectively.)

The proportions of IP in TP were higher in maize land and soybean land than those in reed land and woodland (Table 2). Guo et al. suggested that phosphorus accumulation in soils increased due to the long-term continuous application of phosphorus fertilizers, and the phosphorus accumulated in the soils were mainly transformed into Ca-P (HCl-P) [33]. The result was agreement with the Li Y et al. report, with comparison of the no-fertilizer addition, the long-term single fertilization (inorganic nitrogen and P fertilizer) significantly increased the accumulation of $NaHCO_3$-, NaOH-, and HCl-extractable P-i (residual P) fractions, accounting for two- to three-fold, while the straw incorporation and green manure as fertilizer increased the accumulation of IP, accounting for 12-60% [20]. Therefore, woodland had the highest proportion of OP, probably due to the lower application of inorganic fertilizer or the application of organic fertilizer [34]. Previous studies indicated that large surplus phosphorus inputs were associated with manure application, which could influence the distribution of phosphorus among organic and inorganic forms [13, 35]. Yin Y. concluded that applying organic fertilizer can increase the content of the phosphorus fractions of paddy soil. While with microorganisms present, Al-P and Ca-P can be transformed into moderately labile organic phosphorus and moderately resistant organic phosphorus, and OP can be transformed into highly resistant organic phosphorus [36]. Therefore, the phosphorus fractions in soil under different fertilizers were changeable with the environmental conditions.

The most labile fraction of phosphorus found in soils is undoubtedly NaOH-P, which is easily released from soil to water. NaOH-P of maize land is three times that of reed land. NaOH-P concentration of soybean and wood land samples is two times that of reed land. The reason was probably that the lands of soybean, maize, and wood were all cultivated land, to which was added more inorganic fertilizer [19, 20, 37]. This suggests that soils in maize, soybean, and woodland have higher environmental concern than soils in reed land when this zone would be submerged.

Phosphate Adsorption Isotherm

The phosphate adsorption isotherms are shown in Fig. 3 and the linearly fitted results of phosphate adsorption isotherms are shown in Table 3. The soil C_{EPC} in reed land,

Table 3. The linearly fitted results of phosphate adsorption isotherms.

sites	m (l kg^{-1})	ω_{NAP} (mg kg^{-1})	C_{EPC} (mg L^{-1})	R^2
reed	156.37	0.90	0.006	0.95
wood	139.32	12.39	0.089	0.92
maize	121.99	35.03	0.287	0.99
soybean	101.96	11.24	0.110	0.87

which did not receive fertilizer containing phosphorus, was only 0.006 mg L^{-1}, while those from the maize, soybean, and woodland were 0.287, 0.11, and 0.089 mg L^{-1}, respectively. Maize, soybean, and woodland had higher C_{EPC} than reed land, probably due to long-term fertilization. Shafqat and Pierzynski used the Freundlich model ($A = KC^{1/n}$) to describe phosphorus adsorption to sediments. In the model, *A* represents the amount of P sorbed by the solid phase (mg kg^{-1}), C is the solution P concentration (mg L^{-1}) after equilibration, and K and 1/n are the Freundlich constants. The Freundlich K refers to the ratio of P adsorbed to P in the soil solution, while 1/n describes the non-linearity of the adsorption curve. Shafqat and Pierzynski reported that much higher Freundlich K and smaller 1/n values were observed for the P-deficient soil, which means that the higher the K, the more P adsorbed to sediments, or the stronger the adsorb potential to the sediments; therefore the P was difficult to release to the overlaying water. The result is consistence in our results, and the weed land with P deficient soil has lower C_{EPC} with lower potential for P release [38]. Some of the previous adsorped phosphorus occupied the adsorption sites and blocked further reaction, thus the phosphorus sorption capacity in fertilize in fertilized soils decreased [33].

According to government regulations, after the SNWD project is completed, the water quality of Nansi Lake should be better than grade III of the China surface water quality standard (GB3838-2002), which requires TP concentration below 0.05 mg/L. The TP content of the overlying water after diversion is higher than C_{EPC} at the sample sites of reed land, so the soils in reed land will not release phosphorus and cause water quality concern. But the soils in woodland, maize land, and soybean land with C_{EPC} higher than TP of the overlying water (<0.05 mg L^{-1}) will tend to release phosphorus to overlying water, which has a chance to threaten water quality. Therefore, the inherent phosphorus of the soils of these types of farmland could be of concern to water quality.

In the isotherm equation, the term of ω_{NAP} can be considered to be phosphorus adsorbing on the soil surface mainly by physical effects, and is easily desorbed from the surface into the water [30]. Soils in maize land, soybean land, and woodland had much higher ω_{NAP} than that in reed land. This indicates that more soil phosphorus may be released from maize, soybean, and woodland and cause higher environmental threats than reed land in the future.

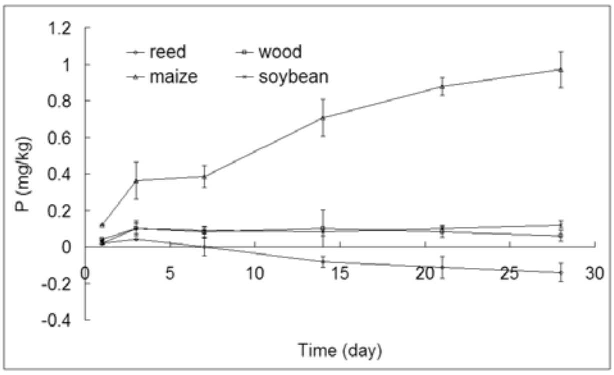

Fig. 4. Soil phosphorus releasing under submerged conditions. (Reed, wood, maize, and soybean represent land with different types of land use, respectively.)

Soil Submerged Experiment

The phosphorus release phenomena from soil under submerged conditions over 28 days are illustrated in Fig. 4. This indicates that the soil sample from the reed land adsorbed phosphorus from the overlying water and the TP concentration decreased gradually with time. Therefore, the quantity of phosphorus released from reed soil (Q_{PR}) was -0.14 mg/kg. Soil phosphorus was released from woodland and soybean land samples under submerged conditions, but the Q_{PR} from both soils were much lower (wood 0.06 mg kg^{-1}; soybean 0.12 mg kg^{-1}). Soil phosphorus from maize land was consistently released throughout the 28-day period, and the Q_{PR} was at least 0.97 mg kg^{-1}. If a longer test period were applied, a higher Q_{PR} would be expected.

Based on the above observations, the soil in reed land adsorbs phosphorus from overlying water, but other soils may release phosphorus into the overlying water at different levels when WLFZ is submerged. Soils in maize land, soybean land, and woodland tend to release phosphorus to overlying water and will threaten the water quality to some extent after SNWD (East route) is completed at the beginning. It may take months or longer to flush out the phosphorus-rich soils until no phosphorus is released.

Reed wetland has been widely used for water purification in many projects [39, 40] in which the phosphorus in soil absorbed by reed can be easily removed by harvesting reed plants. To maintain high water quality, the land in WLFZ should not be utilized for wood, soybean, and maize, and should be switched to plant reed gradually in order to reduce phosphorus loading. The strategy of returning the farmland into the lake shore with reed can ensure not only the water quality of Nansi Lake, but also preserve the lake's beautiful landscape.

Conclusions

The soils in WLFZ near Nansi Lake were characterized for phosphorus release concern in the SNWD project. The C_{EPC} and the quantities of phosphorus released (Q_{PR}) in the submerged experiment indicate that soil in reed land adsorbed phosphorus from overlying water. However, soils in maize, soybean, and woodland released phosphorus into the overlying water at different levels. Phosphorus release from the soils in WLFZ could threaten water quality in the future. Therefore, technical approaches should be taken to reduce the phosphorus release from the lands in WLFZ before the SNWD project is put in use for transporting water from the Yangtze. At present, in order to reduce phosphorus loading, the application of phosphorus fertilizers to the land in the WLFZ should be reduced, and the land uses of wood, soybean, and maize should be changed to reed land gradually, which also can purify the lake water and bring about economic benefits.

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