Baoqing Shan¹
Chunming Hu¹
Wenzhong Tang¹
Yajing Cheng¹

¹Research Center for Eco-Environmental
Sciences, Chinese Academy of
Sciences, Beijing, P. R. China.

Research Article

Variations in Phosphorus Speciation in Pilot Scale Subsurface Flow Wetlands Constructed with Blast Furnace Slag and Gravel

Variations in phosphorus (P) speciation were compared for two types of pilot scale wetlands: a blast furnace slag-based constructed wetland (SCW), and a gravel-based constructed wetland (GCW). Synthetic secondary effluent was used as the influent of the wetlands, which contained 1.1 mg/L P with more than 95% present as soluble reactive P (SRP). However, dissolved organic phosphorus (DOP) and particulate phosphorus (PP) emerged in the water along both wetlands. The levels of these three P species varied between the two wetlands. The GCW was more efficient than SCW at removing SRP, but showed a different trend. SRP decreased continually in the SCW, while it increased at the end of the GCW due to biological release. DOP was constant in SCW and GCW, and the mean value was 0.023 and 0.020 mg/L, respectively. The mean values of PP in the GCW ranged between 0.093 and 0.216 mg/L; much higher than the 0.05 ± 0.01 mg/L measured in the SCW. Sequential extractions showed that iron bound PP (Fe-PP), aluminum bound PP (Al-PP), organic PP (Org-PP) and occluded PP (Oc-PP) were the major components of PP at most locations of the GCW. Fe-PP decreased from 0.53 to 0.14 mg/L in the upper layer, with DO steady at about 0.15 mg/L at the bottom. Oc-PP increased at each layer. Al-PP and Org-PP were steady in the first 140 cm of the GCW, but decreased sharply at the end. Considering the variation of SRP, DOP and PP fractionations, it can be seen that PP exchanged intensively with SRP in the GCW, and might act as an intermediate in the P removal process. Part of the SRP was first transformed into PP, and then absorbed by substrates or deposited in the wetlands. P removal was mainly via Ca precipitation in the SCW, but involved multiple mechanisms in the GCW, such as precipitation, adsorption and biological interactions. The multiple P removal mechanisms might be the reason for the low proportion of SRP, and the better P removal efficiency observed in the GCW.

Keywords: Particulate phosphorus; Phosphorus speciation; Secondary effluent; Wetland

Received: March 19, 2009; *revised:* August 23, 2009; *accepted:* August 26, 2009

DOI: 10.1002/clen.200900059

1 Introduction

Wetlands can satisfactorily remove phosphorus (P) on a short term basis, which is otherwise difficult to degrade by secondary treatment, especially biological treatment systems [1]. Substrate binding was believed to contribute to more than 80% of P removal in constructed wetlands (CW), via complex physical, chemical and micro-

bial interactions [2, 3]. The greatest capacity for long term storage of P in CW is in the substrate through either peat building or adsorption [4]. P adsorption in wetlands is usually controlled by iron (Fe) and aluminum (Al) in acidic conditions, and calcium (Ca) and magnesium (Mg) in alkaline conditions [2, 5]. The process is generally described as a two step process. The first step is the rapid dissociation of P from water and association with the substrate. The second step is the slow penetration of substrate bound P into the solid phase [6].

In order to get a better understanding of the P removal processes, different forms of P and their dynamics were studied by researchers [7–10], such as soluble reactive P [11], dissolved P [12] and organic P [13]. However, all this research treated particulate P as a simple speciation, or just categorized it as inorganic P and organic P. Nor did they explain the transformation of particulate P inside the wetlands. On the other hand, particulate P in sediments and seawater had been studied for a long time and has been extracted into many fractions [14–17].

Correspondence: Professor B.-Q. Shan, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, P. R. China.

E-mail: bqshan@rcees.ac.cn

Abbreviations: Al-PP, Aluminum-bound PP; Ca-PP, Calcium-bound PP; CW, Constructed wetland; DO, Dissolved oxygen; DOP, Dissolved organic phosphorus; Ex-PP, Exchangeable PP; Fe-PP, Iron-bound PP; GCW, Gravel-based constructed wetland; Oc-PP, Occluded PP; Org-PP, Organic PP; PP, Particulate phosphorus; SCW, Blast furnace slag-based constructed wetland; SRP, Soluble reactive phosphorus; TDP, Total dissolved phosphorus; TP, Total phosphorus

Figure 1. Sectional view of the experimental wetland system. The system is 2.4 m long, 0.4 m wide and 0.65 m high. The first 0.1 m in length was the inlet zone and the last 0.1 m was the outlet zone.

In the water column, some P is adsorbed to particles as intracellular storage products and thus forms particulate inorganic P, such as Ca, Al, and Fe bound P, whereas particulate organic P comprises P incorporated in living and detrital organic molecules [17]. Because of the different bioavailability of different kinds of particulate P, information about them are necessary to characterize the effect of wetlands in preventing eutrophication.

Blast furnace slag and gravel are two kinds of substrates used in wetlands. Gravel has traditionally been used while blast furnace slag has been used frequently in the last few decades. Lots of research has shown that slag performed better in P removal from wastewaters [5, 18–20]. However, little research has focused on the performance of these substrates in treating secondary effluent. In this paper, two pilot scale wetlands with different substrates were constructed to treat secondary effluent, a blast furnace slag-based constructed wetland (SCW) and a gravel-based constructed wetland (GCW). P speciation in wetlands was measured, with a special focus on particulate P. The purpose was to study the variation of P speciation in these two wetlands.

2 Materials and Methods

2.1 Experimental Wetland Systems

Two systems of experimental constructed wetlands made of wood were placed in a greenhouse (see Fig. 1), in which the average temperature was 46.4°C in summer and 28.7°C in spring and autumn. Both wetlands were constructed with three layers; 5 cm depth sand layer at the bottom, 20 cm depth soil layer at the top, and 35 cm depth substrate layer in the middle, in which the substrates were 16–30 mm diameter blast furnace slag and gravel, respectively, (SCW and GCW). In both wetland systems, 14 sampling pipes were placed in two layers, at depths of 0.05 and 0.25 m from the bottom. At each depth, the pipes were distributed at 0.2, 0.4, 0.7, 1, 1.4, 1.8 and 2.2 m from the inlet zone. In the experiment, water gathered from the sampling pipe was noted according to the pipe location. For example, if the sampling pipe was 0.25 m from the bottom and 0.2 m from the inlet zone, water gathered from it was noted as Upper-20 cm (U_{20}). So, water gathered from upper pipes were noted as U_{20} , U_{40} , U_{70} , etc., while from the bottom pipes were noted as B_{20} , B_{40} , B_{70} , etc.

The wetlands were constructed in April 2007, and flooded with fresh water for 6 days each week to wash the substrates, used from June 2007, when the reeds had grown well, and paused in November

when the reeds withered. In the next year, the experiment carried on for another 4 months, from March till June.

During the experiment, the water level in the CWs was fixed at 40 cm, and the hydraulic retention time (HRT) was first set at one day (26 Jun – 17 Aug), and then changed to two days. With different HRT, the Hydraulic Loading Rates (HLRs) of the CWs were about either 20 or 10 cm/day. The whole experiment was divided into several phases in order to give the CWs a recovery period to rejuvenate their P adsorption capacities, which had been shown in the study of Drizo et al. [20]. During this recovery period, all of the water was drained out of the CWs.

To control the water quality of the influent, synthetic secondary effluent was made up with the following reagents (> 98% purity): $C_6H_{12}O_6$, KH_2PO_4 , K_2HPO_4 , NH_4NO_3 , $(NH_2)_2CO$, $CaCl_2$, $MgSO_4$, $FeSO_4$, $ZnSO_4$, $CuSO_4$, $(NH_4)_6Mo_7O_{24}$, H_3BO_3 and Al_2O_3 . These were added to provide (mg/L): 1.1 P, 7 NH_4 -N, 8 NO_3 -N, 60 COD and 18 K. P was analyzed every week over the study period with the detected total phosphorus values being 1.1 ± 0.07 mg/L (> 95% as soluble reactive phosphorus). The synthetic secondary effluent was made daily to maintain a constant concentration. Metric pumps were used to transport the secondary effluent into the wetlands constantly.

2.2 Chemical Properties of Substrates

The mineralogical composition of the blast furnace slag and gravel were studied using X-ray photo electron spectroscopy (XPS) before being put into the wetlands. XPS studies were performed on an ESCALAB MK II using Al Ka ($h\nu = 1486.6$ eV) as the exciting source. The binding energies of all elements were standardized for specimen charging using C 1s as the reference at 284.8 eV. Results showed that blast furnace slag includes: O 44.85%, Ca 19.51%, Si 9.43%, Al 1.19%, Fe 1.07% and Mg 1.03%, compared to in gravel: O 46.64%, Ca 8.78%, Si 14.44%, Al 5.71%, Fe 2.60% and Mg 0.88%. Note that Ca is more abundant in blast furnace slag while Fe and Al are more abundant in gravel.

At the end of the study, the BFS and gravel were taken out of the wetlands, dried at 30°C for 1 wk using an oven and later broken into fragments carefully with a hammer. Intact surface fragments were collected and examined by scanning electron microscopy (SEM) and electron dispersive spectrometry (EDS), which were conducted using a Hitachi S-3000N with an EDAX Genesis XM4.

2.3 Water Quality Analyses

Water samples were collected from all 14 sampling pipes at each sampling time and analyzed immediately for pH, dissolved oxygen

(DO), total phosphorus (TP), total dissolved phosphorus (TDP) and soluble reactive phosphorus (SRP) according to the standard methods [21]. Samples for TDP and SRP analysis were filtered using 0.45 μm filters. Based on those, particulate phosphorus (PP = TP - TDP) and dissolved organic phosphorus (DOP = TDP - SRP) were calculated. All the data was processed by OriginPro 7.5 and SPSS 13.0.

2.4 Fractionation of Particulate Phosphorus

On May 16, 2008, PP in GCW samples was extremely high according to the analysis, which meant enough PP could be collected from the water, and fractionation of the PP was possible.

On the same day, 50 mL water samples were individually collected from U_{20} , U_{70} , U_{140} , U_{220} , B_{20} , B_{70} , B_{140} and B_{220} twice every hour. In 3.5 h, 350 mL of water samples were collected from each pipe. Then, the 50 mL water samples were analyzed for traces of Al, Fe and different species of P, while the remaining 300 mL was equally divided into three samples.

A 0.45 μm filter was used first to filter one water sample (100 mL), and then air dried and prepared for P fractionation. Samples were sequentially extracted by five processes following the procedure of Ivanoff as modified by Zhu [15, 21]:

- 30 mL 1 M MgCl_2 (pH 8) was used to obtain exchangeable PP (Ex-PP) by shaking for 2 h followed by centrifugation.
- 30 mL of 0.5 M NH_4F (pH 8.2) was used to liberate aluminum-bound PP (Al-PP) by shaking for 1 h followed by centrifugation.
- 30 mL of 0.1 M NaOH buffered with 0.5 M Na_2CO_3 was used to extract iron-bound PP (Fe-PP) by shaking for 4 h followed by centrifugation.
- To extract occluded PP (Oc-PP), 24 mL of 0.3 M $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 1 M NaHCO_3 and 0.675 g $\text{Na}_2\text{S}_2\text{O}_4$ (pH 7.6) were first added, and stirred for 15 min. Then 6 mL of 0.1 M NaOH was added, shaken for 8 h, followed by centrifugation.
- 30 mL of 1 M HCl was used to release calcium-bound PP (Ca-PP) by shaking for 16 h followed by centrifugation. The residue left was organic PP (Org-PP). The resulting extracted solutions were characterized by ICP-OES.

3 Results and Discussion

3.1 Variation of P Speciation

The concentrations of TP, TDP, SRP, PP and DOP at different locations of both CWs are shown in Fig. 2. Similar decreasing gradients of TP, TDP and SRP were observed with increasing distance from the inlet in each layer of the CW. There was a fluctuation from U_{140} to U_{180} in the GCW, where the TP increased from 0.346 mg/L at U_{140} to 0.402 mg/L, while SRP increased from 0.157 to 0.249 mg/L. The increase of SRP was nearly twofold the TP increase. However, the same phenomenon was not observed in the SCW. We ascribe this to biological release. U_{180} of the GCW was possibly the turning point of DO, where SRP would be largely released from the biological organisms.

DOP could be used as a nutrient source for plants through enzymatic hydrolysis [22, 23], especially when the level of SRP was very low [24]. In each CW, the DOP level remained relatively constant, which was also observed in Monbet's research [25]. However, the mean value of DOP in the SCW was 0.023 mg/L, which was slightly higher than the 0.020 mg/L observed in the GCW. This is likely

Figure 2. Speciation of P in water samples at all the fourteen locations: (a) SCW and (b) GCW. Each box plot is the statistical value of 50 analyses.

caused by different P removal mechanisms in each CW. Removal of P is largely reliant on precipitation in SCW and on adsorption in GCW. Precipitation in CW has no effect on DOP levels [25].

The contents of PP were very different in these two CWs. In the SCW, the mean value of PP was around 0.05 mg/L at all the locations. However, the PP was much larger in the GCW, and a noticeable trend was observed. The mean value of PP decreased slowly from 0.216 to 0.11 mg/L in the upper layer, and from 0.155 to 0.093 mg/L at the bottom. Unlike SRP as the immediate P source for biological uptake, PP provides a long term source of P for aquatic plant growth in surface water [26], and can be biologically available in some special situations like resuspension [27] and anoxic conditions [28]. Dierberg [9] reported a large amount of PP in the effluent of five stormwater treatment wetlands in South Florida. By incubating this PP in a laboratory under oxic or anoxic conditions, the amount of SRP released was very small and quite different from each other,

Figure 3. Percentage of PP, DOP and SRP in TP from (a) water samples in SCW and (b) water samples in GCW.

varying from 2–16%. However, this SRP which was released was only labile P adsorbed on particulates. In natural circumstances, the SRP released from PP would certainly increase. The stability and bio-availability depend on the characteristics of PP and also on the circumstances. Nevertheless, PP causes less eutrophication than SRP.

In the two CWs, the relative contributions of the P species to TP differed from each other (see Fig. 3). In the SCW, PP accounted for 8.7–12.35% of TP, SRP accounted for 80.71–87.67% and DOP accounted for 3.96–7.52%. In comparison with the SCW, the P species in the GCW changed towards a higher proportion of PP (20.13–41.83%) and relatively lower proportions of SRP (53.11–77.06%) and DOP (2.81–5.26%). When considering the Redfield ratio of 106 C/16 N/1 P [29] in surface water with low nutrient concentrations, SRP and DOP are both considered to be available P for organisms [30]. Thus, SRP is available directly and DOP is available through enzymatic hydrolysis, while PP is only a latent pool. The results of this study suggested that the GCW was much better than the SCW in preventing eutrophication because of the lower TP concentration at U₂₂₀ and B₂₂₀, and also the higher proportion of PP in the water column.

3.2 pH and DO of Water

The pH value between the wetlands was different. Compared to the fluctuation of pH in the SCW, the pH in the GCW was relatively stable. The highest mean value of pH was 7.90 at U₂₀, while the lowest was 7.71 at B₂₂₀ (see Fig. 4). pH values did not show any correlation with depth. Considering that the pH in water is affected by ions released from substrates, a stable pH suggested the physical and chemical properties of gravel did not change much throughout the experiment, nor did the P removal mechanism.

High levels of Ca in blast furnace slag resulted in a high pH in the SCW, with a mean value of 9. With time however, the pH in the SCW decreased gradually from 10 to about 8.5. This phenomenon was also observed in Adam's study [31, 32]. The reason might be Ca loss and the formation of precipitates which prevented the metal releasing.

pH plays an important role in the retention of P by substrates and influences P removal mechanisms [26, 33, 34]. In this study, the pH not only differed between two CWs but also varied between the two layers of the SCW, which might result in different P speciation.

Figure 4. pH value of water samples in the fourteen locations for both CWs. Each result is the statistical value of 16 analyses.

Figure 5. DO in the fourteen locations for both CWs. Each result is the statistical value of 16 analyses.

Variations in DO were mainly found between layers (see Fig. 5). At the bottom of both wetlands, DO was almost at the same level, about 0.4 mg/L. In the upper layer, DO decreased quickly in the front and slowly at the end of both wetlands. DO in the upper layer of the SCW was about 0.3 mg/L higher than that of the GCW. DO is generally depleted in four major categories: sediment litter oxygen demand, respiration requirements, carbonaceous and nitrogenous biochemical oxygen demand [35]. Given the same influent, the difference in DO between the two wetlands might result from respiration. Due to the more appropriate pH in GCW, biological activities would be higher in GCW than SCW, and therefore consumed more DO.

3.3 Fractionation of PP in GCW

PP extraction analyses were carried out in May 2008, and the results are shown in Fig. 6. Comparing with SRP and DOP, PP was the major proportion of TP in this part of experiment.

Figure 6. Results of PP extraction analyses and TDP for water samples in the GCW. Data are means of triplicate analysis of samples.

Ex-PP represents weakly adsorbed inorganic P that acts as a buffer maintaining the concentration of P in solution, and thus providing temporary and intermediate storage of P [36]. In the upper layer, Ex-PP was zero at U_{20} and increased gradually to 0.0352 mg/L at U_{220} . This was because of decreasing assimilation by microbes and plants with decreasing DO. At the bottom, the Ex-PP level was relatively constant, indicating that HRT, as well as the microbes and plants, had little effect on it.

Al-PP and Fe-PP are formed by chemical adsorption, which involves ligand exchange. In this experiment, the two fractions were the main portions of the PP and TP, indicating that Al and Fe played important roles in P removal in GCW. Fe-PP differed remarkably with both depth and distance. At U_{20} , Fe-PP was 0.530 mg/L, but decreased to 0.309, 0.214 and 0.140 mg/L at U_{70} , U_{140} and U_{220} , respectively. The Fe-PP levels at the bottom were all below 0.15 mg/L. At the end and bottom of the GCW, DO was relatively low (see Fig. 5) and the majority of Fe ions existed as Fe(II) because of the reducing conditions. The results showed the P could easily be bound to Fe(III) oxide or hydroxide, but reduction of Fe(III) into Fe(II) would lead to the release of P. Except for U_{220} and B_{220} , Al-PP in the samples of the other six locations ranged from 0.231–0.285 mg/L. Compared to Fe-PP, Al-PP was more stable and unaffected by DO or redox conditions, which has also been shown in other research [26, 37].

Oc-PP represents parts of Al-PP and Fe-PP that are covered by Fe oxide or hydroxides. The Oc-PP level increased from 0.005 to 0.069 mg/L in the upper layer, and from 0.040 to 0.098 mg/L at the bottom. The variation of Oc-PP was opposite to that of DO observed in this study. However, Shenker [38] pointed out that P was first adsorbed by Al and Fe and then part of it was occluded by iron oxide or hydroxides. In contrast, P release would proceed from the outer to inner layers with reductive dissolution of Fe oxide or hydroxides, releasing the absorbed P first, then the occluded P. The phenomena observed in this study could be caused by the collective functioning

of Fe-PP, Al-PP and Oc-PP together: i) At B_{20} , B_{70} and B_{140} , where the DO was lowest in the GCW, Fe-PP was maintained at about 0.14 mg/L. The liberation of P still proceeded in the outer layers. Fe ions, Fe-PP and Oc-PP might form an equilibrium which would result in a slight increase of Oc-PP. ii) It had been suggested that a large P retention capability was even possible in anaerobic pore water in wetland soils with a Fe/P molar ratio greater than 3 [39]. Due to the low P level, Fe/P ratios in the GCW were very high in most locations (see Tab. 1). This could be the reason for the abundant Fe-PP and the increasing Oc-PP level.

Ca-PP was a minor portion of PP in the GCW, indicating its minimal effect on the P removal mechanism. Org-PP, which is connected with biota activities, was a certain part of TP at most locations. Org-PP accounted for 15.98% of PP at U_{20} , and then rose to 21.34% at U_{70} , and 29.36% at U_{140} . The ratios were lower but more stable in the bottom, which were 13.94, 16.96 and 15.82% at B_{20} , B_{70} and B_{140} , respectively. These were very different to the high Org-PP in marine water, where Org-PP was always more than 50% of PP due to the higher phytoplankton biomass [17]. In our study, Org-PP levels disappeared at the end of the GCW, indicating that there might be a large amount of storage of organic P at the back-end of the GCW.

Fractions of PP have different behaviors and effects on water and bio-organisms. Ex-PP is quite unstable and can release SRP easily. Fe-PP can be mobile and available for bio-organisms in the environment, especially under anoxic condition [40]. Al-PP is very stable in water and sediments [28]. The mobility of Ca-PP is low in many conditions [41]. But when the environment is abundant with bio-organisms, Ca-P would release P rapidly [40]. Oc-PP is the most inaccessible and is leached the slowest of all inorganic P [42]. The stability of Org-PP was unclear because it also contained various compounds such as inositol phosphates, nucleic acids and phospholipids [13]. However, Reddy suggests that most of the P stored in deep peats is organic [43], and this indicates that Org-PP is relatively stable.

In this study, Oc-PP and Al-PP together accounted for 45.22 and 50.91% of PP at U_{220} and B_{220} , respectively. Fe-PP may be stable and remained in the water column. Only about 10% of the Ex-PP would release SRP to the environment. Furthermore, no Org-PP was detected in the water column, which means that it was all sequestered in the wetland and peats were expected to be formed.

3.4 P-removal Mechanisms

The two wetlands were constructed in a similar manner, including wetland size, plant and substrate diameter. The differences in P speciation could only arise from the characteristics of the different substrates. Figure 7 shows the surface structure and composition of the used blast surface slag and gravel. In the SEM image of the slag, many vesicular materials can be seen on the surface. According to the EDS analysis, Ca (31.04% in wt.) accounted for a large proportion of the whole, with only 1.07% P. Additionally, Fe (6.15%), Al (0.61%) and Mg (0.86%) were all at a low level. Relative to the results for the slag, the materials on the gravel surface were much richer in Mg (6.08%), Fe (12.06%) and Al (1.31%). Also, the P content was 2.12%, twice the concentration in the slag. The content of P found on the substrates was not as much as those reported in other studies [44], which might be because of the low P concentration in the secondary effluent. However, it was quite clear that the P removal mechanisms were mostly linked to Ca in the SCW, and to Fe and Al in the GCW. It should be explained that the different chemical properties of substrates between the results of EDS and XPS was because of these two

Table 1. Concentrations of Al, Fe and SRP for water samples in the GCW.

	U ₂₀	U ₇₀	U ₁₄₀	U ₂₂₀	B ₂₀	B ₇₀	B ₁₄₀	B ₂₂₀
Fe (mg/L)	1.294	1.463	1.481	1.584	1.507	2.955	2.136	2.454
SRP (mg/L)	0.091	0.025	0.012	0.025	0.294	0.261	0.065	0.025
Fe/P (molar)	7.87	32.40	68.32	35.07	2.84	6.27	18.19	54.34

Figure 7. SEM image and EDS analyses for the surfaces of substrates: (a) blast furnace slag and (b) gravel.

analysis methods. The result of XPS showed the elemental proportions of the entire substrates, while the result of EDS showed the proportions of the selected area.

The presence of Ca facilitates P retention via precipitation [20, 33], while Fe and Al can bind P through both precipitation and adsorption [21]. Furthermore, biological activities were higher in the GCW. Therefore, the P-removal mechanism in the SCW was mostly through precipitation, but involves multiple aspects in GCW, such as precipitation, adsorption and biological interactions. Considering the higher PP in the GCW and the high proportion of SRP in the SCW, there may be some inner relationship between the mechanism and speciation. Multiple P-removal mechanisms in wetlands might lead to the low proportion of SRP in the water column.

PP must play an important role in P removal mechanism in GCW, since it was the major component in TP. In the upper layer, PP decreased gradually, especially Fe-PP. However, as the concentration of Fe increased, the SRP level changed little along the wetlands (Tab.

1). This suggested that the deoxidization of Fe-PP did happen in the wetlands, but the released SRP was removed from the water or converted into other P forms. We propose that in the upper layer, the abundant PP exchanged intensively with SRP and acted as an intermediate in the P removal process. At the front of the GCW, a large amount of PP was formed. The biological bodies, their extracellular products and some resuspended particulates may be the nuclei of PP formation. SRP were then transformed into PP by adsorption by these nuclei. When these particulates became larger in size, they were adsorbed on substrates or deposited in the wetlands. Therefore, this part of SRP was removed from water column and sequestered by the wetland.

Phosphorus is sequestered in a variety of forms in wetlands, in which the most important one is organic P [13, 42]. In the SCW, P species that were sequestered could not be traced. In the GCW, it should be both the organic P and Al bound P that were largely sequestered. But whether they would become stable in the wetland floor and stored as peat still needs to be further investigated.

4 Conclusions

Blast furnace slag and gravel are two kinds of substrates frequently used in wetlands. Many researchers showed that slag performed better for P removal from wastewaters than gravel. However, the water quality of secondary effluent is different from wastewater. P was mostly present as SRP in the secondary effluent, while PP dominated in the wastewater.

In this experiment, we found that SRP changed into other P forms in wetlands in treating secondary effluent. DO was found in both SCW and GCW in similar concentrations, while abundant PP was found in the GCW, but little in the SCW. Because of the different availability for organisms, different P forms influence the environment differently. SRP is available directly and DOP is available through enzymatic hydrolysis, while PP is only a latent pool. So, the results of this paper showed that GCW might be better than SCW in treating secondary effluents.

This study was supported by Project for Science and Technology of The Chinese Academy of Sciences to Supporting the Building in Binhai District of Tianjin (No. TJZX1-YW-03); Knowledge Innovation Project of the Chinese Academy of Sciences (No. KZCX1-YW-06-02), and Special Foundation for Science and Technology Innovation of Tianjin (No. 06FZZDSH00900).

The authors have declared no conflict of interest.

References

- [1] C. Hu et al., Effects of Long-term Wastewater Application on Chemical Properties and Phosphorus Adsorption Capacity in Soils of a Wastewater Land Treatment System, *Environ. Sci. Technol.* **2005**, 39 (18), 7240–7245.
- [2] S. P. Faulkner, C. J. Richardson, *Physical and Chemical Characteristics of Freshwater Wetland Soils. Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*, Lewis Publishers, Chelsea, MA **1989**, pp. 41–72.
- [3] M. Sundaravadeivel, S. Vigneswaran, Constructed Wetlands for Wastewater Treatment, *Crit. Rev. Environ. Sci. Technol.* **2001**, 31 (4), 351–409.
- [4] C. J. Richardson, Mechanisms Controlling Phosphorus Retention Capacity in Freshwater Wetlands, *Science* **1985**, 228, 1424–1426.
- [5] L. Johansson, J. P. Gustafsson, Phosphate Removal Using Blast Furnace Slags and Opoka-mechanisms, *Water Res.* **2000**, 34 (1), 259–265.
- [6] E. J. Dunne, K. R. Reddy, M. W. Clark, Phosphorus Release and Retention by Soils of Natural Isolated Wetlands, *Int. J. Environ. Pollut.* **2006**, 28 (3–4), 496–516.
- [7] J. M. Dorioz, E. A. Cassell, A. Orand, K. G. Eisenman, Phosphorus Storage, Transport and Export Dynamics in the Foron River Watershed, *Hydrolog. Process.* **1998**, 12 (2), 285–309.
- [8] T. A. DeBusk et al., An Investigation of the Limits of Phosphorus Removal in Wetlands: A Mesocosm Study of a Shallow Periphyton-dominated Treatment System, *Ecol. Eng.* **2004**, 23 (1), 1–14.
- [9] F. E. Dierberg, T. A. DeBusk, Particulate Phosphorus Transformations in South Florida Stormwater Treatment Areas Used for Everglades Protection, *Ecol. Eng.* **2008**, 34 (2), 100–115.
- [10] C. van der Zee, N. Roelvros, L. Chou, Phosphorus Speciation, Transformation and Retention in the Scheldt Estuary (Belgium/The Netherlands) from the Freshwater Tidal Limits to the North Sea, *Mar. Chem.* **2007**, 106 (1–2), 76–91.
- [11] P. Monbet, I. D. McKelvie, P. J. Worsfold, Combined Gel Probes for the In Situ Determination of Dissolved Reactive Phosphorus in Porewaters and Characterization of Sediment Reactivity, *Environ. Sci. Technol.* **2008**, 42 (14), 5112–5117.
- [12] M. G. Forbes et al., Dissolved Phosphorus Retention of Light-weight Expanded Shale and Masonry Sand Used in Subsurface Flow Treatment Wetlands, *Environ. Sci. Technol.* **2004**, 38 (3), 892–898.
- [13] B. L. Turner, S. Newman, J. M. Newman, Organic Phosphorus Sequestration in Subtropical Treatment Wetlands, *Environ. Sci. Technol.* **2006**, 40 (3), 727–733.
- [14] M. J. Hedley, J. W. B. Stewart, B. S. Chauhan, Changes in Inorganic and Organic Soil Phosphorus Fractions Induced by Cultivation Practices and by Laboratory Incubations, *Soil Sci. Soc. Am. J.* **1982**, 46 (5), 970.
- [15] D. B. Ivanoff, K. R. Reddy, S. Robinson, Chemical Fractionation of Organic Phosphorus in Selected Histosols, *Soil Sci.* **1998**, 163, 36–45.
- [16] H. L. Liu et al., Sedimentary Phosphorus Form Distribution and Cycling in the Littoral Subzones of a Eutrophic Lake, *Clean: Soil, Air, Water* **2008**, 36 (1), 78–83.
- [17] T. Yoshimura et al., Distributions of Particulate and Dissolved Organic and Inorganic Phosphorus in North Pacific Surface Waters, *Mar. Chem.* **2007**, 103 (1–2), 112–121.
- [18] A. Drizo, C. Forget, R. P. Chapuis, Y. Comeau, Phosphorus Removal by Electric Arc Furnace Steel Slag and Serpentine, *Water Res.* **2006**, 40 (8), 1547–1554.
- [19] C. Pratt et al., Phosphorus Removal Mechanisms in Active Slag Filters Treating Waste Stabilization Pond Effluent, *Environ. Sci. Technol.* **2007**, 41, 3296–3301.
- [20] A. Drizo et al., Phosphorus Saturation Potential: A Parameter for Estimating the Longevity of Constructed Wetland Systems, *Environ. Sci. Technol.* **2002**, 36 (21), 4642–4648.
- [21] *Standard Methods for the Examination of Water and Wastewater*, AWWA, Washington, DC **1999**.
- [22] G. W. Zhu, B. Q. Jin, L. Zhang, L. C. Luo, Geochemical Forms of Phosphorus in Sediments of Three Large, Shallow Lakes of China, *Pedosphere* **2006**, 16 (6), 726–734.
- [23] H. K. Pant, A. C. Edwards, D. Vaughan, Extraction, Molecular Fractionation and Enzyme Degradation of Organically Associated Phosphorus in Soil Solutions, *Biol. Fertil. Soils* **1994**, 17 (3), 196–200.
- [24] K. M. Bjorkman, D. M. Karl, Bioavailability of Dissolved Organic Phosphorus in the Euphotic Zone at Station ALOHA, North Pacific Subtropical Gyre, *Limnol. Oceanogr.* **2003**, 48 (3), 1049–1057.
- [25] P. Monbet, I. D. McKelvie, A. Saefumillah, P. J. Worsfold, A Protocol to Assess the Enzymatic Release of Dissolved Organic Phosphorus Species in Waters under Environmentally Relevant Conditions, *Environ. Sci. Technol.* **2007**, 41, 7449–7485.
- [26] H. K. Pant, K. R. Reddy, F. E. Dierberg, Bioavailability of Organic Phosphorus in a Submerged Aquatic Vegetation-dominated Treatment Wetland, *J. Environ. Qual.* **2002**, 31 (5), 1748–1756.
- [27] M. Sondergaard, P. Kristensen, E. Jeppesen, Phosphorus Release from Resuspended Sediment in the Shallow and Wind-exposed Lake Arresø, Denmark, *Hydrobiologia* **1992**, 228 (1), 91–99.
- [28] T. A. Wilson, S. A. Norton, B. A. Lake, A. Amirbahman, Sediment Geochemistry of Al, Fe, and P for Two Historically Acidic, Oligotrophic Maine Lakes, *Sci. Total Environ.* **2008**, 404 (2–3), 269–275.
- [29] A. C. Redfield, B. H. Ketchum, F. A. Richards, The Influence of Organisms on the Composition of Seawater, in *The Sea* (Ed.: M. N. Hill), Vol. 2, Wiley, New York **1963**, pp. 26–27.
- [30] D. M. Karl, G. Tien, J. Dore, C. D. Winn, Total Dissolved Nitrogen and Phosphorus Concentrations at US-JGOFS Station ALOHA: Redfield Reconciliation, *Mar. Chem.* **1993**, 41 (1–3), 203–208.
- [31] K. Adam et al., Phosphorus Retention in the Filter Materials Shell-sand and Filtralite P[®]-Batch and Column Experiment with Synthetic P Solution and Secondary Wastewater, *Ecol. Eng.* **2007**, 29 (2), 200–208.
- [32] A. Drizo et al., New Evidence for Rejuvenation of Phosphorus Retention Capacity in EAF Steel Slag, *Environ. Sci. Technol.* **2008**, 42 (16), 6191–6197.
- [33] C. A. Arias, M. Del Bubba, H. Brix, Phosphorus Removal by Sands for Use as Media in Subsurface Flow Constructed Reed Beds, *Water Res.* **2001**, 35 (5), 1159–1168.

- [34] L. Zeng, X. M. Li, J. D. Liu, Adsorptive Removal of Phosphate from Aqueous Solutions Using Iron Oxide Tailings, *Water Res.* **2004**, 38 (5), 1318–1326.
- [35] R. H. Kadlec, R. L. Knight, *Treatment Wetlands*, Lewis Publishers, Chelsea, MA **1996**.
- [36] M. G. Forbes et al., Recovery and Fractionation of Phosphorus Retained by Lightweight Expanded Shale and Masonry Sand Used as Media in Subsurface Flow Treatment Wetlands, *Environ. Sci. Technol.* **2005**, 39 (12), 4621–4627.
- [37] K. Reitzel et al., Lake Restoration by Dosing Aluminum Relative to Mobile Phosphorus in the Sediment, *Environ. Sci. Technol.* **2005**, 39 (11), 4134–4140.
- [38] M. Shenker et al., Redox Reactions and Phosphorus Release in Re-flooded Soils of an Altered Wetland, *Eur. J. Soil Sci.* **2005**, 56 (4), 515–525.
- [39] D. Zak, J. Gelbrecht, *Phosphorus Retention at the Redox Interface of Peatlands Adjacent to Surface Waters*, The Annual Report of the IGB, Berlin **2001**, pp. 155–164.
- [40] X. Jiang et al., Effects of Oxygen on the Release and Distribution of Phosphorus in the Sediments under the Light Condition, *Environ. Pollut.* **2006**, 141 (3), 482–487.
- [41] L. H. Kim, E. Choi, M. K. Stenstrom, Sediment Characteristics, Phosphorus Types and Phosphorus Release Rates Between River and Lake Sediments, *Chemosphere* **2003**, 50 (1), 53–61.
- [42] L. Frankowski, J. Bolalek, A. Szostek, Phosphorus in Bottom Sediments of Pomeranian Bay (Southern Baltic-Poland), *Estuar. Coast. Shelf Sci.* **2002**, 54 (6), 1027–1038.
- [43] K. R. Reddy, Forms of Soil Phosphorus in Selected Hydrologic Units of the Florida Everglades, *Soil Sci. Soc. Am. J.* **1998**, 62 (4), 1134–1147.
- [44] A. Kaasik et al., Hydrated Calcareous Oil-shale Ash as Potential Filter Media for Phosphorus Removal in Constructed Wetlands, *Water Res.* **2008**, 42 (4–5), 1315–1323.