Modeling the purification effects of the constructed *Sphagnum* wetland on phosphorus and heavy metals in Dajiuhu Wetland Reserve, China

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ABSTRACT

Wetlands play a significant role in the dilution of contamination, purification of wastewater, and the transformation of toxic substances. In the Chinese Dajiuhu Wetland Reserve, a simple and practical simulation box was used to examine the purification effects of a simulated *Sphagnum* wetland (SW) on phosphorus (KH_2PO_4) and bivalent metal ions (Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+}) at four different concentrations (20, 40, 80, and $160\,mg\,l^{-1}$). The modified pseudo-first order kinetics model (Model I) and the pseudo-second order kinetics model (Model II) were used to simulate the purification effect. The results indicated that the purification ability of the SW was remarkable for all of the contaminants; 80.8–98.3% of phosphorus, 71.0–85.4% of Zn^{2+}, 96.8–99.3% of Pb^{2+}, 93.9–99.8% of Cu^{2+}, and 81.4–96.9% of Cd^{2+} were removed from contaminated water after 2 h. The time required for the heavy metal ions to reach equilibrium had a significant positive correlation with their initial concentrations ($p = 0.004$–$0.048 < 0.05$), whereas the correlation was poor for phosphorus ($p = 0.308 > 0.05$). The dilution effect of the SW played an important role during the first 5 min; average contribution ratio of dilution effects (CRDE) value of each contaminant ranged from 43.0% to 77.4%. Model II had a better quality of fit than Model I based on the correlation coefficients and the average relative deviation between the purification ratio at the 120th minute (PR_{120}) and the purification ratio calculated by the model at the 120th minute ($PR_{120,c}$). Empirical formulas for predicting the purification ability of the SW were derived using the parameters of Model II, which could be used for evaluating the purification value of the SW and for providing the scientific basis for the protection and proper utilization of the Dajiuhu *Sphagnum* wetland.

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1. Introduction

Wetlands are known as "Earth's kidney", and they serve many functions, such as water conservation, runoff regulation, peat accumulation, carbon sequestration, pollution purification, toxic substance transformation, and disaster prevention for droughts and floods (Blanken and Rouse, 1996; Zhao, 1999; Chen and Lu, 2003; Peregon et al., 2007; Kayranli et al., 2010; Wang et al., 2010). Hu et al. (2008) demonstrated that the peat layer in wetlands has a significant role in the purification ability of the SW because the peat has a high specific surface area ($>200\,m^2\,g^{-1}$) (Asplund et al., 1972; Babel and Kurniawan, 2003; Hu et al., 2008) and a variety of polar functional groups, such as aldehyde, carboxyl, keto, and phenolic hydroxyl groups (Adler and Lundquist, 1963; Bailey et al., 1999), which have a considerable adsorption capacity for efficiently adsorbing heavy metal ions and some nonmetal contaminants, such

as cyanide, phosphate, and organic matter (Coupal and Lalancette, 1976; Ho and McKay, 2000; Ringqvist and Oborn, 2002). Since the 1950s, the Dajiuhu government has implemented an increasing number of reclamation policies, such as digging drainage ditches on a large scale and planting vegetation for pasturage and farming. These policies have caused a gradual drying up of the wetland and have decreased the wetland area from 708 ha to 179 ha (Yin et al., 2007; Xiao et al., 2009). Because the water holding capacity of the wetland has decreased, the dominant species transitioned from *Carex argyi* to *Sphagnum palustre*, which has weakened the carbon fixation ability and pollutant carrying capacity of the wetland (Coupal and Lalancette, 1976; Yin et al., 2007). Hu et al. (2008) reported that once the wetland is destroyed, the peat resource will be lost, and then the water purification ability (WPA) of the wetland would no longer exist.

Despite the function of the SW for water conservation, most researchers have only focused on its application as a peat resource (Chen et al., 1990; Gardea et al., 1996; Ho et al., 1996; Sedeh et al., 1996; Ho and McKay, 2000, 2004; Ringqvist et al., 2002; Kalmykova et al., 2008). Some researchers have conducted

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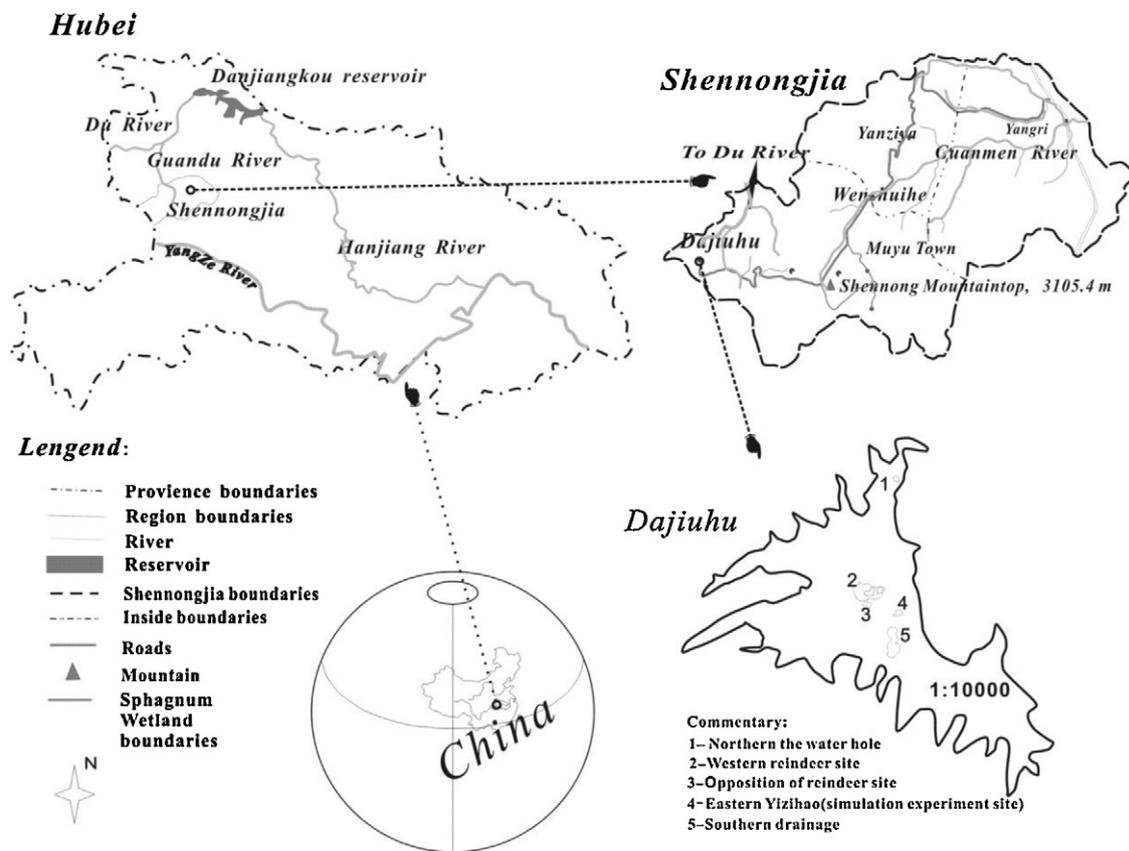*E-mail address:* xufl@urban.pku.edu.cn (F. Xu).

Fig. 1. The geographic location of the experimental site. The lower right-handed part of the figure is the distribution map of the SW, on which simulation experiment is located.

comparative studies of the constructed wetlands' WPA for phosphate when plants existed and when there were not any plants, and concluded that the quality of treated water with plants was better than that without plants (Brix, 1997; Lee and Scholz, 2007; Bindu et al., 2008). Some researchers have used different substrata as a purification material for obtaining the best substratum (Mann, 1997; Sakadevan and Bavor, 1998; Brooks et al., 2000; Xu et al., 2006). Peng et al. (2007) studied the adsorption and release processes under aerobic (>−50 mV) and anaerobic conditions. Some researchers have studied the accumulation and purification of organic matter and heavy metals by the constructed wetlands (von Felde and Kunst, 1997; Tanner et al., 1998; Cheng et al., 2002; Scholz, 2003; Peng et al., 2007). Although all of the above studies were important to our study, they did not directly examine the WPA of the natural SW to the contaminant.

Based on an earlier research conducted at the beginning of August 2007 in the Dajiuhu Wetland Reserve (Hu et al., 2008), this paper further studied the purification effects of the natural SW on nutritious elements of phosphorus (phosphate), cadmium(II), copper(II), lead(II), and zinc(II) through the use of kinetic models to simulate its purification process. The goal of this study was to evaluate the purification value of the SW and to provide the scientific basis for the protection and proper utilization of the Dajiuhu SW. The results from this study will significantly contribute to keeping the water clean for the water source.

2. Materials and methods

2.1. General situation of the study area

The Dajiuhu wetland park is a sub-alpine wetland park, and it is located in the west of the Shennongjia National Nature Reserve

in the western Hubei province of China (Fig. 1). This wetland park has an elevation of 1600–1800 m, an annual mean temperature of 7.4 °C, and a monthly mean maximum temperature of 29.0 °C. The lowest temperature ranges from −18 °C to 22 °C, and the annual mean rainfall is 1585.4 mm with 85.9% occurring between April and October. The research site, Dajiuhu SW, belongs to the north subtropical mountain wetland. The peat deposit was formed in the early Holocene Age, and it has significant scientific research value and considerable economic benefit (Li et al., 2007; Yu et al., 2008). The experimental site is located at the edge of the basin, with flat terrain and hills nearby. The geographic coordinates of the site are 31°29′18.4″N and 110°0′10.5″E. The primary vegetation type is Com. *C. argyi–S. palustre* (Zhao, 1999).

The Dajiuhu *Sphagnum* wetland (SW), which is located in Shennongjia, is a rare type of sub-alpine wetland in China and has a peat layer that is up to 2 m in depth (He et al., 2003). As the source of water for the Duhe River, which is the largest tributary of the Hanjiang River that flows into the Danjiangkou Reservoir—the water source of the Middle Line Project of Water Transfer from the South to the North (MLPWTSN) in China, the Dajiuhu wetland plays a critical role in safeguarding the water quality in the Han River basin and the Danjiangkou Reservoir (Yu et al., 2008).

2.2. Simulation device

First, a hole with a diameter of 35 (±1) mm was drilled at the bottom of the lateral wall of a household plastic box (specifications: 300 mm × 400 mm × 260 mm, wall thickness 2 mm, Jinzun Daily Necessities Co., Ltd., Shanghai, China). Secondly, the hole was blocked with a rubber plug, which contained a glass tube. Thirdly, the tube outside of the box was covered with a latex tube with a spring water stopper and the inside part was covered with gauze.
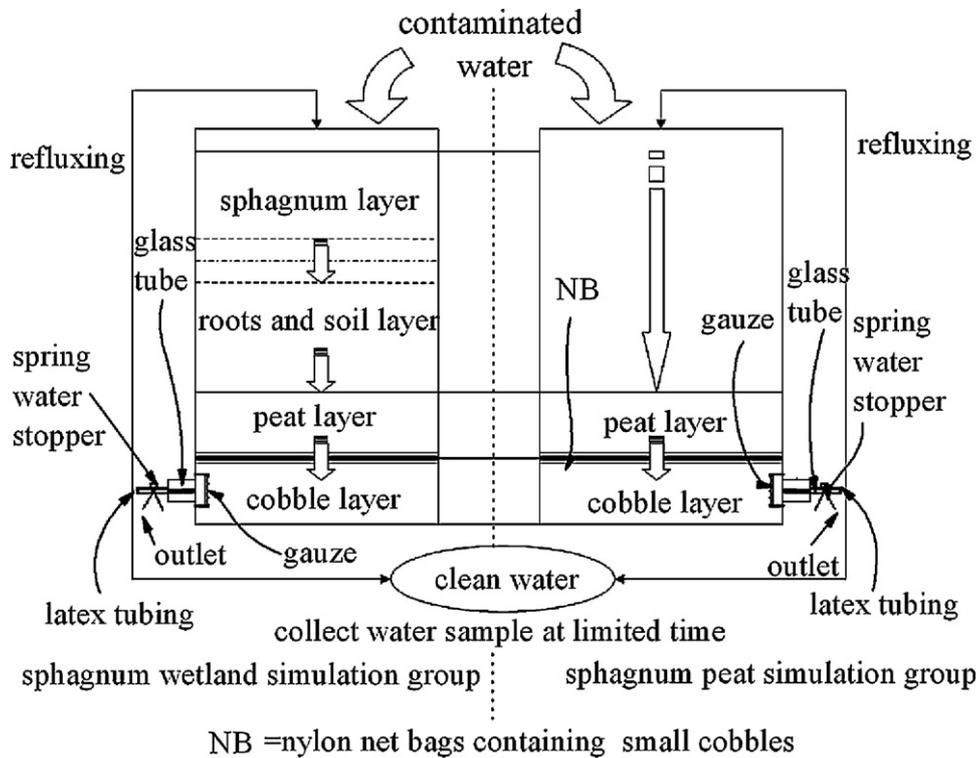
Fig. 2. The process of the SW's purification effects on the contaminated water. The left part of this graph is the SW simulation group; the other is SW peat simulation group which was studied in 2007.

Fourthly, a 50 mm thick layer of cobble was paved at the bottom of the box, which was then covered with a nylon net bag (NB) that contained small cobble. The above design was to prevent the outlet from blocking the cobble and to maintain a normal reflux. Finally, a 10–20 mm thick layer of peat evenly covered the NB, and a *Sphagnum* plant layer with a volume of 300 ($\pm$20) $\times$ 400 ($\pm$20) $\times$ 150 ($\pm$10) mm^3 was layered on the top (Fig. 2).

2.3. Simulation experimental method

A stock solution of 20 g l^{-1} of KH_2PO_4 and the solution of the mixed metal ions (containing Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) were diluted with local well water into four concentrations of 20, 40, 80, 160 mg l^{-1} with a volume of 10 l for each device. The polluted water, which contained TP or metals at four concentration levels, was simultaneously added to each of the four simulation devices. Then, purified water was refluxed using a 600 ml plastic bottle from the outlet to the *Sphagnum* layer. The reflux rate was 2.5–5.0 l min^{-1}. Furthermore, water was evenly sprinkled on the *Sphagnum* layer. Purified water samples were collected at times of 0, 5, 10, 20, 40, 80 and 120 min. The sample at 0 min was collected after two reflux cycles. The volumes of the samples for the TP and metals were 10 and 20 ml, respectively, for each sampling. The total sampling volume of each device was 80–140 ml; therefore, changes in the volume of the pollutants solution was negligible compared to the volume of 10,000 ml of the contaminated water before and after the experiment. A fixed volume of 6 mol l^{-1} of sulfuric acid was added to each metal sample to maintain the water pH $\leq$ 1, while a certain volume of 1 + 9 nitric acid was added to each TP sample to maintain the water pH $\leq$ 2 for storage. After the experiment, the local well water was sampled and preserved with acid, which was used to determine the background value of the studied contaminants; clean *Sphagnum* plants and clean peat were collected to determine the metals content for the background value.

2.4. Storage and processing method for the Sphagnum and the peat

The peat samples, which were obtained in Dajiuhu SW, were dried in air on a plastic cloth in the laboratory, and large pieces of the peat were crumbed into smaller pieces. Subsequently, animal and plant residues were removed. The peat was ground and passed through a 100 mesh sieve and then stored in a 150 ml bottle. The *Sphagnum* plant samples were dried in air under the same conditions as the peat, and then they were cut and ground into small pieces to pass through a 100 mesh sieve.

Approximately 1 g of the pre-treated peat was placed in a 100 ml centrifuge tube that contained 15 ml of 0.1 mol l^{-1} nitric acid, and then the tube was placed in an ultrasonic cleaner for 15 min. The samples were then centrifuged at 4500 rpm for 10 min, and the liquid extract was placed into another tube. The same extraction procedure was conducted two additional times. The collected extract was filtered through a double layer of filter paper and then diluted to a constant volume of 50 ml with 0.2% nitric acid. Approximately 0.2 g of the pre-treated *Sphagnum* plants were placed into a conical flask that contained 10 ml of 1:4 perchlorate-nitric acids, and then the sample was shaken. After standing for 24 h, the sample was thermally digested until the volume was reduced to approximately 2 ml. 0.2% nitric acid was used to dilute the sample that was filtered through three pieces of filter paper to a constant volume of 50 ml.

2.5. Chemical analysis of the sampling water

Each sample was centrifuged and properly diluted for measurement. All measurements were conducted in triplicate, and the average value of the measurements was used. The total P (TP) content of the samples was measured using the molybdenum-antimony anti-spectrophotometric method with a UV-2000 UV-Vis spectrophotometer (Shanghai Precision Instrument Co., Ltd.,

Shanghai, China). The contents of the metals were measured using the TAS-990 atomic absorption spectrometry method (Beijing PuXi General Instrument Co., Ltd.) (Ding, 2006).

2.6. Purification capacity and purification rate

The purification amount (PA or q) was defined as the amount of contaminants removed by the SW due to comprehensive effects, which included dilution of the wetland water, closure and absorption of the Sphagnum, microbial action, and adsorption to the peat and cobble. The purification ratio (PR) was defined as the ratio of the purification amount to the initial amount of contaminant. The dilution process could only reduce the concentration of the contaminants, whereas the removal of the contaminants from the water was the more essential purification process. Therefore, the absorption effect mentioned below was the purification effect, excluding dilution.

The purification amount and the purification ratio were calculated using Eqs. (1) and (2):

$$q_t = (C_0 - C_t)V \qquad (1)$$

And

$$PR_t = \frac{q_t}{C_0 V} \times 100\% \qquad (2)$$

where q_t is the PA of the SW at t min (mg), PR_t is the PR at t min (%), C_0 is the initial concentration of the contaminant (mg l^{-1}), C_t is concentration of the contaminant at t min (mg l^{-1}), V is the volume of the contaminant (l), and V is 10 l in this study.

2.7. Kinetic model

In our earlier study, six models, specifically the pseudo-first order kinetic model, up-limitation-modified pseudo-first order kinetic model, pseudo-second order kinetic model (Model II), Elovich model, two-constant rate model and the hyperbolic diffusion model, were used to study the purification process of SW on TP and copper; the up-limitation-modified pseudo-first order kinetic model and Model II both had a better quality of fit and their own advantages for simulating the purification of SW (Hu et al., 2008). In this paper, the modified pseudo-first order kinetic model (Model I) was different from the one mentioned above and the original model because a new parameter was introduced to calculate the PA, which is primarily caused by the dilution of SW. The model equations are as follows:

Model I

$$q_t = q_e - (q_e - q_0) \times \exp(-k_1 t) \qquad (3)$$

original pseudo-first order kinetic model

$$q_t = q_e(1 - \exp(-k_1 t)) \qquad (4)$$

Model II (Ho and McKay, 2000)

$$q_t = t/(1/k_2 q_e^2 + t/qe) \qquad (5)$$

and the linear form of Model II

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

where q_t is the PA of the SW at t min (mg), q_e is the PA of the SW at the time of the equilibrium point (mg), q_0 is the PA of the SW at 0 min (mg), and the parameters k_1 and k_2 are the rate constants of Model I and Model II, respectively, (min^{-1}) and (mg^{-1} min^{-1}).

Table 1
The background values of material used in the simulation experiment.

	TP	Cd	Cu	Pb	Zn
Dilution water (µg l^{-1})	13.2	1.5	0.0	48.8	35.5
Sphagnum plants (µg g^{-1})	–	5.1	1367.6	19.5	83.7
Peat (µg g^{-1})	–	5.2	207.9	41.5	70.1

The contribution ratio of dilution effects (CRDE) was defined as the ratio between q_0 and all of the contaminants that were added to the SW for each device. This ratio is defined as:

$$CRDE = \frac{q_0}{C_0 V} \times 100\% \qquad (7)$$

where C_0 is the initial concentration of the contaminant (mg l^{-1}), V is 10 l, and $C_0 V$ is the total content of contaminants.

To evaluate the fit of the models, the difference between the fitted values and the experimental data were expressed by the relative deviation between $PR_{120,c}$ and PR_{120}, specifically the RD, which is defined as:

$$RD = \frac{|PR_{120,c} - PR_{120}|}{PR_{120}} \times 100\% \qquad (8)$$

where $PR_{120,c}$ is the PR of the contaminant at the time point of 120 min, which can be calculated using the fitted values, and PR_{120} is the determined PR of the contaminant at the time point of 120 min.

Model II can be used to evaluate the initial time of the purification equilibrium, and it is expressed as:

$$R_{\Delta t} = \frac{q_{t_2} - q_{t_1}}{C_0 V} \qquad (9)$$

where $R_{\Delta t}$ is the ratio of $(q_{t_2} - q_{t_1})$ to $C_0 V$, $\Delta t = t_2 - t_1$, and Δt is assigned as 5 min in the present study. According to Eq. (5), $R_{\Delta t}$ value can be calculated at every 5 min interval, and $R_{\Delta t}$ value tends to be 0. If $R_{\Delta t} < 0.5\%$, we assume the purification approached the equilibration status and the initial time of purification equilibration was t_2 at that 5 min interval.

There is a certain relationship between the parameters q_e and C_0 (a linear relationship) and between k_2 and C_0 (a nonlinear relationship). q_e and k_2 are regressed against C_0 using Eqs. (10) and (11). The empirical formulas were derived using the fitting parameter and Eq. (5); therefore, the PA could be calculated when time t and the initial concentration C_0 are known. Eqs. (10) and (11) were related to those used by Ho and McKay (1999, 2000) as follows:

$$q_e = A + B C_0 \qquad (10)$$

and

$$k_2 = \frac{C_0}{a C_0 + b} \qquad (11)$$

where A and B are parameters of Eq. (10), (mg) and (l), and a and b are parameters of Eq. (11), (mg min^{-1}) and (mg^2 min l^{-1}).

3. Results

3.1. Background values

The background values of the dilution water (DW), Sphagnum plants and peat are presented in Table 1. The contents of copper(II) in the Sphagnum plants and peat were greater than the other metals, and the amount of copper(II) in the Sphagnum plants was greater than that in the peat. The contents of cadmium(II), lead(II) and zinc(II) in the Sphagnum plants and peat were all very low. The amounts of contaminants in the DW were too low to have any effects on the initial concentrations. The concentration of lead was slightly high, occupying 0.24% of the lowest concentration gradient of 20 mg l^{-1}, and the effect of the dilution water was negligible.
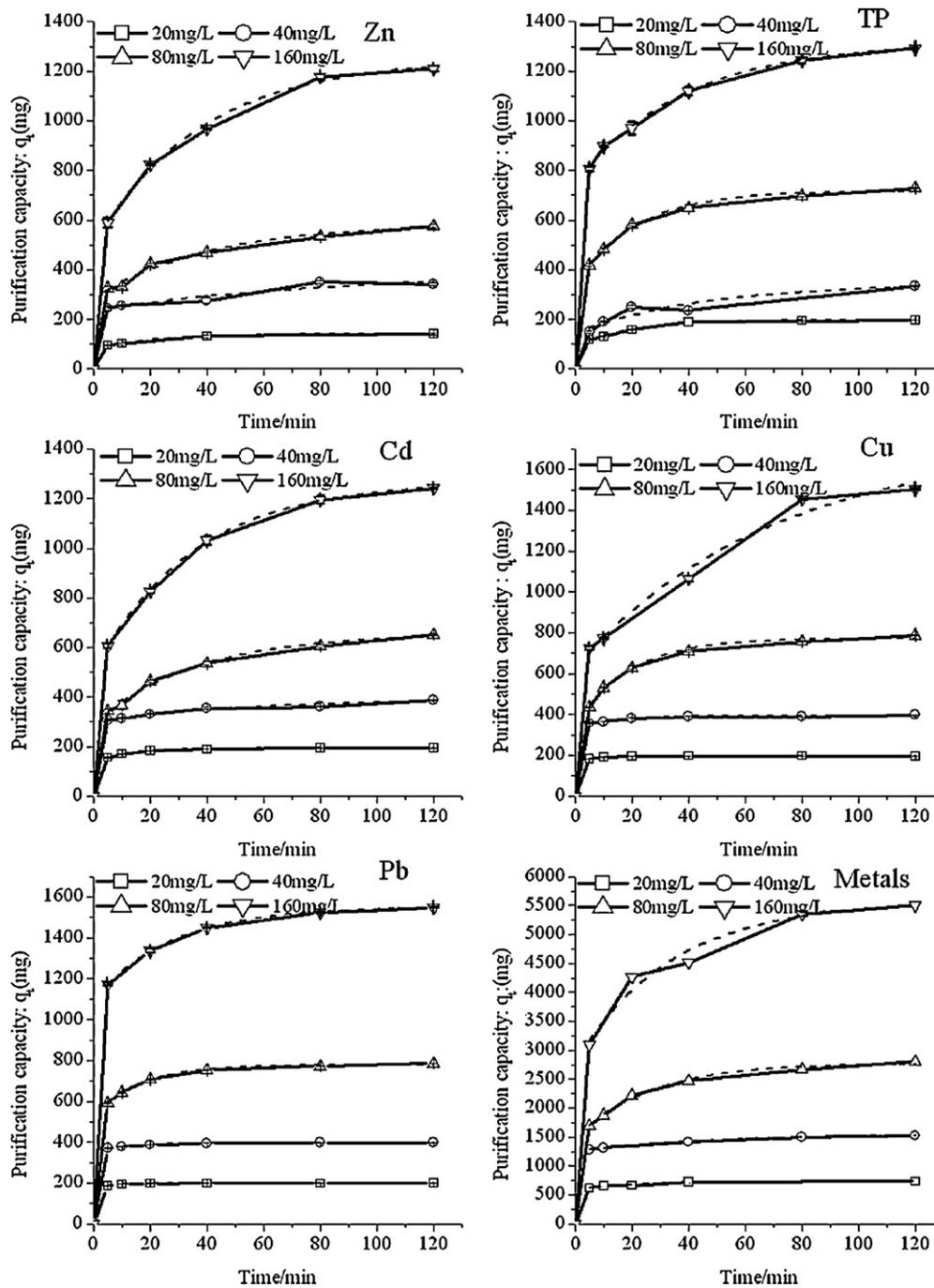
Fig. 3. The purification amount of SW to different contaminants versus time (solid line + symbol) and the fitting curves using Model I (dash line) at various initial concentrations.

3.2. Purification of the SW to TP

The average purification velocity (APV), which is an important parameter that reflects the purification dynamic process of the SW, was defined as the PA within a specified time. In Fig. 3, the APV value between two adjacent sampling time points was calculated as the absolute value of the slope of the line between two points, and the APV value between nonadjacent sampling points was calculated as the absolute value of the slope of the regression line using the two points and those between them, neglecting the fitting degree. The APV values for the TP during the first 5 min in ascending order were 23.89 mg min^{-1}, 30.03 mg min^{-1}, 83.69 mg min^{-1} and 161.36 mg min^{-1}, which indicated that with the increase of the initial concentration, the APV value at the beginning of the purification increased. During each of the following adjacent time segments, the APV of the higher concentration was greater than that of the lower one. According to Fig. 3, the absolute value of the slope between adjacent points clearly decreased with time. This result indicated that the APV of the SW decreased with increasing time. 80 mg l^{-1} of the TP group is taken as an example: The APV values of 5–10 min, 10–20 min, 20–40 min, 40–80 min and 80–120 min were 12.67 mg min^{-1}, 10.00 mg min^{-1}, 3.33 mg min^{-1}, 1.25 mg min^{-1} and 0.75 mg min^{-1}, respectively, which reveals that the purification process approached equilibrium. The purification curve became flat more quickly with lower initial concentrations, which indicated that lowest concentration approached the equilibrium point the fastest.

Table 2
The PR_{120} of phosphorus and metal contaminants at 120th minutes.

Concentration (mg l^{-1})	PR_{120} (%)					
	P	Zn	Pb	Cu	Cd	Metals
20	98.32	71.01	99.51	97.95	96.86	91.34
40	83.70	85.42	99.39	99.83	97.00	95.41
80	91.06	71.97	98.11	98.48	81.44	87.50
160	80.84	75.60	96.80	93.92	77.59	85.98
Average	88.48	76.00	98.45	97.55	88.22	90.06

Notes: Metals represents the average PR_{120} value of the four metals at the same concentration gradient.

3.3. Purification of SW to bivalent metal ions

The same purification laws were observed in the bivalent metal groups, similar to the TP groups, as shown in Fig. 3. During the first 5 min, the APV values of each metal were apparently larger than those of the following time segments because the dilution effect played a significant role at the beginning of the process. During the time of 5–120 min, the APV values decreased with increasing time. The phenomena in the higher concentration groups (initial concentrations of 80 mg l^{-1} and 160 mg l^{-1}) were especially obvious. For the lower concentration groups (initial concentrations of 20 mg l^{-1} and 40 mg l^{-1}), and especially those of copper and lead, the curve became flat after 20 min; therefore, the changes could not be easily distinguished, which indicated that the lower concentration groups require less time to approach the equilibrium point, which was similar to the TP groups. In addition, the time required for different metals to approach the equilibrium varied at the same concentration gradient as indicated by APV values of 5–10 min, 10–20 min, 20–40 min, 40–80 min and 80–120 min. The heavy metal with lower APV values approached equilibrium more rapidly. For the lower concentration groups, the time required to approach the equilibrium for the four metals could be ranked as follows: $Pb^{2+} < Cu^{2+} < Cd^{2+} < Zn^{2+}$. And for the higher concentration groups it could be ranked as follows: $Pb^{2+} < Zn^{2+} < Cd^{2+} < Cu^{2+}$.

4. Discussion

4.1. Purification ability of the SW to various contaminants

The PA is an essential parameter for describing the purification ability of the SW, and the PR_{120} of the SW for each contaminant was computed using Eq. (2) when t was 120 min, as shown in Table 2. The PR_{120} of the simulated wetland tended to decrease with the increase of the initial concentration. The PR_{120} of each metal was observed to be considerably larger than that of the TP, which suggested that the SW had greater purification potential than the TP for metal ions. By considering the average value of the various concentrations for each element, the purification ability of the SW to pollutants could be ranked as follows: Zn < Cd < TP < Cu < Pb.

Due to the limitations of the field simulation experiment, it was difficult to ensure that each SW in the simulation had the same content of peat, *Sphagnum* plants and wetland water. Consequently, an accurate quantitative relationship between the PR_{120} value and the initial concentration was not calculated, but only estimated. However, a comparison among each ion in every gradient could be performed. In total, the purification for lead and copper were both significant, and the PR_{120} values at all concentrations were greater than 90%. Taking 40 mg l^{-1} copper liquid as an example, the PR_{120} was up to 99.83%. The effect for zinc was the poorest, and PR_{120} value at every concentration was lower than that of the other three ions.

The results of an earlier study revealed that the peat had a significant contribution to the purification of SW for copper ion,

accounting for more than 90% of the PA (Hu et al., 2008). Because peat had a strong adsorption of bivalent metal ions (Rock et al., 1985; Ho and McKay, 2000; Ringqvist and Oborn, 2002), any comparison of the purification effect of SW on different, metal ions was actually a comparison to that of peat. Kalmykova et al. (2008) reported that the peat adsorption effect size order for four ions was in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$, and the same conclusion could be made in our study. The affinity between lead & peat and copper & peat was greater than that between cadmium & peat and zinc & peat. Ringqvist and Oborn (2002) suggested that the adsorption effect decreased when the copper ion concentration increased. Because adsorption sites most likely existed for different ions on the peat surface and zinc did not have its own sites, adsorption competition occurred with the other three metal ions, which affected the adsorption of zinc to the peat (Sprynskyy et al., 2006). In addition, when the solution pH were less than 4.0, there were many hydrogen ions and competition would occur between H^+ and the metal ions for the adsorption site (Chen and Wang, 2007). The poorest purification effect of SW to zinc was limited, resulting from weakest affinity between peat and zinc and large amount of H^+ (the pH of SW is 3–4) (Chen et al., 1990; Ringqvist and Oborn, 2002; Kalmykova et al., 2008).

4.2. Kinetic models for modeling the purification effects of the constructed Sphagnum wetland

Based on the above results, the dilution effect of the SW played an important role in the first 5 min of the purification process. Under the assumption that the process of dilution was completed in 5 min, a nonlinear relationship was obtained using the experimental data after the time point of 5 min to construct a plot of q_t versus t, as shown in Fig. 3 (the dashed line). The constants in Model I (Eq. (3)) are presented in Table 3, where the practical meaning of q_0 was the contribution of the dilution effect to the purification of the simulated wetland. The fitted values of the parameter q_e, which is the equilibrium purification amount in Model I, conformed to reality; in other words, they were smaller than the initial values. The values of rate constant, k_1, were observed to be greater at lower concentrations than that at higher ones. The data exhibited good agreement with the proposed modified pseudo-first order equation (Eq. (3)) because the regression coefficients were between 0.9069 and 0.9999, with the majority of the coefficient greater than 0.99.

The contribution ratio of the dilution effect (CRDE) to the purification effects of the SW could be calculated using Eq. (7), and their values are presented in Table 4. For the bivalent metal ions, CRDE was the greatest at the initial concentration of 40 mg l^{-1}. Overall, the CRDE was greater at higher initial concentrations than that at lower ones, which indicated that the adsorption of metal ions by the simulated wetland was greater with higher initial concentrations, that is, the value of the initial absorption rate of the SW to contaminants increased with changes of the initial concentration. The average CRDE of the four metal ions at different concentrations decreased in the order of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$.

The results once again suggested that peat had a different adsorption amount and initial adsorption rate for different metal ions, among which Pb was the largest for both of them. Using the experimental data, a linear relationship was obtained from the plot of t/q_t versus t, which indicated that the linear form of Model II (Eq. (6)) was more applicable to the system studied because the regression coefficients were between 0.9855 and 1, as shown in Table 3. The equilibrium purification amount, q_e, increased with the increase of the initial concentrations of the contaminants, whereas the values of the rate constant in Model II, k_2, were observed to decrease when C_0 increased from 20 mg l^{-1} to 160 mg l^{-1}. The value of k_2 decreased by one order of magnitude when the initial concentration increased by one-fold for copper. Among the

Table 3
Parameters of Model I and Model II.

Parameters, C_0 (mg l^{-1})	Model I						Model II				
	q_e (mg)	q_0 (mg)	k_1 (10^{-2} min^{-1})	R^2	PR$_{120,c}$ (%)	RD (%)	q_e (mg)	k_2 (10^{-4} mg^{-1} min^{-1})	R^2	PR$_{120,c}$ (%)	RD (%)
Cd											
20	193.23	134.99	8.80	0.9954	96.6	−0.3	196.46	36.65	1.0000	97.1	0.3
40	391.07	299.82	1.97	0.9615	97.8	0.8	389.11	8.61	0.9980	94.9	−2.1
80	655.59	292.40	2.82	0.9913	81.9	0.6	684.93	1.72	0.9971	80.0	−1.8
160	1269.63	499.34	2.87	0.9994	79.4	2.3	1347.23	0.69	0.9969	77.3	−0.4
Cu											
20	198.63	168.88	18.57	0.9972	99.3	1.4	196.85	507.93	0.9999	98.3	0.4
40	397.94	362.67	6.26	0.9996	99.5	−0.3	400.00	26.15	0.9998	99.2	−0.6
80	778.48	527.61	6.11	0.9966	97.3	−1.2	819.67	2.22	0.9997	98.0	−0.5
160	1551.19	1095.36	3.72	0.9997	96.9	3.2	1603.69	0.64	0.9855	92.7	−1.3
Pb											
20	197.22	163.95	17.19	0.9837	98.6	−0.9	199.60	193.08	1.0000	99.6	0.1
40	395.27	343.39	6.19	0.9644	98.8	−0.6	400.00	53.42	1.0000	99.6	0.2
80	773.66	345.23	5.27	0.9921	96.7	−1.4	800.00	5.44	0.9999	98.1	0.0
160	1726.52	630.54	1.46	0.9839	107.9	11.5	1581.86	2.15	0.9997	96.5	−0.3
Zn											
20	142.76	83.39	4.18	0.9970	71.4	0.5	149.03	10.49	0.9921	70.7	−0.4
40	386.14	234.51	1.22	0.9069	96.5	13.0	355.87	5.75	0.9928	85.5	0.1
80	583.74	285.20	2.50	0.9806	73.0	1.4	602.41	2.09	0.9965	70.6	−1.9
160	1249.96	501.24	2.64	0.9956	78.1	3.3	1315.45	0.70	0.9960	75.4	−0.3
TP											
20	197.55	93.12	5.14	0.9921	98.8	0.5	204.50	11.03	0.9993	98.6	0.3
40	335.38	95.08	5.15	0.9999	83.8	0.2	355.87	2.70	0.9861	81.9	−2.2
80	717.83	344.86	4.61	0.9932	89.7	−1.5	757.58	2.36	0.9994	90.5	−0.6
160	1315.61	746.83	2.64	0.9971	82.2	1.7	1342.92	1.28	0.9984	80.1	−1.0
Metals											
20	733.32	596.93	4.54	0.9562	91.7	0.4	740.74	9.80	1.0000	91.5	0.2
40	1556.87	1256.55	1.98	0.9983	97.3	2.0	1543.45	3.25	0.9998	94.9	−0.5
80	2771.03	1477.72	3.85	0.9922	86.6	−1.0	2895.26	0.63	0.9995	86.5	−1.1
160	5560.47	2783.17	3.00	0.9715	86.9	1.0	5699.40	0.32	0.9983	85.2	−1.0
ARD[a]						2.1					0.7

[a] Average of the values above in RD column of each model.

different contaminants, the rate constant values clearly varied, even at the same concentration levels and especially at lower concentrations.

The rate constant values for copper and lead were approximately one order of magnitude greater than those for cadmium and zinc when the concentrations were 20 mg l^{-1} and 40 mg l^{-1}. At higher initial concentrations, i.e., 80 mg l^{-1} and 160 mg l^{-1}, the rate constant value for copper was the same order of magnitude as that for cadmium and zinc with little difference, whereas the rate constant value for lead was clearly greater than that of the other metals, which suggests that the SW has the highest purification amount for lead.

Two parameters, the relative deviation (RD) and the average relative deviation (ARD), were introduced for evaluating the two kinetic models. For Model I, the RD was between −1.5% and 13.0% and the ARD was 2.1%, whereas for Model II, the RD was between −2.2% and 0.4% and the ARD was 0.7%. When the regression coefficient, the RD and the ARD are considered, it can be concluded that Model II provided the best fit to the studied purification system, which is consistent with the results of a previous study (Hu et al., 2008).

Model II fitted the experimental data very well; therefore, this model could be used to estimate the equilibration time of the purification system. The system was considered to have reached equilibrium if no changes in greater than 0.5% of the initial value of the purification amount were observed at a certain time segment (Kalmykova et al., 2008). The fitting effect of Model II was satisfactory; therefore, the experimental data at each time point could be calculated using the parameters of Eq. (6). Then, by using Eq. (9) to calculate purification rate $R_{\Delta t}$, if $R_{\Delta t} < 0.5\%$, the equilibration time was t_2, as shown in Table 5. The equilibration time of each contaminant varied from 15 min to 95 min, and longer times were required to reach steady state conditions for contaminants with higher initial concentrations. When the initial concentrations were 20 mg l^{-1} and 40 mg l^{-1}, lead and copper had equilibration times of 15–35 min, whereas cadmium, zinc and TP required 2–3 times longer to reach equilibrium. When the initial concentrations were 80 mg l^{-1} and 160 mg l^{-1}, the equilibration time for all of the contaminants were between 70 and 95 min, except for lead, which had values of 50 min and 55 min, respectively. The time required for the heavy metal ions to reach equilibrium had a significant positive correlation with their initial concentrations ($p = 0.004–0.048 < 0.05$), whereas the correlation was poor for phosphorus ($p = 0.308 > 0.05$).

Table 4
The contribution ratio of dilution effects to the purification of the simulated wetland.

Concentration (mg l^{-1})	CRDE ($q_0/C_0 \cdot V$) (%)					
	P	Zn	Pb	Cu	Cd	Metals
20	45.47	41.69	84.44	81.98	67.49	68.90
40	36.61	58.63	90.67	85.85	74.95	77.53
80	43.11	35.65	65.95	43.15	36.55	45.33
160	46.68	31.33	68.46	39.41	31.21	42.60
Average	42.97	41.83	77.38	62.60	52.55	58.59

Table 5
The expected equilibration time of different contaminants.

Concentration (mg l^{-1})	Equilibration time (min)				
	Cd	Cu	Pb	Zn	P
20	40	15	20	65	70
40	55	35	25	65	90
80	80	75	50	75	75
160	90	95	55	90	70

The relationship of the equilibrium PA, q_e, the rate constant, k_2, and the initial concentration, C_0, in Table 3 could be described using Eqs. (10) and (11), respectively, and the fitting parameters were calculated. The fit quality was so good that the correlation coefficient was 0.9953–1.000 for Eq. (10), and it was 0.8629–0.9987 for Eq. (11). By substituting the parameters into Eqs. (10) and (11) and then into Eq. (5), the empirical formulas for q_t expressed by C_0 and t were obtained, as shown in Eqs. (12)–(17):

for Cd:

$$q_t = \frac{(44.55 + 8.13C_0)^2 C_0 t}{3.43 \times 10^3 C_0 - 6.32 \times 10^4 + (44.55 + 8.13\,C0)^2} \tag{12}$$

for Cu:

$$q_t = \frac{(1.24 + 10.05C_0)^2 C_0 t}{1.26 \times 10^3 C_0 - 2.49 \times 10^4 + (1.24 + 10.05C_0)^2} \tag{13}$$

for lead:

$$q_t = \frac{(5.28 + 9.87C_0)^2 C_0 t}{0.60 \times 10^3 C_0 - 1.10 \times 10^4 + (5.28 + 9.87C_0)^2} \tag{14}$$

for Zn:

$$q_t = \frac{(-8.48 + 8.19C_0)^2 C_0 t}{4.44 \times 10^3 C_0 - 6.99 \times 10^4 + (-8.48 + 8.19C_0)^2} \tag{15}$$

for TP:

$$q_t = \frac{(50.65 + 8.19C_0)^2 C_0 t}{6.50 \times 10^3 C_0 - 11.18 \times 10^4 + (50.65 + 8.19C_0)^2} \tag{16}$$

for Metals:

$$q_t = \frac{(13.83 + 9.54C_0)^2 C_0 t}{9.00 \times 10^3 C_0 - 15.95 \times 10^4 + (13.83 + 9.54C_0)^2} \tag{17}$$

Eqs. (12)–(17) present the contaminants purified by the simulated wetland as a function of contact time and initial concentration; therefore, the equations could be used to predict the purification amount of the five contaminants at any reaction time and at any given initial concentrations between 20 mg l^{-1} and 160 mg l^{-1} using the system studied in this paper.

4.3. Importance of the Sphagnum wetland and further study

The Dajiuhu SW has recently experienced significant ecological and environmental changes, such as an increase in the discharge amount and planting of vegetation on the wetland, which leads to a gradual degradation of the wetland (Yu et al., 2008). All of these activities have caused considerable damage to the ecological functions of the SW. Furthermore, the impact of agricultural non-point source pollution to water source area of MLPWTSN might occur in the near future unless we protect the remaining SW and recover the lost wetland. The conclusion of this paper emphasizes the importance of the Dajiuhu wetland, such as SW to the preservation of the water source, suggesting that measures should be taken to prevent further reclamation and to protect and restore the wetland as soon as possible.

Due to the protection and sensitivity of the study area, a large scale in situ study was not designed. Therefore, there were some disadvantages in using a box simulation research near the area. These disadvantages included: (1) the simulation time lasted only 120 min; therefore, absorption of the Sphagnum plants and microbial action were not studied; (2) a small scale study cannot reflect the purification potential of the entire Sphagnum wetland; (3) non-point resource of the farmland near the wetland was not considered during the evaluation of the importance of the Sphagnum wetland purification function; (4) the depth of the wetland, especially the

depth of the peat layer, is considerably greater than the simulated depth in the box; therefore, the purification of the wetland might be underestimated; (5) the concentration of the contaminated water in this study might be slightly higher than that in the environment, hence, a lower concentration should be added. In consideration of the actual situation of the Dajiuhu and the disadvantages of the box simulation, a further study that comprises two directions will be performed. The first objective is to determine the potential purification effects of the Sphagnum wetland on the total phosphate from the farmland on a large-scale over a long time period. The second objective is to evaluate the potential purification effects of the entire Sphagnum wetland using the box simulation data, remote sensing data, geological structure data and parameters of the contamination transport model.

5. Conclusions

The purification ability of the SW was remarkable for all of the contaminants; 80.8–98.3% of phosphorus, 71.0–85.4% of Zn^{2+}, 96.8–99.3% of Pb^{2+}, 93.9–99.8% of Cu^{2+}, and 81.44–96.9% of Cd^{2+} were removed from contaminated water after 2 h. The time required for the heavy metal ions to reach equilibrium had a significant positive correlation with their initial concentrations ($p = 0.004$–$0.048 < 0.05$), whereas the correlation was poor for phosphorus ($p = 0.308 > 0.05$). The dilution effect of the SW played an important role during the first 5 min; the average CRDE value of each contaminant ranged from 43.0% to 77.4%. Empirical formulas for predicting the purification ability of the SW were derived using the parameters of Model II, which could be used for evaluating the purification value of the SW and for providing the scientific basis for the protection and proper utilization of the Dajiuhu Sphagnum wetland.

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