Phosphorus release: A biogeochemical insight from a restored lakeside wetland in the Yangtze-Huaihe region, China

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Abstract

The heavy intensification of agriculture in East China since the 1980s caused the decrease of lake area and water storage capacity with impediment of regulation, lake eutrophication and frequent floods. Many restoration projects have been conducted. However, the knowledge of biogeochemical factors that drive nutrient cycles during the early stage of restoration is still limited. We studied the effect of the remediation of a patch of near-shore shallow wetland on the northern bank of Chaohu Lake in the Yangtze-Huaihe region, China, which was used as rice paddy for many years, on the behavior of phosphorus. Redox potential (ORP), temperature and dissolved oxygen were monitored in situ from May 2006 to November 2007. Samples of soil pore water were collected during this time for the determination of different forms of iron and phosphorus. ORP showed a clear transition of the wetland soil from an oxidized state in winter to a reduced state in summer. The decrease of ORP correlated with the release of large amounts of Fe and P. The maxima of total dissolved Fe and total dissolved P in the summer of the second year were (13.8 ± 6.8) mg/L and (0.88 ± 0.27) mg/L, respectively. It is worth noticing that P concentration far exceeded the critical value of lake eutrophication (0.02 mg/L). The pressure of P release to the adjacent lake during the first two years of wetland restoration from rice fields should be taken into account by environmental policy makers.

Key words: wetland restoration; phosphorus; eutrophication; redox potential; iron

DOI: 10.1016/S1001-0742(09)60114-5

Introduction

Lakeside wetlands have been recognized as buffer zones between uplands and lake ecosystems. They can effectively trap pollutants and retain nutrients from catchments (NOAA et al., 2003). Consequently, the protection and restoration of lakeside wetlands have become a useful method for water quality improvement (Weller et al., 1996). The ability of wetlands to retain or release pollutants depends on the physical, chemical and biological characteristics of associated soils (Reddy and Patrick, 1993). The properties and biogeochemical processes of wetland soil hence have become a key link in the restoration process. However, the properties of wetland soil in restored lakeside wetlands have been highly altered through years of agricultural uses. The alteration of soil properties has been so intense that restoration efforts were not successful on the short term for most locations, especially not for nutrients N and P (Bruland et al., 2003). There is no information about how the history of the soil influences the processes of wetland restoration. Malakoff (1998) and Zedler (2000) found that created wetlands accumulated less nitrogen and produced less organic matter than a nearby reference wetland, so it is debatable whether it is possible to restore wetlands to work like in their natural state. Phosphorus is the most critical nutrient affecting wetland restoration and water quality at least in the initial phase of eutrophication – the key limiting nutrient for lake primary production (Correll, 1998; Liu et al., 2006). Phosphorus can be adsorbed or released by wetland soil and the processes involved are controlled by various environmental factors, i.e., pH, temperature, redox potential, phosphorus availability in the substrate, microbial activities (Christophoridis and Fytianos, 2006).

The Yangtze-Huaihe region, with abundant lake and river systems, is one of the eight natural wetland regions in China (An et al., 2007) and has a large population and developed economy. Under the pressure of the steady increase in population and relative scarcity of available land, 13,000 km² lake wetlands (20% of the total wetland area in China) were claimed as farmland in this region from the 1950s to the 1980s (Shi and Zhou, 2006). Meanwhile, many levees and dams were constructed for water storage and flood control. These activities were accompanied by the disappearance of typical lakeside areas (Jin and Liu, 2003). Lake and ecosystem structures changed greatly, which affected lake functions even further. The natural regulation and storage capacity of lakes declined, which...
was followed by the biodiversity loss and water quality deterioration (Liu and Zhao, 2003).

Agricultural cultivation in the region has been intensified since the agricultural reform in the 1980s (Zhang and Shan, 2008). The average dosage of chemical fertilizers increased from 750 kg/km² in the 1950s to 120,000 kg/km² in the 1990s in the Chaohu catchment (Zhang, 2005). A large proportion of N and P entered the lake because of improper use. Non-point pollution from agricultural runoff gradually became a major factor affecting lake water quality (Yan et al., 1999). With the onset of lake eutrophication and frequent floods, especially the flood disaster of the Yangtze River catchment in 1998, the local government gradually realized the importance of lakeside wetlands for pollutants barrier and floodwater storage and “Returning farmland to lake” had been developed as a national policy (Jiang et al., 2004). Subsequently, several studies were carried out in the region to investigate the P budget and cycle in an agricultural catchment near a lake (Yan et al., 1999), the P retention capacity of a wetland area (Fu et al., 2005), and P historical distribution under the intensely agricultural activities (Zhang and Shan, 2008). However, the dynamic mechanisms and transformation processes of P during the early stage of wetland restoration were still unclear and few studies had been performed in this field.

In this work, a typical agricultural sub-catchment near Chaohu Lake in the Yangtze-Huaihe region was selected to study the behavior of P during the early stages of lakeside area restoration. The redox processes and phosphorus biogeochemistry of soils that were heavily affected by agriculture were monitored during the first two years after restoration, PVC pipes (diameter 32.5 cm, length 70 cm) were drilled into the pipe walls. The pipes were 10 cm exposed to the surface. Many holes about 2 mm in diameter were drilled vertically along the side) were placed at each sampling point. The PVC pipes were hammered into the soil to 60 cm depth with only 10 cm exposed to the surface. Many holes about 2 mm in diameter were drilled into the pipe walls. The pipes were then wrapped by three layers of gauze with different apertures. The pipe top was covered by gauze to prevent other matter from entering.

1 Materials and methods

1.1 Study area

Chaohu Lake (30°58′N–32°06′N, 116°24′E–118°00′E) is one of the five largest freshwater lakes in China, located in the center of Anhui Province and emptying into the Yangtze River. It covers an area of 755 km² and its catchment area is 12,938 km². The catchment has a transitional monsoon climate between subtropical and warm temperate. The annual average precipitation is 900.5 mm. The mean annual temperature is 16.1°C. It is a typical intensified agricultural area in the Yangtze-Huaihe region, and many lakeside areas had disappeared due to land reclamation since the 1950s. For flood control, levees and dams were constructed, especially on the northern bank. Chaohu was influenced by such intense artificial control that the fluctuation of the water level was minor and the annual average water level was 8.03 m. Chaohu is hypertrophic since the 1980s, partly because large amounts of fertilizers and pesticides were used in this area in the effort to produce high crop yields (Zhang and Shan, 2008). By the year 2000, the mean application of phosphate fertilizer of the Liuchahe catchment (which was near the studied watershed and had similar agricultural structure and land pattern) was as high as 27,000 kg/km², nearly eight times that used 20 years before.

This study focused on a sub-catchment named the Duotang catchment, with an area of 0.5 km² (Fig. 1). It is close to the northern bank of Chaohu Lake. This region had intensified agriculture and no industrial production. Its land use was mainly composed of forests, villages, rice fields, farmlands and ponds. The study site had a length of 155 m and a width of 60 m and was downstream of the Duotang catchment where rice fields had been cultivated for many years. This was a typical high-yield agricultural area and large amounts of fertilizers and pesticides had been applied to the rice fields every year. Tillage ceased at the end of 2005 and restoration began in early 2006. We only removed the lakeside obstructions to restore the water exchange with the lake and constructed an earth dike to divert the upstream agricultural inflow. Soil and vegetation characteristics were investigated pre- and post-restoration. The site originally had no weed other than the residual stubbles of the rice.

A transect next to Chaohu was selected for sampling (Fig. 1). It was a swampy lakeside zone and the depth range of the surface water was generally less than 10 cm. Three sampling points 20 m apart were set along a transect. To monitor the biogeochemical processes during the restoration, PVC pipes (diameter 32.5 cm, length 70 cm, with 2 mm diameter holes drilled vertically along the side) were placed at each sampling point. The PVC pipes were hammered into the soil to 60 cm depth with only 10 cm exposed to the surface. Many holes about 2 mm in diameter were drilled into the pipe walls. The pipes were then wrapped by three layers of gauze with different apertures. The pipe top was covered by gauze to prevent other matter from entering.

Fig. 1 Location of the study area and sampling site. Three locations were selected in a transect with distances of 20 m.
1.2 In situ monitoring

In order to trace the changes of the redox system during two years of wetland restoration, the redox potential (ORP), temperature and dissolved oxygen (DO) were monitored in situ. Monitoring was carried out once a month from May 2006 to November 2007 (due to instrument malfunctioning, bad weather etc., measurements are missing from July 2006, February, July and September 2007). An Orion 4-star pH/ISE portable meter (Thermo, USA) (range ± 1999.9 mV; resolution ± 0.1 mV; relative accuracy ± 0.2 mV) and a triode electrode (Orion 9179 BNMD, Thermo, USA, with a silver/silver chloride reference electrode) were used to monitor the redox potential and temperature of the soil pore water in the pipe. The readout of the instrument delivers the redox potential relative to the standard hydrogen electrode. A portable dissolved oxygen meter (YSI 550A, YSI, USA, range 0–50 mg/L; resolution 0.01 mg/L, relative accuracy 0.3 mg/L) were used to monitor DO.

A portable device was made for monitoring and sampling. Its main body was a wooden stand with two broad bases which could be placed in a steady position on the wetland soil. A motile strait batten with holes placed every centimeter passed through the center of the stand vertically, which could be fixed at each scale manually. A redox electrode connected with a motile end was vertically moved into the PVC pipe. The equipment was operated slowly to avoid disturbance of the pore water. Data were recorded with a resolution of 1 cm for ORP and temperature, and 20 cm for DO in the vertical direction.

1.3 Sample collection and analysis

Along with the in situ monitoring, water samples were collected synchronously. A long latex tube was fixed to the electrode that was moved into the PVC pipe. The other end of the tube was fixed to a 100-mL glass syringe. When the ORP was measured, 100 mL water samples for P analyses were extracted from 20, 40 and 60 cm depth. The samples were collected in polyethylene bottles, sent to the laboratory and stored at 4°C. Another set of samples for Fe was collected in the same way but infused into the bottles pre-acidified (10% hydrochloric acid) to pH < 2 by nitric acid.

Total phosphorus (TP) and dissolved total phosphorus (DTP) were determined after peroxysulphate digestion in the unfiltered and filtered samples (using 0.45 µm cellulose acetate membrane), respectively. Soluble reactive phosphorus (PO$_4^{3-}$-P) levels were determined colorimetrically with the molybdenum blue method. Fe(II) was measured by direct phenanthroline colorimetry and total Fe after reduction to Fe(II) with hydroxylamine hydrochloride. Fe(III) was calculated by total Fe minus Fe(II) (APHA, 1998). These tests were all completed within two days in the field lab near our sampling site.

Data from the three sampling locations were considered as triplicate sets because of similar altitude, surface water level and soil properties, thereby data of latter figures were the average of three pipes. Data processing and graphics making were accomplished using Excel 2003, Origin 8.0 and SPSS 13.0 for windows.

2 Results

2.1 Redox potential

Redox potential of the soil pore water showed a clear seasonal trend during the two years of monitoring (Fig. 2). The soil pore water was reduced in the summer and the lowest values of the year were observed between May and August with (126.2 ± 88.9) mV in June 2006 and (136.5 ± 86.4) mV in August 2007. The ORP then gradually increased to reach the high level of 310–340 mV from November to January, and maxima occurred in December 2006 (360.9 ± 13.2 mV) and in January 2007 (359.5 ± 16.2 mV). Transitional periods of four months from March to April and September to October with intermediate values were observed. Correspondingly, DO concentration was a mirror image of the redox potential (Fig. 2a) and rose from about 0.1 mg/L in summer to 12 mg/L in winter, while the range of temperature varied from approximately 28°C in summer to 6°C in winter. The seasonality of the water level and rainfall is shown in Fig. 2b. The water level of Chaohu Lake had a similar trend with ORP level. While in some months, they could not follow this rule, which may be ascribed to the rainfall. The rainfall of the watershed did not have immediate relation with ORP, but the high...
Intensity rainfall could largely alter the water level (such as in August 2006 and August 2007) and then indirectly affected ORP levels.

A clear inflection point of ORP in soil pore water could be found vertically during the two years of monitoring, below which was an amplitude layer. In this layer, ORP was unstable and had a drastic change as expressed in Fig. 3, where four typical months were chosen to display this phenomenon. The locations of the inflection points (18 and 22 cm below the ground) were close in summer for the two years (June 2006 and 2007), with the ORP values near this point ranging from 253 to 246 mV (2006) and from 252 to 235 mV (2007). A lower location, 55 cm below the ground, was found in March 2007, with the value near this point changing from 373 to 288 mV. No inflection point could be observed in November 2006. The phenomena of inflection points expressed the transition from oxidation state to reduction state. Inflection points may appear at about 20 cm below the ground in the summer and decline along with the change of season, eventually reaching a point below our monitoring depth of 60 cm in winter.

2.2 Iron

The total amount of Fe in the soil did not change greatly during the two years of wetland restoration. The value was $(25.71 \pm 3.56)$ g/kg ($n = 18$) in November 2005 and $(26.84 \pm 7.77)$ g/kg ($n = 36$) in November 2006. The content and forms of Fe in the soil pore water changed greatly with season during the two years (Fig. 4). The concentration of total Fe rose in summer and then descended in winter. It remained at a high state in first summer and was higher in the second summer, with a maximum of $(27.31 \pm 3.58)$ mg/L at 60 cm below the ground in August 2007 (Fig. 4a). Fe$^{2+}$ displayed a consistent trend with the total Fe and had a maximum of $(24.78 \pm 1.75)$ mg/L at the same depth with total Fe in August 2007 (Fig. 4b). However, the concentration of Fe$^{3+}$ had no obvious rise until the next year, with a maximum of $(7.29 \pm 6.26)$ mg/L also at the same depth in June 2007 (Fig. 4c). Fe$^{2+}$ accounted for the majority of the total Fe during this period. None of the three forms of Fe showed any obvious variation with low concentrations of less than 1.5 mg/L (total Fe) from November to the next January and Fe$^{3+}$ was predominant during this period. The concentration of Fe was little higher than that in winter months during the transitional months with the predominant form alternating.

Similar with the vertical variation of ORP, the forms of Fe in the soil pore water also varied with depth during the two years of monitoring (Fig. 4). The concentration of total Fe and Fe$^{2+}$ increased greatly along with depth in summer, and this increase was more prominent during the second summer. The concentration of Fe$^{3+}$ did not exhibit a great difference at different depths until the second summer.

2.3 Phosphorus

The concentration of TP in the soil pore water had a larger fluctuation and four clear peaks appeared during the two years of monitoring (Fig. 5). The first two peak values were $(0.24 \pm 0.07)$ mg/L and $(0.31 \pm 0.19)$ mg/L at 20 cm below the ground in August and November 2006, respectively. In the next year, the peak values reached
The concentrations of $\text{PO}_4^{3-}\text{-P}$ and DTP exhibited no clear difference with depth in the first year. However, some variation was observed in the second year. Their concentrations were not widely different at the depths of 20 and 40 cm, but had a leap at 60 cm. The huge release of three forms of P during the second summer was probably related to the release of Fe, since the two had similar layer patterns. In addition, the content of all P forms far exceeded that of Chaohu Lake and the critical level of the lake eutrophication (0.02 mg/L) (Fu et al., 2006).

3 Discussion

3.1 Relation between ORP, Fe, and P

Nutrient cycling in wetland ecosystems is controlled by ORP and by the microbial transformations of nutrient elements that occur under conditions in which oxygen is not always abundant (Schlesinger, 1997). Therefore, understanding the changing trend of ORP is very important in the process of wetland restoration. Existing research mostly considered that the soil redox potential was mainly controlled by the water level fluctuation (Catallo, 1999; Dwire et al., 2006). At our study site, the fluctuation of the water level in Chaohu Lake was minor because of the regulation of the downstream dam. Our sampling sites were flat in topography and the depth range of the surface water was generally less than 10 cm; it could be characterized as a swampy wetland. The fluctuation of water level and rainfall only had minor influence on the redox process (Fig. 2b). The seasonal variation of ORP in the soil pore water at our sampling sites could be mainly ascribed to the change of temperature and DO (Fig. 2a). In summer, the rise of temperature accelerated microbial activity and depleted DO. The soil pore water was anoxic and in a reduced state, which displayed a lower ORP value. In winter, although the soil was also inundated sometimes, the lower environmental temperature restricted microbial activities and DO was abundant. For this reason, soil pore water in the spring was oxidized, with high ORP values. At the same time, an amplitude layer could be found in the vertical gradient with a similar seasonal trend. This was a transitional layer from the oxidation state to the reduction state. In summer, the microorganisms at high temperature constantly consumed the oxygen of the soil pore water. When the oxygen was exhausted, the ORP would decline sharply, which caused the phenomena of inflection points. Microbial activities were very active in this layer, thus the ORP value was accordingly unstable. We could confirm the negative correlation between ORP and temperature ($r^2 = -0.652, p = 0.01$) and the positive correlation between ORP and DO ($r^2 = 0.664, p = 0.01$) from Table 1. Water level and rainfall had no statistical relation with ORP, which has not been listed in the table.

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Fe in the soil was constant, the concentration of Fe\(^{3+}\) would decrease accordingly. In winter, Fe\(^{2+}\) was oxidized to Fe\(^{3+}\) and combined with the soil minerals again since the soil pore water was aerobic. Then the concentrations of all Fe forms were very low and no seasonal difference could be found during these months. The vertical variation of Fe was similarly controlled by the transition from an oxidation state to a reduction state. The correlation analysis (Table 1) between forms of Fe and ORP confirmed that Fe\(^{2+}/Fe^{3+}\) were the main electron pairs and were controlled predominantly by the redox processes (Donahoe and Liu, 1998). For the higher release of Fe during the second year, it may be explained by the hysteresis of soil Fe dissolution.

The release of P in soil pore water at our sampling sites was mainly related to the total amount of soil P and P forms. Fe-bound P was as high as 150 mg/kg, accounted for a large proportion (24%) of the high soil P content according to a P-particle test in the nearby Liuchah watershed (Zhang and Shan, 2008). This was also a labile redox-sensitive form of P. Under oxidation conditions (in winter), P was fixed by Fe\(^{3+}\) in the form of oxyhydroxide flocs. Once the ORP dropped to the reduction state, P was released from the flocs along with the reduction of Fe\(^{3+}\) (Aldous et al., 2005). This process was primarily controlled by the content of Fe and may conversely influence the redox process (Table 1). But the extent to which P could alter biogeochemical processes may depend on its relative availability in organic substrates (Sundareshwar et al., 2003). In our study, there was a clear seasonal trend of TP in both of the study years, but a hysteresis and weaker effect of PO\(_4^{3-}\)-P in the first year, which may be explained by the release of not inorganic P, but organic P, from the microbial biomass in the first year (Turner and Haygarth, 2001). Additionally, P release may also originate from the decline of soil pH, which had a direct effect on the dissolution of Ca-bound P minerals (Hambright et al., 2004) or the release of organic P along with the decomposition of organic matter (Wang et al., 2008).

### 3.2 Potential pressure of P release to lake water quality

The importance of lakeside wetland restoration had been generally acknowledged by local governments since the large area outbreak of lake eutrophication. Many lakeside wetlands in the Yangtze-Huaihe region were restored in a gradual and orderly manner. For example, the vegetation pattern stabilized after 2–4 years of restoration in Dongting Lake (Jiang et al., 2004). Our study sites also had prosperous vegetation and considerable biomass in two years. This showed that nature had strong restoration capabilities, and most species could be established in the first two years (Weyembergh et al., 2004). However, existing research showed that the ecological function of restored wetlands usually could not reach the desired criterion or substitute for a real system (Malakoff, 1998; Kaiser, 2001). This may be due to our lack of knowledge about the biogeochemical processes of wetland soil during restoration.

In our research, the use of phosphorus fertilizers in this region gradually increased year by year. Only 20%–30% of the total dosage of the fertilizers could be absorbed and used by crops (Zhou and Wang, 2007). A large amount of P fertilizers would accumulate in the soil profiles or flow into adjacent waters. Yan et al. (1999) investigated the nutrient budget of the Liuchah watershed near our study site and found that the nutrient input was larger than the output as a result of fertilization. Therefore, the nutrient transformation was very strong during the early stage of restoration. It has been shown by our study that a mass of P (the maximum (0.88 ± 0.27) mg/L) was released from the wetland soil to the pore water in summer at least in the first two years of restoration and the concentration had already far exceeded the critical level of P (0.02 mg/L) of lake eutrophication. Our study site was near the lake and the sandy lakeshore, which was favorable for water exchange. Once the soil was inundated, large amount of P would be released to the overlying water or directly inpon to the lake (Liu et al., 2004). The release of P might be temporary and would reach equilibrium, on which occasion the wetland would act as a net P sink eventually (Qiu and McComb, 1994; Aldous et al., 2007). However, these months of release were also periods of outbreaks of algal bloom, which was particularly important. This would inevitably increase the input of nutrients into Chaohu Lake and exacerbated the eutrophication process. Thus the release of P in the early years of lakeside wetland restoration could not be neglected by environmental managers since the duration of release was at least two years and had a trend of deterioration with time.

### 4 Conclusions

Redox potential of soil pore water in the lakeside wetland showed a clear seasonal trend during the first two

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**Table 1** Correlation analysis of main indexes in the soil pore water at the sampling sites from May 2006 to November 2007

<table>
<thead>
<tr>
<th>ORP</th>
<th>T</th>
<th>DO</th>
<th>Total Fe</th>
<th>Fe(^{2+})</th>
<th>Fe(^{3+})</th>
<th>TP</th>
<th>DTP</th>
<th>PO(_4^{3-})-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORP</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>-0.652(^a)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DO</td>
<td>0.664(^a)</td>
<td>-0.654(^a)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Fe</td>
<td>-0.788(^a)</td>
<td>0.384(^a)</td>
<td>-0.460(^b)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>-0.735(^a)</td>
<td>0.306(^a)</td>
<td>-0.374(^a)</td>
<td>0.967(^a)</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>-0.530(^a)</td>
<td>0.466(^a)</td>
<td>-0.496(^a)</td>
<td>0.546(^a)</td>
<td>0.316(^a)</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TP</td>
<td>-0.194(^b)</td>
<td>0.179</td>
<td>-0.073</td>
<td>0.348(^a)</td>
<td>0.379(^b)</td>
<td>0.098</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>DTP</td>
<td>-0.267(^a)</td>
<td>0.256</td>
<td>-0.179</td>
<td>0.379(^b)</td>
<td>0.392(^a)</td>
<td>0.151</td>
<td>0.787(^a)</td>
<td>1</td>
</tr>
<tr>
<td>PO(_4^{3-})-P</td>
<td>-0.358(^a)</td>
<td>0.211(^b)</td>
<td>-0.166</td>
<td>0.532(^a)</td>
<td>0.533(^a)</td>
<td>0.248(^b)</td>
<td>0.683(^a)</td>
<td>0.812(^a)</td>
</tr>
</tbody>
</table>

\(^a\) Correlation is significant at 0.01 level (2-tailed); \(^b\) correlation is significant at 0.05 level (2-tailed).
years of restoration. It transformed from an oxidizing state in winter to a reduction state in summer. The seasonal changes of the redox front could be followed by the gradient of the ORP. The great variation of ORP was directly correlated with the release of a large amounts of dissolved Fe and, simultaneously, the release of large amounts of Fe-bound P in the summer. The maximum P concentration (0.88 ± 0.27 mg/L) far exceeded the critical level for lake eutrophication, and may exacerbate the water quality of Chaohu lake.

Acknowledgments

This work was supported by the National Basic Research Program (973) of China (No. 2006CB403306) and the National Natural Science Foundation of China (No. 50679087). The authors would like to thank Dr. Honglei Liu for his helpful suggestions and Dr. Beat Mueller in Swiss Federal Institute of Aquatic Science and Technology (Eawag) for English improvement.

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