Hong Zhang¹
Benoît Pernet-Coudrier²
Shengfang Wen¹
Beat Müller³
Baoqing Shan¹

¹State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, P. R. China

²Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland

³Eawag, Swiss Federal Institute of Aquatic Science and Technology, Kastanienbaum, Switzerland

Research Article

Budget and Fate of Phosphorus and Trace Metals in a Heavily Loaded Shallow Reservoir (Shahe, Beijing City)

Shahe Reservoir in the headwater of the Wenyu River, Beijing City, was selected for a case study evaluating the effects of both urbanization and agricultural intensification on the cycling of phosphorus (P), as well as Cr, Cu, and Ni. This study showed that the construction of the reservoir in 1960 resulted in an increased retention of P, Cr, Cu, and Ni in its sediment. The load of these elements to the river system has sharply increased since the 1980s. For P, the mean sediment content was 890 ± 270 mg/kg before 1980, but thereafter increased to 1540 ± 700 mg/kg. Most of the sedimentary P was apatite P (47%). The average sediment contents of Cu and Ni increased from 37.3 and 28.8 g/kg to 61.6 and 60.7 mg/kg, respectively. According to mass balance calculations, the actual annual input loads were 110 t P, 500 kg Cr, 520 kg Cu, and 600 kg Ni. Whereas the reservoir retained about 50% of the trace metal loads in its sediment, P retention was only 7%. Hence, the sediment contribution to the P balance of the reservoir is almost negligible and sediment manipulation cannot be a measure for the mitigation of eutrophication in this reservoir.

Keywords: Surface water pollution; Trace elements; Urbanization; Water quality

Received: March 24, 2013; *revised:* September 19, 2013; *accepted:* September 25, 2013

DOI: 10.1002/clen.201300231

Additional supporting information may be found in the online version of this article at the publisher's web-site.

1 Introduction

The contamination of surface water with nutrients as well as trace metals and organic xenobiotics has increased in China in the past 30–40 years as a consequence of rapid urbanization, economic growth, intensification of agricultural productivity, and water scarcity [1, 2]. Drinking water production requires increasingly laborious and expensive techniques, and surface water ecosystems are under great threat with respect to biodiversity and ambient quality [3–5]. Rivers in urban areas are particularly vulnerable due to the lack of sufficient sewage treatment facilities and increasing overexploitation of their headwaters [6, 7]. In addition, dams and floodgates constructed for water storage, irrigation, and flood control destroyed their lateral and longitudinal connectivity, thus impairing self-purification [8, 9]. Due to the high loads of organic matter and nutrients, the reservoirs are highly eutrophic and turn anaerobic below a shallow photic zone, making them unattractive for public use. However, acting as sedimentation basins, they may buffer the impacts of anthropogenic

pollutants on downstream communities [10]. Moreover, their sediments may provide chronological records of anthropogenic and natural inputs [11]. Such information provides insight into matters related to environmental quality concerns [12, 13] and is essential for the development of river restoration strategies [14, 15].

Recently, the Shahe Reservoir and its catchment have been studied with respect to their water quality and water balance [16, 17] as it is the headwater of the Wenyu River and North Canal, the main receiving water system of Beijing. Shahe Dam, built in 1960, was the first dam on the Wenyu River. Nowadays, the reservoir's environment has been developed for leisure activities and fishing, and the water is occasionally used for irrigation of Cuihu Park along the southern bank. An earlier water sampling campaign conducted by the authors in July and August 2009 resulted in the discovery of unexpectedly high concentrations of dissolved inorganic phosphate, ammonium, nickel, copper, and chromium, suggesting anthropogenic pollution that might impair the value of this recreation area.

To estimate the impact of urbanization and intense agricultural development on the reservoir's water quality, this study establishes a mass balance budget for total phosphorus (TP), NH_4^+ , Ni, Cu, and Cr including element net-retention in the reservoir's sediment. Based on its sediment archive we (a) reconstruct the pollution history of the reservoir, (b) evaluate its increasing pollutant loads caused by urbanization and agriculture, and (c) evaluate the effect of the Shahe Reservoir as a pollutant sink on the water quality of the downstream Wenyu River.

Correspondence: Dr. H. Zhang, State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Rd., Haidian District, 100085 Beijing, P. R. China
E-mail: hongzhang@rcees.ac.cn

Abbreviations: GDP, gross domestic production; TDP, total dissolved phosphorus; TP, total phosphorus

2 Materials and methods

2.1 Study area and background

The catchment of the Shahe (meaning “sandy river”) is located on the upper reach of the Wenyu River (renamed the North Canal when leaving Beijing). The Wenyu River, a tributary in the large catchment of the Haihe River basin, has its source in the south of Yanshan Mountain and flows from north to south through Haidian, Changping, Shunyi, Chaoyang, and Tongzhou Districts situated in the core area of Beijing City (Fig. 1). Three tributaries, i.e., the East, North, and South Shahe Rivers (East Shahe River flows into North Shahe River before reaching the reservoir), discharge into the reservoir. They drain a catchment area of 1099 km², 55.9% forested and 23.1% cultivated farmland, 10.3% urban and 9.1% rural areas, and 1.6% rivers and reservoirs in 2005, respectively, compared to 52.5% forest, 35.5% agricultural land, 2.6% urban and 7.7% rural areas, and 1.7% rivers and reservoirs in 1980. The predominant soil type is cinnamon soil [16]. A weather monitoring station is located adjacent to the Shahe dam. The average annual temperature is 11.6°C and average annual precipitation amounts to 582 mm (for the period 1956–2000), with >80% between June and September. The average annual evapotranspiration of 1175 mm exceeds the average annual precipitation by a factor of two. In recent years, at least one-third of the water supplied to Shahe Reservoir was wastewater, and the reservoir is subjected to high loads of organic matter and nutrients.

Based on the monitoring data from the Hydrology Department in Beijing City, the average water depth of Shahe Reservoir is about 2.2 m and its surface area extends >1.86 km², resulting in a capacity of 4 × 10⁶ m³, and an average water residence time of approximately 1.5 month. The average annual outflow to the downstream Wenyu River is 67.4 × 10⁶ m³/year (1980–2010), but in

recent years, the discharge has shrunk due to acute water scarcity, to about 40 × 10⁶ m³/year since 2005. The average inflow is approximately 57 × 10⁶ m³/year in recent years, the infiltration is about 15 × 10⁶ t/year, and the evaporation amount is 2 × 10⁶ m³/year. Because one-third of the inflow to the reservoir is wastewater, its headwaters never dry up although the annual evapotranspiration exceeds the average annual precipitation in their catchments.

2.2 Sample collection and analysis

Samples for water quality analyses were collected monthly at 20 cm below the surface from July 2009 to June 2010 at the outlet of Shahe Dam to calculate the annual effluent loads for TP, Cr, Ni, and Cu. The time schedule is given in Supporting Information Tab. S1. Water samples for total dissolved phosphorus (TDP) were filtered through 0.45 µm pore size cellulose acetate membranes (Whatman). TDP and TP were analyzed after digestion with K₂S₂O₈ for 2 h at 120°C in an autoclave with the molybdenum blue method [18]. Particulate phosphorus was calculated from the difference between TP and TDP. Dissolved Cr, Cu, and Ni were analyzed in HNO₃-acidified samples after filtration through 0.45 µm pore size cellulose acetate membranes (Whatman) with an inductively coupled plasma spectrophotometer (Perkin-Elmer Elan 6000). Particulate Cr, Cu, and Ni retained on the filter membranes. After filtering, a defined amount of water was analyzed with the same method as the sediment.

Six sediment cores were sampled from Shahe Reservoir in April and August 2009 (Fig. 1) using a Uwitec® gravity corer (www.uwitec.at) with an inner diameter of 59.5 mm and a length of 600 mm. Site a was located near the Shahe Dam, while sites e and f were near the inlet of North and South Shahe, respectively. The other three sites (i.e., b–d) were in the central area of the reservoir. Surface water samples were collected from 20 cm below the surface of the reservoir. For overlying water sampling, a plastic pipe connected with a syringe was penetrated carefully nearly to the sediment surface (within 1 cm) in each core, then pull the syringe slowly to collect overlying water. Temperature (T) and pH were measured with a YSI Professional Plus (ProPlus, YSI, USA). Basic information of the six cores is listed in Tab. 1.

The sediment cores were extruded and sectioned in 9 mm slices before the depth of 35.1 cm, and then 18 mm for the rest in the laboratory. Water content was determined from a subsample of each slice, and pore water was extracted by vacuum filtration using another subsample. Grain size distribution of the sediments was determined as described in the Supplementary material, and the remaining material freeze-dried for further analysis. Dried sediments were ground in an agate mortar and sieved (100 µm) prior to analysis.

TP of sediment samples was analyzed by the HClO₄/H₂SO₄ digestion method [19], and P fractionation was determined according to the procedure of van Eck [20] as described in detail by Zhang and Shan [21] (detailed information is given in Supporting information). The determination of organic matter was carried out following the method of residual titration of K₂Cr₂O₇ [21]. For trace metal analysis, 0.1 g sediment sample was digested with 6 mL aqua regia and 2 mL hydrofluoric acid at 180°C for 20 min in a microwave digestion apparatus (CEM MARS 5, USA) following the procedure recommended by the United States Environmental Protection Agency (USEPA, no. 3051a).

Hydrological data on water discharge rates and water level variations in the reservoir were provided by the Hydrology Departments in Beijing City, with monthly resolution during the sampling

Figure 1. Map of the Shahe Catchment with sampling sites.

Table 1. Basic information of the six sediment cores and surface water quality in Shahe Reservoir

Site	Location (N, E)	Water depth (m)	Core length (cm)	T (°C)	pH	TP (mg/L)	DIP (mg/L)	Sampling date
a	40° 7'53.65", 116°19'50.59"	–	36.6	18.7	9.21	3.32 ± 2.57	2.65 ± 2.51	April 2010
b	40° 7'54.37", 116°19'37.60"	5.0	35.1	29.0	8.61	2.90 ± 3.31	2.43 ± 2.71	August 2010
c	40° 7'53.36", 116°19'16.90"	6.5	37.8	29.5	8.66	2.90 ± 3.17	2.48 ± 2.83	August 2010
d	40° 7'53.69", 116°18'58.79"	5.7	38.6	29.8	8.65	2.77 ± 2.98	2.48 ± 2.65	August 2010
e	40° 8'7.62", 116°18'6.44"	1.3	37.8	30.6	9.06	1.62 ± 2.58	1.25 ± 2.44	August 2010
f	40° 7'41.20", 116°18'2.20"	0.4	48.6	29.1	8.59	2.42 ± 2.62	2.18 ± 2.36	August 2010

period. The regional socio-economic data of Beijing from 1949 to 2009 was obtained from the Beijing Municipal Bureau of Statistics, including population data, gross domestic production (GDP) data, wastewater treatment efficiency data, and fertilizer data.

Areal fluxes of TDP, Cu, Cr, and Ni across the sediment–water interface were calculated from pore-water concentration gradients with a one-dimensional transport–reaction model [22] based on Fick's first law of diffusion.

2.3 Quality assurance and quality control of results

Quality assurance and quality control of the analytical procedure for sediment P, Cr, Ni, and Cu determinations was carried out by using method blanks and certified reference material (GBW 07305) purchased from the National Research Center for Certified Reference Materials of China. Five blanks were treated identical to the samples in each batch, and the mean concentrations over all batches were 4.5 ± 1.8 (mean $\pm$ SD) mg/kg P, 1.8 ± 0.26 mg/kg Cr, 0.57 ± 0.19 mg/kg Ni, and 1.5 ± 0.9 mg/kg Cu assuming 0.1 g of the weight, respectively, which had been subtracted correspondingly from sediment samples. Recoveries for P, Cr, Ni, and Cu were 84.3, 94.1, 95.0, and 92.7% averaged over all batches, respectively. Five replicates of the certified reference standards showed relative standard deviations for P, Cr, Ni, and Cu of 4.6, 4.2, 3.9, and 4.4%, respectively. Each sample was analyzed in triplicates and the results averaged. Sediment samples were also analyzed at Eawag (Swiss Federal Institute of Environmental Science and Technology) using standard methods described above for cross-checking.

2.4 Methods for average sedimentation rate estimation and annual budget calculations

An initial attempt of dating the sediment cores of the Shahe Reservoir by their ^{210}Pb activity rendered far too small sedimentation rates leading us to the assumption that the transport of ^{210}Pb from the atmosphere to the sediment must have changed in time. Consequently, we resigned from core dating but instead intended to find a mark in the geochemical sediment profiles that could serve as an indication for the dam construction in 1960. Several observations led us to the assumption that the time of the dam construction 50 years ago lay at 30 cm depth: (1) A change in the porosity profile at 30 cm depth may indicate the change from a flow regime causing a dense silting of the river bed to a still water situation allowing more pore spaces, leading to increasing water content (Fig. 2). (2) A peak in the grain size profile at 26–29 cm depth that may indicate a single event such as construction work in the surrounding area (Fig. 2), but also a flooding event. (3) Moreover, a sedimentation rate in the order of 5–8 mm/year was determined in other shallow eutrophic lakes (Chaohu Lake and Taihu Lake) supporting the above

interpretations [23, 24]. Using an average of 30 cm sediment depth for the change 50 years ago results in an estimated sedimentation rate of 6.0 mm/year. With a total weight of all the layers above 30 cm of 360 g and a diameter of the corer of 5.95 cm we calculate a mass accumulation rate of $2.6 \text{ kg m}^{-2} \text{ year}^{-1}$.

Annual loads of element i , including export load from the outlet ($L_{e,i}$), pore-water flux ($L_{p,i}$), sedimentation load ($L_{s,i}$), and atmospheric input load ($L_{a,i}$) to the reservoir were calculated for the period of July 2009 to June 2010 (detailed description of the methodology for these parameter calculations is included in the Supplementary material). Then the annual input load of element i ($L_{i,i}$) could be calculated based on the differential equation for the element budget of a lake (reservoir) as following:

$$V(dC_i/dt) = L_{i,i} + L_{a,i} - L_{e,i} - L_{s,i} + L_{p,i} \quad (1)$$

where V is the water volume of the lake, C_i is the mean concentration of element i in lake water. Since the annual increase of the lake content is relatively small compared to all other contributions, the steady-state assumption was made for the input calculation, which implied that on an annual basis the change in the element content of the lake is approximately zero.

3 Results and discussion

3.1 Phosphorus in sediments

Prior to reservoir construction, sediment TP contents at all sampling sites, except for site a, were about $750 \pm 126 \text{ mg/kg}$ (Fig. 3) and changed relatively little until the 1980s, when the contents first at

Figure 2. Water content of sediment cores (a–f) taken from different part of Shahe Reservoir, as well as grain size, and organic matter contents.

Figure 3. Total phosphorus concentrations in six sediment cores a–f of the Shahe Reservoir showing the sediment history of P.

sites c and then d, b, and e increased steeply within 1986–1992, 1993–2005, 1998–2006, and 2001–2005, respectively. At site a, the TP content was already about twice as high at that time, increasing by about another 1000 mg/kg soon after damming.

The sediment TP content is the combined result of the interplay of various circumstances. The increasing TP content observed at site a immediately after damming is explained primarily by the physical effects of decreased flow velocity and increased water residence time, resulting in an increased sedimentation of fine organic matter of allochthonous and autochthonous origin. In contrast, we relate the TP increases of all other cores observed after the 1990s to increased P loads to the Shahe Reservoir.

The socio-economic development of Beijing City is shown in Fig. 4. The urbanization process was slowed between 1960 and 1980 with a

total urban population of five million, which was two-thirds of the total population of Beijing (Fig. 4). Since the 1980s, the urbanization was greatly accelerated, and the GDP increased sharply (Fig. 4), suggesting a quickly increasing wastewater production. However, as shown in Fig. 4, the wastewater treatment efficiency remained at a very low level of about 10% during the 1980s. This contradiction between fast socio-economic development and neglected municipal wastewater treatment resulted in the steep increase of effluents to city rivers, which we observe in the sediments of the Shahe Reservoir. Furthermore, since the agricultural reform in the 1980s, agricultural cultivation in the suburbs of Beijing was intensified under the pressure of the steady increase of the population and the relative scarcity of arable land. This resulted in a dramatic increase in fertilizer application. Figure 4 gives an overview of P and N fertilizer

Figure 4. Development of population, GDP, percentage of wastewater treated, and fertilizer (N and P) usage of Beijing City. Data were obtained from the Beijing Municipal Bureau of Statistics.

Figure 5. Fractions of phosphorus in sediment core a taken from the Shahe Reservoir.

use in the Beijing area during the past 30 years. Before 1980, the amount of phosphate fertilizer usage was only 0.1 t P/km^2 but then increased sharply to 1.2 t P/km^2 in 1990. It has been pointed out that over-fertilized soils become increasingly important as a P source to surface waters [25]. Only 10–15% of phosphate fertilizer is absorbed by the soil [26], while the rest is carried from the land into runoff and/or subsurface flow [25]. This explains how under the pressure of both rapid urbanization and agricultural intensification, the input of TP to Shahe Reservoir increased greatly during the last three decades.

In order to refine our information on P sedimentation and benthic metabolism, we performed sequential P extraction of sediment of core a. Figure 5 depicts the sudden increase in the organic and residual P fractions after the damming of the Shahe River in 1960. As the cold NaOH treatment extracted a proportion of organic P

essentially consisting of P associated with humic and fulvic acids, a part of the residual P must be deemed to the highly resistant residual organic P [27]. Apparently, organic and refractory P increased after damming the Shahe River. Sediments with transiently lower organic P contents probably were deposited when the inflows to the reservoir imported increased amounts of allochthonous inorganic soil particles, rich in apatite and Al/Fe-bound P diluting the allochthonous sediment.

Excluding the layers where the organic and residual P content was diluted, it becomes more explicit that the average organic-bound P content before damming ($45.4 \pm 6.7 \text{ mg/kg}$) increased suddenly fivefold to $216 \pm 100 \text{ mg/kg}$ after damming. Concurrently, average residual P nearly doubled from 283 ± 148 to $474 \pm 80 \text{ mg/kg}$ after damming.

3.2 Trace metals in sediments

Cu, Cr, and Ni contents of the reservoir sediments shared the trend observed for P. Although trace metal contents varied in a site-dependent fashion, Cu and Ni contents clearly increased since the 1980s (Fig. 6). As observed for P, the trace metal content increased preferentially at sites b–d, after 1990. However, contrary to the P content, damming by itself did not affect the trace metal content of the sediment at sites a and f. Mean contents were $37.3 \pm 9.5 \text{ mg/kg}$ Cu, $28.8 \pm 7.1 \text{ mg/kg}$ Ni, and $48.9 \pm 10.0 \text{ mg/kg}$ Cr averaged over all cores before 1980, and subsequently increased to $61.6 \pm 29.2 \text{ mg/kg}$ Cu, $60.7 \pm 34.3 \text{ mg/kg}$ Ni, and $63.1 \pm 14.9 \text{ mg/kg}$ Cr, respectively. The increased heavy metal contents (especially Cu and Ni) reflect the growing trace metal load during the last decades in parallel to the rapid urbanization and economic development in Beijing and the reservoir's drainage basin. The possible risks of elevated trace metal concentration with respect to the river ecosystem and the quality of the envisioned recreation area deserve additional careful studies.

Figure 6. Trace metal contents of Cu, Cr, and Ni in sediment cores from Shahe Reservoir.

3.3 Annual budget of phosphorus and trace metals in Shahe Reservoir (2009–2010)

The annual export from the Shahe Reservoir via its outflow from July 2009 to June 2010 (estimated as the product of water discharge time average reservoir concentration) yielded 106 t P/year, 230 kg Cr/year, 230 kg Cu/year, and 346 kg Ni/year (Tab. S1). Fluxes of dissolved elements across the sediment–water interface showed the release of 4 t P/year and 1.1 kg Cr/year, while 2.2 kg Cu/year and 1.3 kg Ni/year were taken up (Supporting information Tab. S2 and Fig. S1). For the past 50 years, sedimentation yielded an average benthic mass accumulation of $2.6 \text{ kg m}^{-2} \text{ year}^{-1}$ (Fig. 2). Considering the average TP, Cr, Cu, and Ni contents observed at the sediment surface (Figs. 5 and 6) and the reservoir's surface area of 1.86 km^2 yields recent annual net sedimentation rates of about 8 t P/year [28], 301 kg Cr/year, 317 kg Cu/year, and 277 kg Ni/year [29], respectively (Supporting information Tab. S3). The direct atmospheric input of those elements to the reservoir from July 2009 to June 2010, was 41 kg P/year, 33 kg Cr/year, 33 kg Cu/year, and 26 kg Ni/year, respectively (Supporting information Tab. S4).

As summarized in Fig. 7, >70% of the annually exported P, Cu, and Ni were dissolved, while Cr was mainly associated with particles (166 kg Cr). On an annual basis the change in the P content of the lake is approximately zero, which we think is justified since the annual increase of the lake content is relatively small compared to all other contributions. Thus assuming steady state and solving the element mass balance equation, yields annual input rates of 110 t P, 497 kg Cr, 516 kg Cu, and 598 kg Ni.

The pollution source census campaign conducted by the Chinese Ministry of Environmental Protection in 2007 identified 100-point sources in the Shahe catchment, including 46 food factories, twelve machine shops, eleven petrochemical factories, eight metallurgical factories, and six pharmaceutical factories, as well as ten wastewater treatment plants. Major pollutants are organic matter, ammonia, phosphorus, and heavy metals, which were directly discharged to tributaries of the upper Shahe River, or indirectly discharged by wastewater treatment plants. Based on the pollution source census campaign conducted by the Environmental Protection

Agency of China in 2007, 106 t of TP was generated in sewage within this watershed, while the average P-removal efficiency of the wastewater treatment plants in Beijing City was reported as 60% by Cao et al. [30]. Accordingly, after removal of 60% of the wastewater TP, the wastewater treatment plants contributed 42 t/year to the TP load of the Shahe Reservoir, leaving 68 t P/year to non-point sources. Relating this amount to the area of cultivated farmland within the Shahe Reservoir's drainage basin (254 km^2) yields an annual TP transfer to the Shahe River of $268 \text{ kg P km}^{-2} \text{ year}^{-1}$, a value exceeding values estimated for intensively fertilized Swiss soils twofold [31].

Figure 7 indicates that Shahe Reservoir sediments retained only 7.3% of the TP input. As the water residence time is very short (1.5 month), only a small fraction of the produced phytoplankton is buried in the sediments while most of it is flushed into the river. In addition, Fig. 7 shows that 80% of TP leaving the reservoir is dissolved P, emphasizing that in this reservoir P is definitely not the growth-limiting factor. Contrary to phosphorus, trace metals were subject to physical deposition at the reservoir bottom. Consequently the reservoir retained 61% of its Cr load, 61% of its Cu load, and 46% of its Ni load. In conclusion, damming a polluted river significantly lowers the trace metal load, but has little effect on its trophic state. In addition, as Fig. 7 illustrates, P release from reservoir sediments contributes only 4% to the TP export from the reservoir. This strongly indicates that sediment dredging would not solve lake internal problems related to eutrophication.

4 Concluding remarks

As an example for many water resources in North China, this case study conducted in the drainage basin of the Shahe River illustrates that urbanization and overexploitation of soils used for agricultural crop production resulted in increased TP and trace metal loads, and hence severe ecosystem deterioration. It shows that damming a heavily polluted river may significantly lower the trace metal load to its downstream reaches but has little influence on its trophic state. The study further explains why dredging of sediment enriched with nutrients can neither mitigate lake eutrophication nor improve water quality.

Figure 7. Synoptic presentation of the annual budgets of TP, Cr, Cu, and Ni of the Shahe Reservoir. PS, point sources; NPS, nonpoint sources; SF, soluble fraction; PF, particulate fraction. Input loads in dashed boxes were extrapolated from output loads, sedimentation, and pore-water fluxes. Data of PS for P (42 t) was obtained by the total amount of PS generated (106 t based on the pollutants census campaign of the Environmental Protection Agency of China) and the treatment efficiency (60%). Accordingly, the load from NPS must equal $110 - 42 = 68 \text{ t/year}$.

Acknowledgments

The authors gratefully acknowledge Xuehong Kong and Dr. Yu Zhao for taking sediment cores, and Wenqiang Zhang and Wei Zhang for trace metal analysis, as well as Dr. Chao Wang for drawing the maps of Shahe Reservoir. Appreciation is extended to Dr. René Gächter for inspiring discussion, and Ruth Stierli and Caroline Stengel at Eawag for cross-checking of phosphorus and trace metals in sediment cores. This work was supported by the External Cooperation Program of the Chinese Academy of Sciences (Grant No. GJHZ0908) and the Major Science and Technology Program for Water Pollution Control and Treatment (2012ZX07203-006).

The authors have declared no conflict of interest.

References

- [1] J. Chen, C. Tang, Y. Sakura, J. Yu, Y. Fukushima, Nitrate Pollution from Agriculture in Different Hydrogeological Zones of the Regional Groundwater Flow System in the North China Plain, *Hydrogeol. J.* **2005**, 13 (3), 481–492.
- [2] W. Tang, B. Shan, H. Zhang, Z. Mao, Heavy Metal Sources and Associated Risk in Response to Agricultural Intensification in the Estuarine Sediments of Chaohu Lake Valley, East China, *J. Hazard. Mater.* **2010**, 176 (1–3), 945–951.
- [3] J. Liu, Z. Yang, Ecological and Environmental Water Demand of the Lakes in the Haihe-Luanhe Basin of North China, *J. Environ. Sci.* **2002**, 14 (2), 234–238.
- [4] J. Xia, H. Feng, C. Zhan, C. Niu, Determination of a Reasonable Percentage for Ecological Water-Use in the Haihe River Basin, China, *Pedosphere* **2006**, 16 (1), 33–42.
- [5] C. Yuan, G. Jiang, L. Liang, X. Jin, J. Shi, Sequential Extraction of Some Heavy Metals in Haihe River Sediments, People's Republic of China, *Bull. Environ. Contam. Toxicol.* **2004**, 73 (1), 59–66.
- [6] B. Malmqvist, S. Rundle, Threats to the Running Water Ecosystems of the World, *Environ. Conserv.* **2002**, 29 (2), 134–153.
- [7] C. Walsh, A. Roy, J. Feminella, P. Cottingham, P. Groffman, R. Morgan, The Urban Stream Syndrome: Current Knowledge and the Search for a Cure, *J. N. Am. Benthol. Soc.* **2005**, 24 (3), 706–723.
- [8] J. Onema, D. Mazvimavi, D. Love, M. Mul, Effects of Selected Dams on River Flows of Insiza River, Zimbabwe, *Phys. Chem. Earth* **2006**, 31 (15–16), 870–875.
- [9] X. Wang, C. Yin, B. Shan, The Role of Diversified Landscape Buffer Structures for Water Quality Improvement in an Agricultural Watershed, North China, *Agric. Ecosyst. Environ.* **2005**, 107 (4), 381–396.
- [10] L. Svendsen, B. Kronvang, P. Kristensen, P. Græsbøl, Dynamics of Phosphorus Compounds in a Lowland River System: Importance of Retention and Non-Point Sources, *Hydrol. Process.* **1995**, 9 (2), 119–142.
- [11] L. Xiang, X. Lu, D. Higgitt, S. Wang, Recent Lake Sedimentation in the Middle and Lower Yangtze Basin Inferred from ^{137}Cs and ^{210}Pb Measurements, *J. Asian Earth Sci.* **2002**, 21 (1), 77–86.
- [12] J. Graney, T. Eriksen, Metals in Pond Sediments as Archives of Anthropogenic Activities: A Study in Response to Health Concerns, *Appl. Geochem.* **2004**, 19 (7), 1177–1188.
- [13] H. Zhang, B. Q. Shan, Historical Records of Heavy Metal Accumulation in Sediments and the Relationship with Agricultural Intensification in the Yangtze-Huaihe Region, China, *Sci. Total Environ.* **2008**, 399 (1–3), 113–120.
- [14] M. Bowes, J. Smith, J. Hilton, M. Sturt, P. Armitage, Periphyton Biomass Response to Changing Phosphorus Concentrations in a Nutrient-Impacted River: A New Methodology for Phosphorus Target Setting, *Can. J. Fish Aquat. Sci.* **2007**, 64 (2), 227–238.
- [15] J. Elser, M. Bracken, E. Cleland, D. Gruner, W. Harpole, H. Hillebrand, J. Ngai, et al., Global Analysis of Nitrogen and Phosphorus Limitation of Primary Producers in Freshwater, Marine and Terrestrial Ecosystems, *Ecol. Lett.* **2007**, 10 (12), 1135–1142.
- [16] Y. Zhang, J. Xia, J. Chen, M. Zhang, Water Quantity and Quality Optimization Modeling of Dams Operation Based on SWAT in Wenyu River Catchment, China, *Environ. Monit. Assess.* **2011**, 173 (1–4), 409–430.
- [17] B. Pernet-Coudrier, W. Qi, H. Liu, B. Müller, M. Berg, Sources and Pathways of Nutrients in the Semi-Arid Region of Beijing–Tianjin, China, *Environ. Sci. Technol.* **2012**, 46 (10), 5294–5301.
- [18] M. Reinhardt, R. Gächter, B. Wehrli, B. Müller, Phosphorus Retention in Small Constructed Wetlands Treating Agricultural Drainage Water, *J. Environ. Qual.* **2005**, 34 (4), 1251–1259.
- [19] S. D. Bao, *Chemical Analysis for Agricultural Soil*, China Agriculture Press, Beijing **2000**.
- [20] G. van Eck, Forms of Phosphorus in Particulate Matter from the Hollands Diep/Haringvliet, The Netherlands, *Hydrobiologia* **1982**, 91–92, 665–681.
- [21] H. Zhang, B. Shan, Historical Distribution and Partitioning of Phosphorus in Sediments in an Agricultural Watershed in the Yangtze-Huaihe Region, China, *Environ. Sci. Technol.* **2008**, 42 (7), 2328–2333.
- [22] B. Müller, Y. Wang, M. Dittrich, B. Wehrli, Influence of Organic Carbon Decomposition on Calcite Dissolution in Surficial Sediments of a Freshwater Lake, *Water Res.* **2003**, 37 (18), 4524–4532.
- [23] Y. Han, J. Cao, T. Kenna, B. Yan, Z. Jin, F. Wu, Z. An, Distribution and Ecotoxicological Significance of Trace Element Contamination in a ~150 yr Record of Sediments in Lake Chaohu, Eastern China, *J. Environ. Monit.* **2011**, 13, 743–752.
- [24] S. Ding, D. Xu, X. Bai, S. Yao, C. Fan, C. Zhang, Speciation of Organic Phosphorus in a Sediment Profile of Lake Taihu, II. Molecular Species and Their Depth Attenuation, *J. Environ. Sci.* **2013**, 25 (5), 925–932.
- [25] A. Sharpley, R. Menzel, The Impact of Soil and Fertilizer Phosphorus on the Environment, *Adv. Agron.* **1987**, 41, 297–324.
- [26] Y. Xiong, Q. Li, *Soils of China*, 2nd Ed., Scientific Press, Beijing **1990**.
- [27] K. R. Reddy, O. A. Diaz, L. J. Scinto, M. Agami, Phosphorus Dynamics in Selected Wetlands and Streams of the Lake Okeechobee Basin, *Ecol. Eng.* **1995**, 5 (2–3), 183–207.
- [28] B. Liang, *MSc Thesis (in Chinese)*, Capital Normal University, Beijing **2005**.
- [29] Y. Cong, Y. Chen, Z. Yang, Q. Hou, H. Wang, Dry and Wet Atmospheric Deposition Fluxes of Elements in the Plain Area of Beijing Municipality, China (in Chinese), *Geol. Bull. China* **2008**, 27 (2), 257–264.
- [30] B. Cao, X. Huang, K. Atsushi, Y. Yang, D. Yang, Pilot Test on Enhanced Biological Nitrogen and Phosphorus Removal by Using A2/O-MBR, *China Water Wastewater* **2007**, 23 (3), 22–26 (in Chinese).
- [31] R. Gächter, J. Ngatiah, C. Stamm, Transport of Phosphate from Soil to Surface Waters by Preferential Flow, *Environ. Sci. Technol.* **1998**, 32 (13), 1865–1869.