

# Potential effects of sediment processes on water quality of an artificial reservoir in the Asian monsoon region

Kiyong Kim,<sup>1</sup> Bomchul Kim,<sup>2\*</sup> Klaus H. Knorr,<sup>3</sup> Jaesung Eum,<sup>2</sup> Youngsoon Choi,<sup>2</sup> Sungmin Jung,<sup>2</sup> and Stefan Peiffer<sup>1</sup>

<sup>1</sup> *Department of Hydrology, BayCEER, University of Bayreuth, Bayreuth, Germany*

<sup>2</sup> *Department of Environmental Science, Kangwon National University, Gwangwon, Republic of Korea*

<sup>3</sup> *University of Muenster, Nordrhein-Westfalen, Germany*

\* *Corresponding author: bkim@kangwon.ac.kr*

Received 29 March 2015; accepted 31 December 2015; published 14 July 2016

## Abstract

Sediment processes in lakes may affect water chemistry through the internal loading of phosphorus, ammonia, and sulfides released under anoxic conditions. Lake Soyang is a deep warm monomictic reservoir with a dendritic shape, located in the Asian summer monsoon region, South Korea. During summer, the lake is stratified and receives a large nutrient input via storm runoff, which forms a turbid intermediate layer with high concentrations of suspended particles. The lake water, the main inflowing stream (the Soyang River), bottom sediment, and porewater of the lake sediments were studied over a 2-year period (2012–2013). After intensive monsoon rain events, particulate organic carbon (POC), total phosphorus (TP), and turbidity were high in the inflowing water (C: 1.21 mg L<sup>-1</sup> in June 2013) and in the metalimnion (2.8 mg L<sup>-1</sup>, 17.6 µg L<sup>-1</sup>, and 58.5 NTU, respectively in July 2013). Higher concentrations of iron (Fe) and manganese (Mn) were also associated with the turbid intermediate layer (37 and 8 µg L<sup>-1</sup>, respectively, in July 2013). During the summer stratification period, oxygen started to deplete in the hypolimnion (down to 0.5 mg L<sup>-1</sup> in September 2013), and sediment became anoxic, showing negative oxidation redox potential (ORP) in core samples. Diffusion of dissolved inorganic P and ammonia from sediment to the water column can be substantial, considering the concentration difference between the porewater and hypolimnetic water. Fe and Mn were abundant in the sediment porewater at the dam site, implying inorganic nutrients and minerals are well transported along the 60 km long lake axis by the density current of storm runoff. Sulfate and reduced sulfur were larger in the porewater of the top sediment than in the lower layer of the sediment core (below 10 cm). The results show that substantial amounts of inorganic nutrients and minerals are supplied to the lake by storm runoffs during monsoon and distributed through the lake by a density current, controlling the material cycle and flux at the sediment surface.

**Key words:** artificial reservoir, Lake Soyang, monsoon, porewater, sediment

## Introduction

Lake sediments are frequently studied to understand and determine changes of water quality and internal processes occurring within lakes (De Boer 1994, Marce et al. 2006, Mushtaq et al. 2015). Lake sediments are used to derive historic changes of catchment processes such as previous changes in land use and agricultural activities (Morellón et al. 2011, Giguët-Covex et al. 2014) and also impact

water quality through internal loads of nutrients and toxic materials (Perkins and Underwood 2001, Liu et al. 2013). Artificial lakes are increasingly created for agricultural and hydroelectric purposes worldwide, especially in many Asian countries (WCD 2000, Gupta et al. 2012), including South Korea, in the monsoon climate area (An and Jones 2000, Bae et al. 2008).

Reservoirs constructed in the middle reach of a river system generally have a higher ratio of watershed area to

reservoir surface area than natural lakes of comparable size, resulting in relatively larger inputs of carbon and nutrients (Knoll et al. 2013). Nutrients and eroded soils from agricultural nonpoint sources are major problems for impounded water quality management in many places (Heathcote et al. 2013, Michalak et al. 2013). Typically, nonpoint source pollution increases when intensive cultivation is combined with monsoon rainfall events, resulting in large amounts of pollutants transported by heavy runoff to receiving waterbodies (Hu and Huang 2014).

Phosphorus (P) is typically the limiting nutrient in freshwater and causes eutrophication by promoting massive algal growth (Correll 1999, Wetzel 2001, Xu et al. 2015). P is easily adsorbed onto soil particles in the watershed and mobilized through soil erosion and enters lakes or reservoirs via storm runoffs or inflowing streams (Ekholm and Lehtoranta 2012). After entering lakes, P can be released from the sediment to the water column, especially under anoxic conditions, enhancing eutrophication in lakes (Søndergaard et al. 2003, Kangura et al. 2013,

Martins et al. 2014, Nikolai and Dzialowski 2014, Kowalczevska-Madura et al. 2015, Tang et al. 2015). Additionally, toxic materials such as ammonia ( $\text{NH}_4^+$ ) and dissolved sulfides ( $\text{S}^{2-}$ ) are released under anoxic conditions, depending on the concentrations of nitrogen (N), sulfur (S), and decomposable organic matter (Besser et al. 1998, Holmer and Storkholm 2001), and can harm the aquatic ecosystem (Wang and Chapman 1999). Thus, the internal load from lake sediment processes is considered an important factor in lake water quality management.

Previous Lake Soyang studies investigated its trophic state, phytoplankton–zooplankton successions, and C dynamics (Kim et al. 1985, 2000, 2001, Lee et al. 2013), but we found no study that focused on the interaction between lake water quality and sediment processes in artificial reservoir systems located in the monsoon climate. In this study, the effects of internal sediment processes on the water quality was studied in a deep, stratified reservoir (Lake Soyang, South Korea) by measuring the vertical and horizontal distribution of nutrient contents in the sediment along the main axis from the dam site to the tributary inlet site. We also assessed the external input of nutrients via monsoon runoff of the main inflowing river. The objectives of this study were to (1) assess the effects of inorganic nutrient input from intensive rainfalls on the lake sediment process, and (2) evaluate the potential effects of sediment processes by determining the distribution of elements in the bottom sediment and porewater of the lake sediments.

## Study site

Lake Soyang, South Korea, was constructed in 1973 on the North Han River system for electrical power generation and flood control and today serves as an important drinking water resource for the Seoul metropolitan area (Jo and Park 2010, Bartsch et al. 2014). It is the largest and deepest reservoir in South Korea, with a maximum depth of 120 m, a main axis length of 60 km (Kim et al. 2001), a mean width of the lake of only 0.5 km, and a typical dendritic shape (Fig. 1). The watershed (total area 2703 km<sup>2</sup>; WAMIS 2003) of Lake Soyang is scarcely populated, mostly covered by forest (>85% of the watershed). It also includes small areas of cropland with increasingly intensive agricultural activities (Jung et al. 2012), and agricultural soil erosion has become a major source of suspended solids the lake (Shope et al. 2013). The Soyang River is the main inflowing stream to Lake Soyang, and most of the nutrients and organic matter are exported from the watershed during the summer monsoon season (May–Aug). The mean annual precipitation in the watershed is 1100 mm (WAMIS 2003), more than half of which occurs in summer, a season of episodic heavy rains

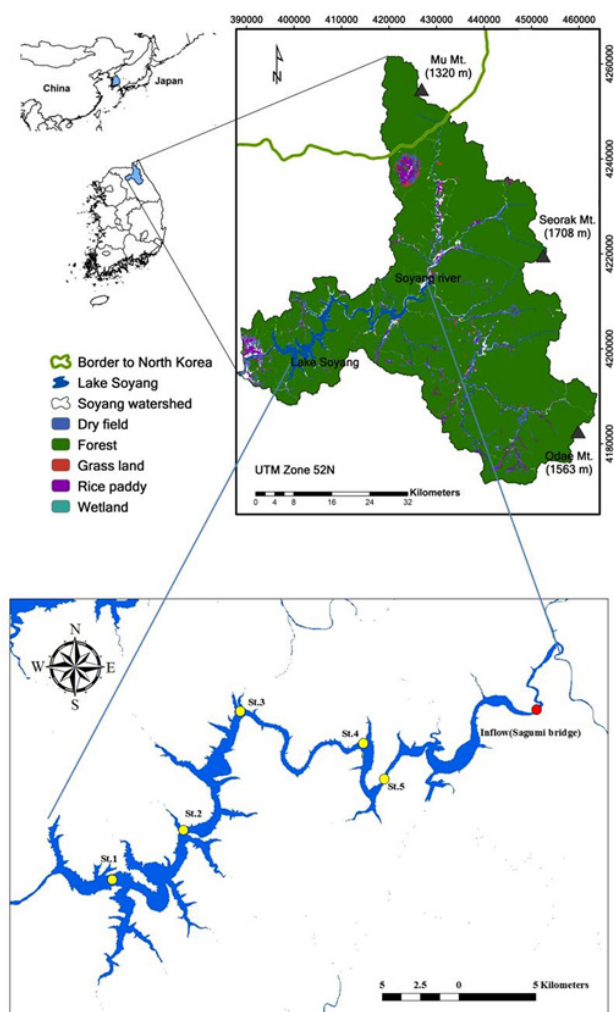


Fig. 1. Lake Soyang watershed in South Korea and study sites.

(Hwang et al. 2003, Park et al. 2010). The trophic state of Lake Soyang has varied over time. Although it was oligotrophic at the beginning of impoundment, it has become eutrophic following the input of nutrients from fish farming (Kim et al. 2001). The water quality and trophic state are currently improving, however (Seo et al. 2014), presumably due to the removal of fish farms.

## Methods

Five sampling sites (St. 1–5; Fig. 1) were selected along the main axis from the dam site (St. 1) to the upstream inlet site (St. 5) for collecting water and sediment. Lake water samples were collected once a month in 2012 and 2013 at St. 1 at depths of 0, 2, and 5 m, and at 10 m intervals below 10 m to the bottom. Water samples were also collected in the Soyang River on a monthly basis (inflow; Fig. 1). Core or grab-type sediment samples were collected with a gravity corer (UWITEC, Mondsee, Austria) and a grab sampler (Wild Co., USA) at each site before and after the summer monsoon period in both 2012 and 2013. Porewater samples were extracted by centrifugation from the sliced sediment core samples. Dissolved oxygen (DO), temperature, and turbidity were measured on site with a portable multiparameter probe (Hydrolab Quanta, Loveland, USA). On 2 additional occasions, vertical profiles of these parameters were measured at a 1 m depth resolution for detailed information.

Water samples were filtered with glass fiber filters (Whatmann GF/F) for dissolved total P, organic carbon, nitrate ( $\text{NO}_3^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), and other major and trace elements. Before filtration, total P (TP) of water samples was analyzed by the ascorbic method after persulfate digestion (APHA 2012). Filtered water samples were used to measure dissolved organic carbon (DOC) using a TOC analyzer (Shimadzu TOC 5000, Kyoto, Japan). Particulate organic C (POC) was measured by combusting the dried glass fiber filters using a Yanaco MT-5 CHN analyzer.  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and chloride ion ( $\text{Cl}^-$ ) concentrations in the porewater samples were determined by the ion chromatography method (Metrohm modular IC system 762, Herisau, Switzerland). Iron (Fe) and manganese (Mn) concentrations in water samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 3200XL, Perkin Elmer, Waltham, MA, USA).

Sediment core samples were sliced with a customized core cutter device at 1, 2, or 5 cm intervals according to the visual identification of layers. Sliced samples were freeze-dried, and the contents of TP, Fe, total reduced inorganic sulfur (TRIS), and other elements, including aluminum (Al), calcium (Ca), potassium (K), and sulfur (S) were determined. Fe was analyzed after HCL extraction using the phenanthroline assay (Tamura et al. 1974) to differenti-

ate ferric ( $\text{Fe}^{3+}$ ) and ferrous ( $\text{Fe}^{2+}$ ) iron in the sediment samples. TRIS species ( $\text{S}_2^{2-}$ ,  $\text{S}^{2-}$ , and  $\text{S}^0$ ) were extracted from sediment samples following chromium reduction (Canfield et al. 1986) and trapped as  $\text{H}_2\text{S}$  in NaOH solution. Reduced S concentration was measured by the methylene blue assay method (Williams 1979) using a UV-VIS-photometer. Further elements in the sediment samples were measured by ICP-OES method after 1 N HCl extraction.

## Results

### Seasonal changes in water quality parameters of lake and inflowing stream

#### Vertical stratification

The vertical variations of temperature, DO, and turbidity were measured on a monthly basis at the dam site (St. 1) in 2012 and 2013. The temperature varied between 5 and 30 °C, typical for a warm monomictic lake. The profiles of temperature in summer clearly showed a stable stratification in both years. DO was depleted at the hypolimnion, and the metalimnetic oxygen minimum was observed occasionally between 10 and 20 m depth during the stratification period. DO (as  $\text{O}_2$ ) decreased to  $<4 \text{ mg L}^{-1}$  in the bottom layer after the onset of stratification for both years. The DO depletion lasted until the end of September, with DO values  $<2.5 \text{ mg L}^{-1}$  in 2012 and 2013 (Fig. 2 and 3). The thermocline disappeared in winter, and the lake water was entirely mixed until the next stratification period. Turbidities were higher in the metalimnion (20–50 m depth) than in the other water layers in both summer monsoon seasons (Fig. 4). Based on average turbidity values, however, the turbidity of water in the metalimnion was different between the 2 survey years; the mean turbidity was only  $1.1 \pm 0.3 \text{ NTU}$  in 2012 but was  $15.9 \pm 11.7 \text{ NTU}$  in 2013. The maximum turbidity of 58.5 NTU was observed at 30 m depth in July 2013 following intensive rainfalls. Turbidity varied in the same pattern as POC and TP (Fig. 4 and 5).

#### Water chemistry

During our study period, the median POC in the inflowing water was  $0.5 \text{ mg L}^{-1}$ . The maximum concentration of POC in the Soyang River reached  $2.1 \text{ mg L}^{-1}$  after heavy rainfall in 2012. POC remained  $<1.0 \text{ mg L}^{-1}$  in most other monthly observations (range  $0.04\text{--}0.96 \text{ mg L}^{-1}$ ) but was notably higher during the monsoon season ( $2.1$  and  $1.2 \text{ mg L}^{-1}$  in Jul 2012 and 2013, respectively). Two different forms of organic C were also measured in the lake at St. 1 on a monthly basis during the study period. POC and DOC were uniform in the whole lake water and at all depths except during the summer season, when they reached a metalimnetic maximum, as did turbidity. The POC profile showed the highest value at the hypolimnion ( $4.0 \text{ mg L}^{-1}$ ), but it also

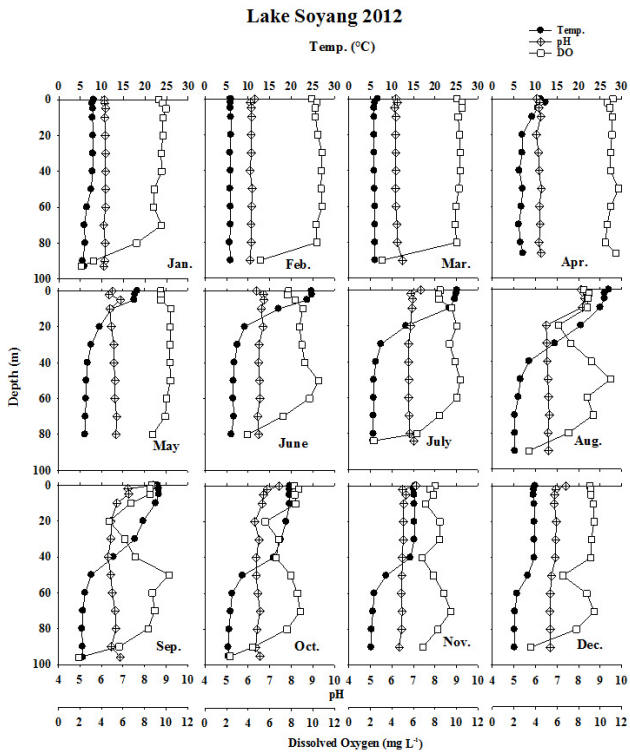


Fig. 2. Vertical variations of temperature, DO, and pH in the Lake Soyang water in 2012

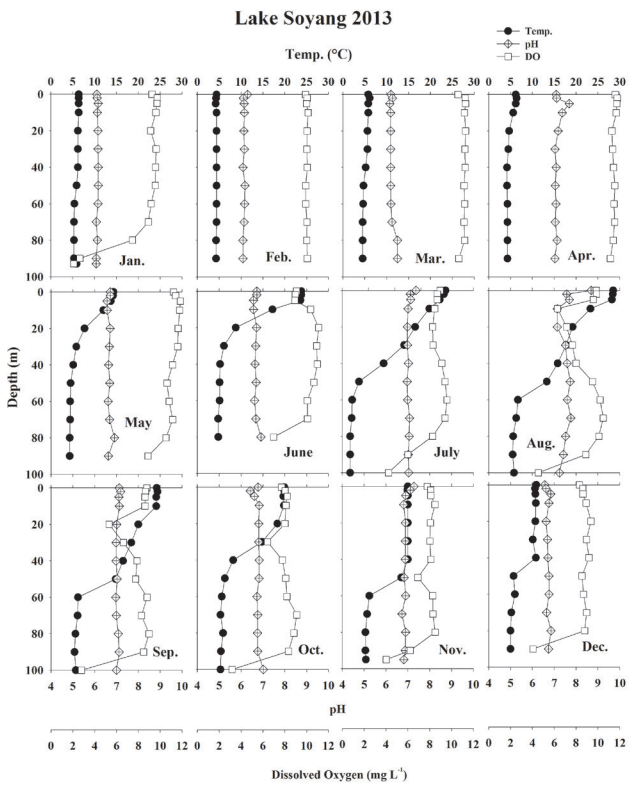


Fig. 3. Vertical variations of temperature, DO, and pH in the Lake Soyang water in 2013.

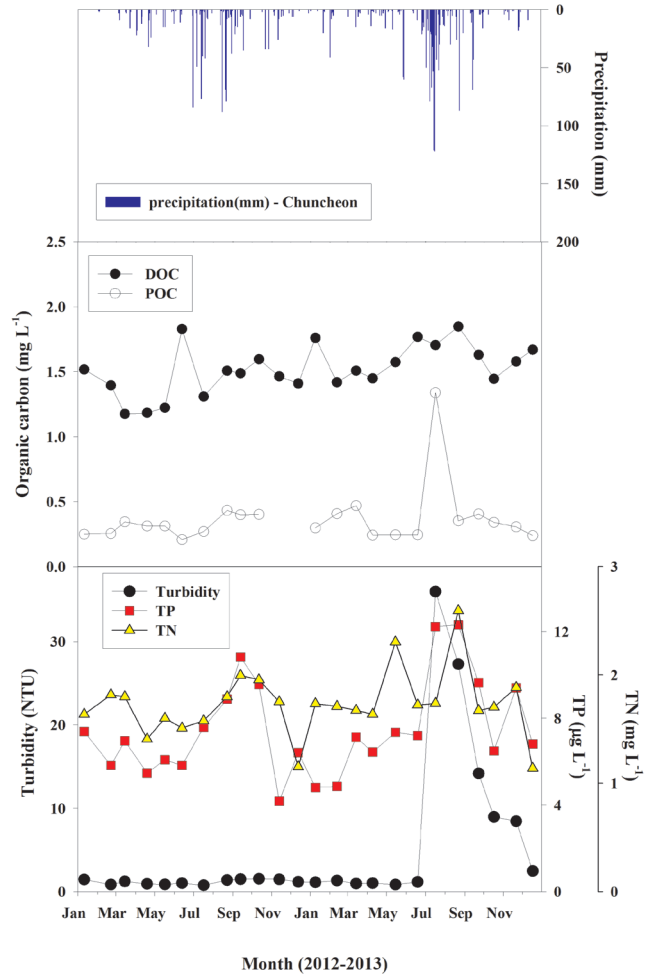


Fig. 4. Records of daily precipitation in Lake Soyang watershed and seasonal variations of DOC, POC, turbidity, TN, and TP in a metalimnion (20–50 m) of the lake for the 2 study years (2012–2013).

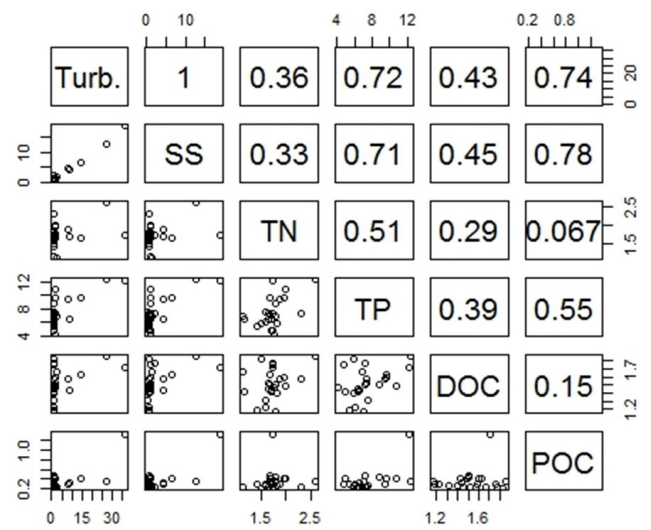


Fig. 5. Scatter plots with correlation coefficient values among water quality parameters in the Lake Soyang metalimnion in 2012–2013.

showed a peak at the metalimnion ( $2.8 \text{ mg L}^{-1}$ ) in July after heavy precipitation of  $>430 \text{ mm}$  within 8 days (8–15 Jul 2013; Fig. 4; KMA 2009). DOC, however, showed a smaller seasonal variation varying between  $1.1$  and  $1.9 \text{ mg L}^{-1}$ .

TP variation was associated with the variation of turbidity in both years. The annual averages of TP and TN were similar in both years (P:  $7.7 \pm 2.7$  and  $7.5 \pm 2.5 \text{ } \mu\text{g L}^{-1}$ ; N:  $1.6 \pm 0.2$  and  $1.8 \pm 0.5 \text{ mg L}^{-1}$  in 2012 and 2013, respectively). TP in the metalimnion was much higher than in the other layers after monsoon rainfalls in July and August 2013 ( $17.6 \text{ } \mu\text{g L}^{-1}$  at 30 m water depth;  $19.5 \text{ } \mu\text{g L}^{-1}$  at 40 m water depth, respectively; Fig. 4).

Fe and Mn of the inflow stream and reservoir water were determined for summer season in 2013. Concentrations of Fe and Mn in the inflowing water were  $>20$  and  $2 \text{ } \mu\text{g L}^{-1}$ , respectively. Fe and Mn concentrations showed 2 peaks, one in the metalimnion ( $17 \pm 14$  and  $5 \pm 3 \text{ } \mu\text{g L}^{-1}$ , respectively) and another in the hypolimnion ( $197$  and  $8585 \text{ } \mu\text{g L}^{-1}$ , respectively) in July 2013 after heavy rainfall (Fig. 6). The concentrations of Fe and Mn were highest in the hypolimnion during the oxygen depletion phase after the onset of stratification (Fig. 3 and 6).

### Porewater and sediment analysis

#### Porewater chemistry

Oxidation redox potential (ORP) and pH were measured with electrodes in core sediment samples at St. 1 in May and St. 5 in June. The pH remained virtually constant over depth, varying between  $6.4$  and  $6.7$  at St. 1 and  $6.6$  and  $6.9$  at St. 5; sediment pH was similar to the

bottom water ( $6.6$  and  $6.9$ , respectively; data not shown). ORP indicated completely anaerobic conditions in the sediment samples. ORP decreased toward the bottom of sediment and was lower than  $-100 \text{ mV}$  below  $10 \text{ cm}$  depth in both core samples (St. 1 and 5; data not shown). Dissolved inorganic phosphorus (DIP) and  $\text{NH}_4^+$  concentrations of the porewater were measured at  $2 \text{ cm}$  resolution to determine the distribution of mobile forms of P and N. Both P and N showed an almost identical depth profile, with a maximum at  $4 \text{ cm}$  depth ( $23.0$  and  $251.5 \text{ } \mu\text{g L}^{-1}$ , respectively) and decreased at the sediment surface ( $15.9$  and  $150.6 \text{ } \mu\text{g L}^{-1}$ , respectively, at  $2 \text{ cm}$  depth). P and N increased again, however, deeper in the core ( $19.5 \pm 5.0$  and  $201.1 \pm 71.3 \text{ } \mu\text{g L}^{-1}$ , respectively; Fig. 7). Concurrently, the P and N concentrations of DIP and  $\text{NH}_4^+$  in the lake bottom water were  $0.9$  and  $16 \text{ } \mu\text{g L}^{-1}$ , respectively (data not shown), much lower than the uppermost porewater of the sediment. Hence, large concentration gradients exist between the sediment porewater and the overlying bottom water.

$\text{NO}_3^-$  was depleted in all sediment samples from St. 1 to St. 5 ( $<0.2 \text{ mg L}^{-1}$ ; Fig. 8). Concentrations of  $\text{SO}_4^{2-}$  showed sharp gradients between  $0$  and  $4 \text{ cm}$  depth, with S ranging from  $3.3$  to  $0.7 \text{ mg L}^{-1}$  and remaining constantly low in deeper zones. Furthermore, the concentrations of  $\text{SO}_4^{2-}$  were lower ( $2.2 \pm 1.2$  to  $1.1 \pm 0.6 \text{ mg L}^{-1}$ ) in the top sediment porewater (below  $3 \text{ cm}$ ) at St. 1 after the monsoon than concentrations before the monsoon period. Chloride concentrations were on average  $3.7 \pm 0.8$  and  $3.0 \pm 0.3 \text{ mg L}^{-1}$  in the samples before and after the monsoon period, respectively. Dissolved concentrations

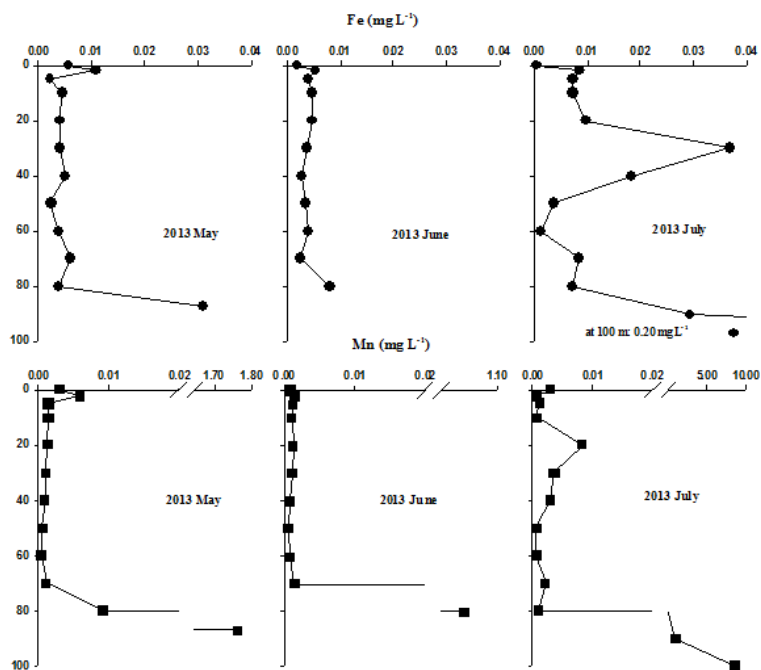


Fig. 6. Distributions of Fe and Mn in Lake Soyang water during monsoon season in 2013.

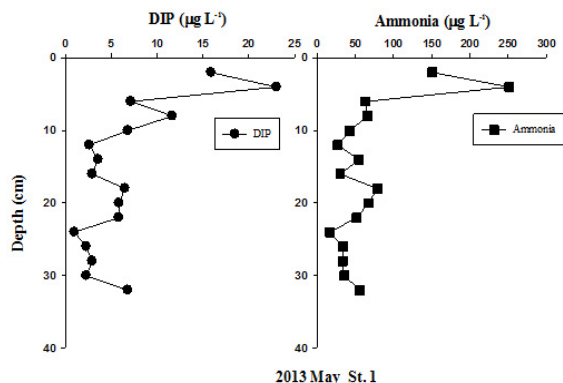


Fig. 7. Distributions of DIP and ammonia in Lake Soyang porewater samples of the core at St. 1 in 2013.

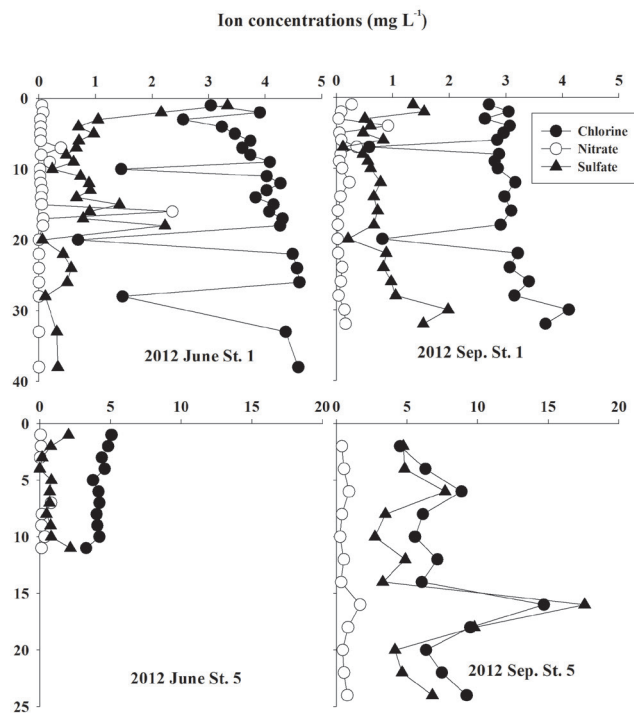


Fig. 8. Distributions of chloride, nitrate, and sulfate ions in Lake Soyang porewater of sediments samples at St. 1 and St. 5 in 2012.

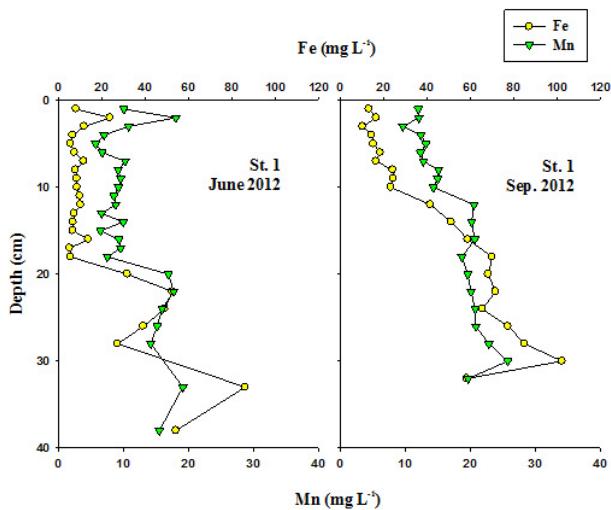


Fig. 9. Vertical profiles of Fe and Mn in Lake Soyang porewater at St. 1 before and after monsoon season in 2012.

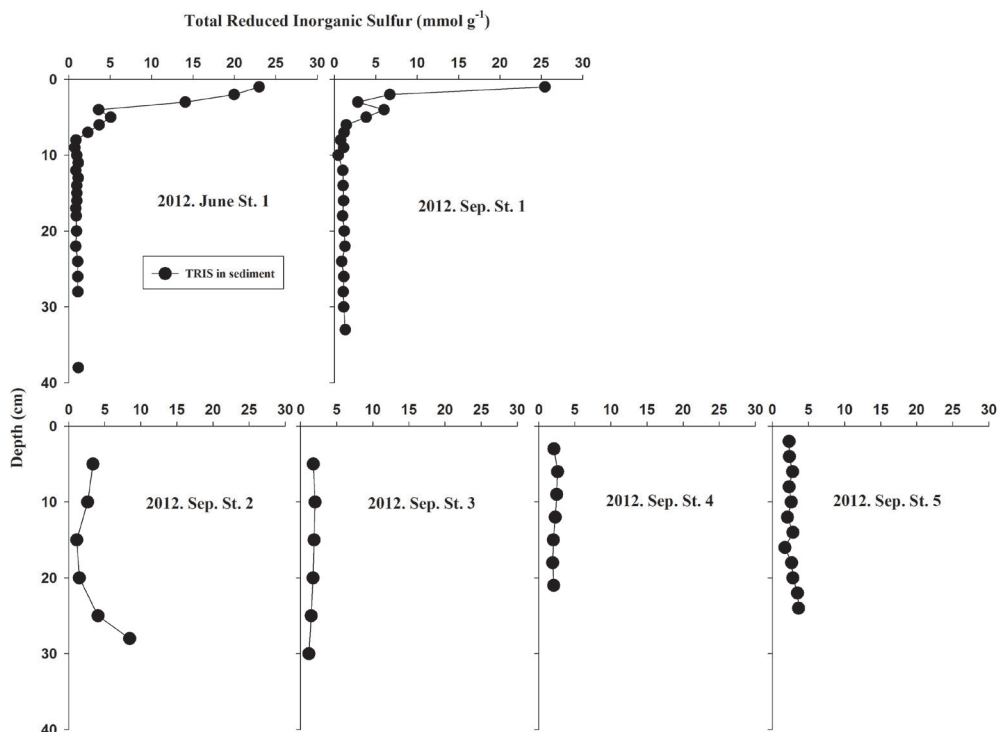
of Fe and Mn were higher below 20 cm depth compared to the concentrations in the other depths in porewater of St. 1 sediment (Fig. 9).

**Sediment chemistry**

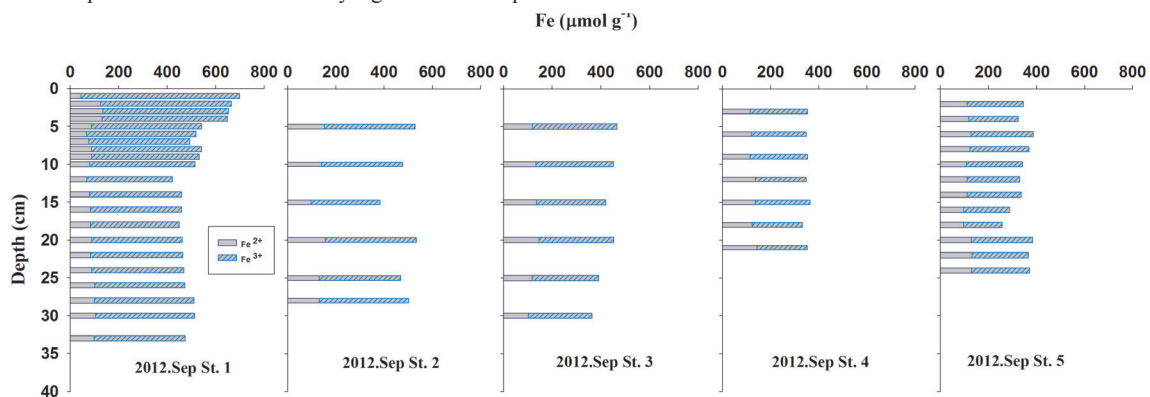
The average TP for all depths in the sediment core at St. 1 was  $1.6 \pm 0.1 \text{ mg g}^{-1}$ . The amount of P decreased from the top to the bottom layers of the sediment. A strong gradient of TRIS existed between the top surface of the sediment and 4 cm depth, with concentrations decreasing sharply from 23.0 to 3.6  $\text{mmol g}^{-1}$ . Below 4 cm, TRIS concentrations further decreased and leveled off at an average concentration of  $1.0 \pm 0.1 \text{ mmol g}^{-1}$  below 8 cm. TRIS exceeded 20  $\text{mmol g}^{-1}$  in the top sediment samples at St. 1 before and after the monsoon in 2012. TRIS in the deeper

layers, especially below 10 cm, of the sediments was  $<5 \text{ mmol g}^{-1}$  (Fig. 10). The vertical distributions of TRIS in the sediment from St. 2 to St. 5 were different from St. 1 (Fig. 10); the concentrations of TRIS were  $<5 \text{ mmol g}^{-1}$  over the entire depth down to 30 cm.

Solid phase Fe was determined as 2 forms ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ) in sediment cores from St. 1 to St. 5 in 2012 (Fig. 11). St. 1 had the highest Fe contents of the 5 sampling sites, and the concentrations continuously decreased along the lake axis from the dam (St. 1) toward the upstream site (St. 5). More than 80% of Fe was in the ferric form at all depths and at all sites. Accordingly, the ratio of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  was approximately constant from St. 1 to St. 5, despite substantial concentrations of TRIS and the differences in TRIS observed between the sites.



**Fig. 10.** Vertical profiles of TRIS in Lake Soyang sediment samples from St. 1 to St. 5 before and after monsoon season in 2012.



**Fig. 11.** Fractions and amounts of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in Lake Soyang sediment samples from St. 1 to St. 5 in 2012.

## Discussion

### Material input from the watershed during the summer monsoon season

The median value of POC in the inflowing stream was much lower than the worldwide median value of POC in rivers ( $2.0 \text{ mg L}^{-1}$ ); however, the highest POC values emerged after heavy rainfall in each year, stressing the relevance of POC loading during high flow. The ratio of DOC to POC was  $<1:1$  in the metalimnion of the lake, much lower than data collected from other eutrophic lakes (6:1; Wetzel 2001). This low value indicates that intensive summer rainfalls cause a large amount of particulate organic matter to enter the lake via storm runoffs, which leads to higher POC concentrations in the lake, as reported earlier in Lake Soyang (Kim et al. 2000, 2009) and other reservoirs (Aryal et al. 2014). Moreover, a high amount of coarse woody debris (CWD), which is not included in POC measurements because of its large size ( $>2 \text{ mm}$ ), was observed floating on the surface of the lake during field surveys after monsoon rainfalls. CWD may provide a high contribution to the C load of the lake water and of the sediment over the long term (Wipfli et al. 2007, Seo et al. 2008); therefore, also quantifying CWD input to the lake waterbody would be useful. Nevertheless, the observed POC concentrations compared well with previous measurements made at St. 1 (highest concentrations  $2.4 \text{ mg L}^{-1}$  in 1996: Kim et al. 2000; and  $\sim 3 \text{ mg L}^{-1}$  in 2008: Kim et al. 2009), and the seasonal and vertical variations coincided with the results of previous studies on POC distribution in this particular reservoir (Kim et al. 2000, 2009). We therefore calculated a C sedimentation rate based on the annual average of POC concentration in this study and a previously reported C settling velocity in the same reservoir (POC  $0.9 \text{ m d}^{-1}$  in 2009; Kim 2009 and unpublished data), yielding a POC sedimentation of  $453 \text{ mg m}^{-2} \text{ d}^{-1}$ . This result is similar to the C sedimentation rates in the other reservoirs but higher than in natural lakes (Teodoru et al. 2013, Clow et al. 2015).

The ratios of DOC to POC varied over depths and seasons, possibly because of changes in stratification. High input of POC and TP caused by intensive rainfalls is a regular annual occurrence during the monsoon period in Lake Soyang (Kim et al. 1995, 2000). A previous study investigated the annual variation of input TP load into Lake Soyang for 16 years (1991–2006), and the P load was highest ( $\sim 1200 \text{ t yr}^{-1}$ ) in 2006 during an intensive rainfall of the summer monsoon season (Kim and Jung 2007). This input is presumably amplified by the disturbances in forested areas and agricultural practices of overusing P fertilizer and frequent soil disturbances (Park et al. 2010). Consequently, a high load of P is deposited

into the sediment in reservoir systems (Tang et al. 2015), a common occurrence in lake waters like Lake Soyang surrounded by intensively managed agricultural regions (Carpenter 2005). Interestingly, Fe and Mn concentrations were also high in the metalimnion during the summer monsoon, caused by an inflow of high amounts of Fe and Mn ( $137$  and  $25 \text{ } \mu\text{g L}^{-1}$ , respectively), as already observed at an adjacent site during the summer monsoon in a previous study (Hong et al. 1989). Previous studies have attributed these high amounts of Fe, Mn, and S to input of particulate matter from the watershed, along with high amounts of P adsorbed to these particles (Stewart and Tiessen 1987, Gleyzes et al. 2002); therefore, the observed high concentrations of Fe and Mn in the hypolimnion seem to have resulted from diffusive fluxes from the sediment under anoxic condition (Graham et al. 2012).

### Stratification and formation of anoxia

The metalimnetic DO depletion ( $3.8 \text{ mg L}^{-1}$  at 14 m in Sep 2013) observed in this study was presumably driven by the density current induced by flooding from the monsoon rainfall (Kim and Cho 1989, Lee et al. 2013), which supplied a large amount of labile C from the watershed. A hypolimnetic anoxia was formed after the eutrophication period in the 1980s in Lake Soyang (Kim and Cho 1989), and, accordingly, the ORP in sediment cores from St. 1 were negative for the entire depth, comparable to values in anoxic sediments in Japanese lakes (Bibi et al. 2007). Under these conditions, oxidized Fe, Mn, and S phases can be favorable electron acceptors (Gambrell et al. 1983). Sulfate reduction is an important respiratory pathway in anoxic sediments (D'Hondt et al. 2002), which explains the observed high concentrations of TRIS in the upper layers of Lake Soyang sediment cores. We therefore presume that anoxic conditions happen frequently, but significant amounts of unreduced Fe oxides seem to be present that may thus still trap P to some extent.

### Processes in the sediment

The mean TP in the sediment at St. 1 was higher than in other shallower reservoirs of South Korea (Kim et al. 2003) and in other eutrophic lakes of China (Zhang et al. 2008). The higher concentrations of DIP and  $\text{NH}_4^+$  in porewater than in bottom water can result in internal loading by diffusion, as proposed earlier in a hypereutrophic lake and reservoirs (Reddy et al. 1996, Wang and Liang 2015, Yang et al. 2015). A substantial amount of  $\text{NH}_4^+$  seems to be released from the sediment into the overlying lake water, evidenced by the highest  $\text{NH}_4^+$  concentration just above the sediment. But rapid decrease of  $\text{NH}_4^+$  concentration



toward upper layer of the hypolimnion implies rapid oxidation of  $\text{NH}_4^+$  in oxic conditions.  $\text{NO}_3^-$  showed the opposite distribution of  $\text{NH}_4^+$ , decreasing drastically under oxygen depletion (hypolimnetic DO of  $1.9 \text{ mg L}^{-1}$ ) just below the boundary of the oxic and anoxic layers (e.g., Sep 2012; Fig. 12).

Despite the high concentrations of DIP and  $\text{NH}_4^+$  in the bottom water layer during stratification, however, the average concentration of DIP and  $\text{NH}_4^+$  remained constantly low after the monsoon season (Sep 2012 to Dec 2013), when the onset of strong oxygen depletion was observed in the hypolimnion. DIP concentration in the epilimnion was  $1.8 \pm 1.2 \text{ } \mu\text{g L}^{-1}$  and the  $\text{NH}_4^+$  concentration was  $0.018 \pm 0.008 \text{ mg L}^{-1}$ , which is significantly lower than in the hypolimnion. We therefore assume that DIP and  $\text{NH}_4^+$  do not reach the epilimnion after being released from the bottom sediment. The maximum lake depth of 120 m could be mainly responsible; in other words, DIP can be resettled and  $\text{NH}_4^+$  can be oxidized when they enter the oxic layer on the way to the epilimnion. Although not measured in this study, turbulence energy in Lake Soyang is thought to be low because it is located in the midst of a high, mountainous area and well sheltered from wind action at the lake surface. Additionally, the removal of nutrients by the intermediate density current discharged from the dam through the outlet at the middle depth of the dam could also explain why nutrients from the sediment cannot easily reach the epilimnion (Fig. 2 and 3). The major transport mechanism of nutrients from the sediment to the epilimnion is thought to be the winter turnover circulation in January and February.

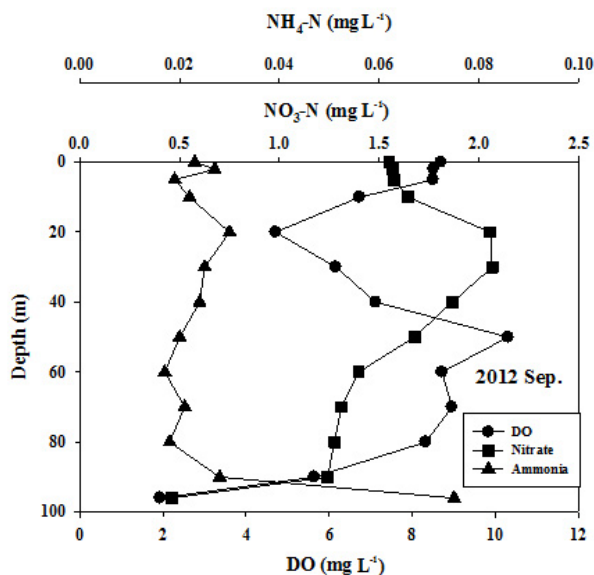


Fig. 12. Vertical profiles of DO, nitrate, and ammonia in Lake Soyang water columns in Sep 2012.

The high abundance of Fe and Mn was considered to be delivered by input from the lake watershed (especially agricultural areas) after monsoon rainfall, based on the high concentrations of Fe and Mn in the metalimnion of the lake after precipitation (Fig. 5). Previous studies noted that Fe, Mn, and Al can originate from soil particles, which also carry high amounts of P (SanClements et al. 2009). A horizontal concentration gradient of Fe was observed from the inlet to the outlet, which implies that finer particles can be transported as far as the dam area, and an especially high amount of Fe and P is included in this fine particle fraction compared to coarse particles more associated with Mg and K (Delfino et al. 1969, Zan et al. 2011). High amounts of Fe in the sediment commonly act as P traps through strong adsorption (Wang et al. 2005, Doncheva 2010).

The  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ratio was interestingly similar over the whole sediment depth, but the underlying reasons could not be elucidated in this study. We hypothesized, however, that the presence of a sulfate reduction reaction of sulfide with Fe oxide surfaces may lead to a passivation, impeding further reduction. Sulfate in the porewater sharply decreased in the top sediment, and TRIS concentrations were higher in the same depth. This finding supports the occurrence of  $\text{SO}_4^{2-}$  reduction in the sediment, leading to high amounts of reduced S trapping available cations as insoluble sulfides (Wersin et al. 1991, Burton et al. 2006, Yu et al. 2015). In the case of Lake Soyang, formation of Fe sulfides is likely due to a constant and high supply of Fe by inflow from the watershed (Hong et al. 1989). Additionally, a previous study revealed that TRIS in lake sediments mostly consisted of FeS and FeS<sub>2</sub> (Canfield et al. 1986). To form Fe sulfides, ferric Fe becomes reduced by sulfide (Wan et al. 2014). After formation of sulfides, their interaction with Fe and other metals controls and modifies mobilization of phosphate ( $\text{PO}_4^{3-}$ ),  $\text{NH}_4^+$ , and hydrogen sulfide. Internal loads from sediments seem to be driven by not only anoxic conditions, but also by sedimentations of Fe, Mn, S, and C (Gächter and Müller 2003).

Based on our findings, we established a conceptual model of the hypothesized seasonal variation of biogeochemical and hydrological processes in the Soyang reservoir located in the monsoon area (Fig. 13). In the pre-monsoon season (Fig. 13a), the reservoir begins to stratify and receives only low amounts of C, N, and P from the watershed because of low precipitation and few agricultural activities in the watershed. DO is thus still available for decomposition in the hypolimnion. During the monsoon season (Fig. 13b), a significant amount of suspended materials carrying substantial amounts of labile C, N, P, and other biogeochemically important elements (Fe, Mn) are added to the waterbody by intensive rain

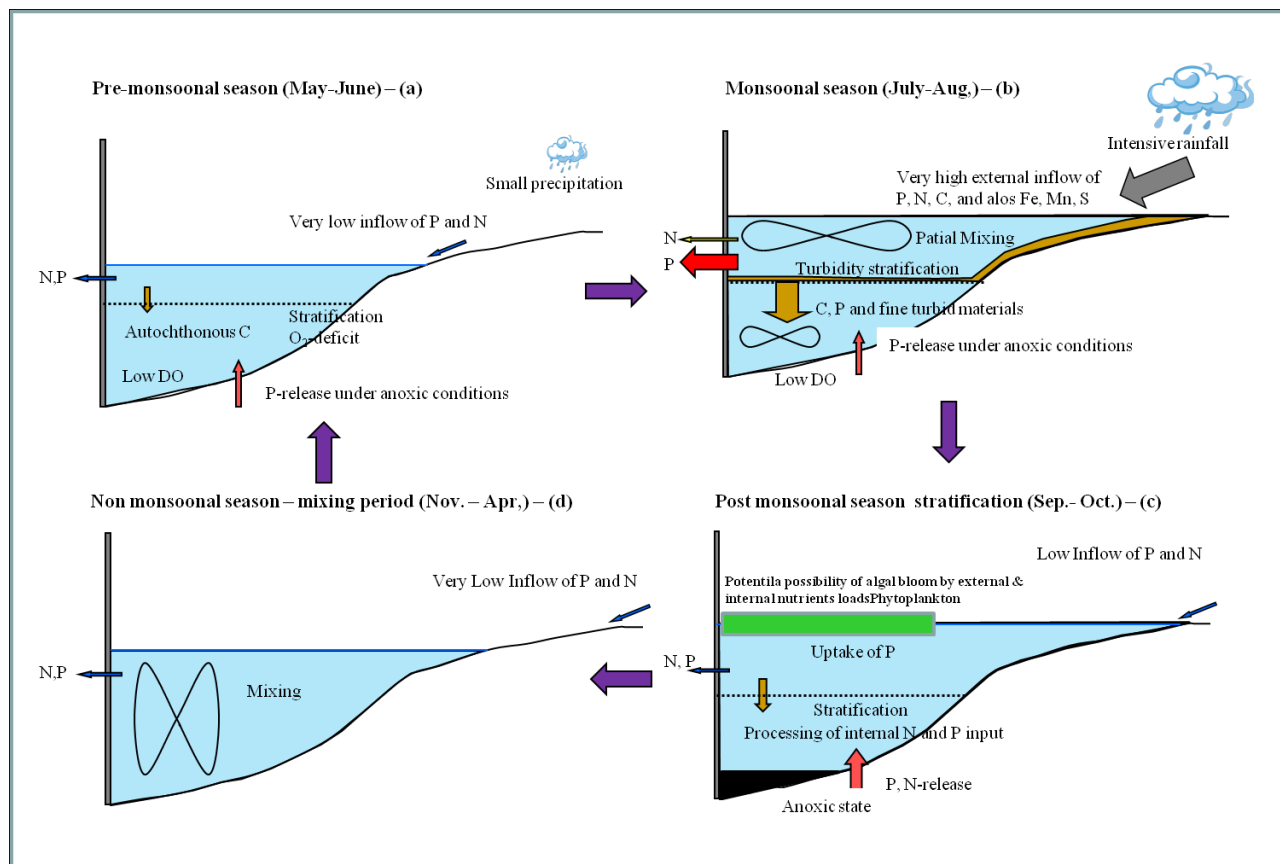


Fig. 13. Seasonal changes of processes in the Soyang Reservoir under summer monsoon climate.

events and concomitant mobilization in the watershed. A turbidity layer establishes at a depth of 30–50 m. After the monsoon season (Fig. 13c), decomposition of the large pulse of allochthonous organic matter, especially in its particulate form, starts and leads to strong oxygen depletion. Under these conditions,  $\text{PO}_4^{3-}$  is released upon dissolution of solid phase electron acceptors (Fe (III), Mn (IV)) to which  $\text{PO}_4^{3-}$  is bound in the sediment. Finally, during the winter season, the reservoir water is mixed entirely, and ferrous Fe and Mn reoxidize, reestablishing conditions for sequestration of  $\text{PO}_4^{3-}$  at the sediment–water interface (Fig. 13d). The situation may differ under conditions of high discharge when a much larger fraction of the suspended material becomes dissipated in the entire waterbody, releasing a pulse of biogeochemically reactive substances into the entire waterbody. Nevertheless, we assume that our conceptual model represents many big artificial reservoirs located in the summer monsoon region (An and Park 2002, Wang et al. 2012).

Overall, heavy rainfalls caused acute increases of C, P, Fe, and Mn in the lake via turbid density currents during monsoon seasons. This increased availability of easily decomposable organic matter controlled the internal loads of  $\text{PO}_4^{3-}$ ,  $\text{NH}_4^+$ , and reduced S released from the sediment

because electron acceptors are consumed under anoxic conditions in the sediment. Our study has implications for reservoir management in monsoon climate regions. Sediment processes and internal loads must be constantly checked while monitoring inflowing water quality for effective reservoir management because the input of the nutrients with eroded soil from the agricultural watershed is consistently high from overuse of fertilizer and frequent soil disturbance.

## Acknowledgements

This study was carried out in the framework of the International Research Training Group TERRECO (GRK 1565/2), funded by the Deutsche Forschungsgemeinschaft (DFG) at the University of Bayreuth (Germany) and the Korean Research Foundation (KRF) at Kangwon National University (South Korea).

## References

- An K-G, Jones JR. 2000. Temporal and spatial patterns in salinity and suspended solids in a reservoir influenced by the Asian monsoon. *Hydrobiologia*. 436:179–189.

- An K-G, Park SS. 2002. Indirect influence of the summer monsoon on chlorophyll–total phosphorus models in reservoirs: a case study. *Ecol Model.* 152:191–203.
- [APHA] American Public Health Association, American Water Works Association, and Water Environment Federation. 2012. Standard methods for the examination of water and wastewater. 22<sup>nd</sup> ed. Washington (DC).
- Aryal R, Grinham A, Beecham S. 2014. Tracking inflows in Lake Wivenhoe during a major flood using optical spectroscopy. *Water.* 6:2339–2352.
- Bae DH, Jung IW, Chang H. 2008. Long-term trend of precipitation and runoff in Korean river basins. *Hydrol Process.* 22:2644–2656.
- Bartsch S, Frei S, Ruidisch M, Shope CL, Peiffer S, Kim B, Fleckenstein JH. 2014. River-aquifer exchange fluxes under monsoonal climate conditions. *J Hydrol.* 509:601–614.
- Besser JM, Ingersoll CG, Leonard EN, Mount DR. 1998. Effect of zeolite on toxicity of ammonia in freshwater sediments: implications for toxicity identification evaluation procedures. *Environ Toxicol Chem.* 17:2310–2317.
- Bibi MH, Ahmed F, Ishiga H. 2007. Assessment of metal concentrations in lake sediments of southwest Japan based on sediment quality guidelines. *Environ Geol.* 52:625–639.
- Burton ED, Bush RT, Sullivan LA. 2006. Elemental sulfur in drain sediments associated with acid sulfate soils. *Appl Geochem.* 21:1240–1247.
- Canfield DE, Raiswell R, Westrich JT, Reaves CM, Berner RA. 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chem Geol.* 54:149–155.
- Carpenter SR. 2005. Eutrophication of aquatic ecosystems: bistability and soil phosphorus. *P Natl Acad Sci-USA.* 102:10002–10005.
- Clow DW, Stackpole SM, Verdin KL, Butman DE, Zhu Z, Krabbenhoft DP, Striegl RG. 2015. Organic carbon burial in lakes and reservoirs of the conterminous United States. *Environ Sci Technol.* 49:7614–7622.
- Correll D. 1999. Phosphorus: a rate limiting nutrient in surface waters. *Poultry Sci.* 78:674–682.
- De Boer DH. 1994. Lake sediments as indicators of recent erosional events in an agricultural basin on the Canadian prairies. In: Loughran RJ, Kesby JA, editors. Variability in stream erosion and sediment transport. Proceedings of the Canberra Symposium, International Association of Hydrological Sciences. IAHS Publications. 224:125–132.
- D'Hondt S, Rutherford S, Spivack AJ. 2002. Metabolic activity of subsurface life in deep-sea sediments. *Science.* 295:2067–2070.
- Delfino JJ, Bortleson GC, Lee GF. 1969. Distribution of manganese, iron, phosphorus, magnesium, potassium, sodium, and calcium in the surface sediments of Lake Mendota, Wisconsin. *Environ Sci Technol.* 3:1189–1192.
- Doncheva V. 2010. Nutrients in pore water from surface sediment layer along the eutrophication gradient (Varna Lake–Varna Bay case study). *Cr Acad Bulg Sci.* 63:547–554.
- Ekholm P, Lehtoranta J. 2012. Does control of soil erosion inhibit aquatic eutrophication? *J Environ Manage.* 93:140–146.
- Gächter R, Müller B. 2003. Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface. *Limnol Oceanogr.* 48:929–933.
- Gambrell R, Reddy C, Khalid R. 1983. Characterization of trace and toxic materials in sediments of a lake being restored. *J Water Pollut Control Fed.* 55: 1271–1279.
- Giguët-Covex C, Pansu J, Arnaud F, Rey P-J, Griggo C, Gielly L, Domaizon I, Coissac E, David F, Choler P. 2014. Long livestock farming history and human landscape shaping revealed by lake sediment DNA. *Nature Comm.* doi:10.1038/ncomms4211
- Gleyzes C, Tellier S, Astruc M. 2002. Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures. *Trac-Trend Anal Chem.* 21:451–467.
- Graham MC, Gavin KG, Kirika A, Farmer JG. 2012. Processes controlling manganese distributions and associations in organic-rich freshwater aquatic systems: the example of Loch Bradan, Scotland. *Sci Total Environ.* 424:239–250.
- Gupta H, Kao S-J, Dai M. 2012. The role of mega dams in reducing sediment fluxes: a case study of large Asian rivers. *J Hydrol.* 464:447–458.
- Heathcote AJ, Filstrup CT, Downing JA. 2013. Watershed sediment losses to lakes accelerating despite agricultural soil conservation efforts. *PLoS One.* 8:e53554.
- Holmer M, Storkholm P. 2001. Sulphate reduction and sulphur cycling in lake sediments: a review. *Freshwater Biol.* 46:431–451.
- Hong GH, Kim SH, Kim KT. 1989. Watershed geochemistry of Lake Soyang, Korea. *Korean J Limnol.* 22:245–260.
- Hu H, Huang G. 2014. monitoring of non-point source pollutions from an agriculture watershed in south China. *Water.* 6:3828–3840.
- Hwang S-J, Kwun S-K, Yoon C-G. 2003. Water quality and limnology of Korean reservoirs. *Paddy Water Environ.* 1:43–52.
- Jo K-W, Park J-H. 2010. Rapid release and changing sources of Pb in a mountainous watershed during extreme rainfall events. *Environ Sci Technol.* 44:9324–9329.
- Jung B-J, Lee H-J, Jeong J-J, Owen J, Kim B, Meusburger K, Alewell C, Gebauer G, Shope C, Park J-H. 2012. Storm pulses and varying sources of hydrologic carbon export from a mountainous watershed. *J Hydrol.* 440:90–101.
- Kangura M, Puusepp L, Buhvestovab O, Haldnab M, Kangurb K. 2013. Spatio-temporal variability of surface sediment phosphorus fractions and water phosphorus concentration in Lake Peipsi (Estonia/Russia). *Est J Earth Sci.* 62:171–180.
- Kim B-C, Cho K-S. 1989. The hypolimnetic anoxic zone and the metalimnetic oxygen minimum layer in a deep reservoir, Lake Soyang. *Korean J Limnol.* 22:159–166
- Kim B, Choi K, Kim C, Lee U-H, Kim Y-H. 2000. Effects of the summer monsoon on the distribution and loading of organic carbon in a deep reservoir, Lake Soyang, Korea. *Water Res.* 34:3495–3504.
- Kim B-C, Heo W-M, Hwang G-S, Kim D-S, Choi K-S. 1995. The distribution of phosphorus fractions in Lake Soyang. *Korean J Limnol.* 28:151–157. Korean
- Kim B, Jung S. 2007. Turbid storm runoff in Lake Soyang and their environmental effect. *J Korean Soc Environ Eng.* 29:1185–1190. Korean

- Kim B, Park J-H, Hwang G, Jun M-S, Choi K. 2001. Eutrophication of reservoirs in South Korea. *Limnology*. 2:223–229.
- Kim B-C, Shim JH, Cho K-S. 1985. Temporal and spatial variation of chlorophyll *a* concentration in Lake Soyang. *J Korean Soc Water Qual*. 1:18–23.
- Kim K, Kim B, Eom J, Choi Y, Jang C, Park H-K. 2009. The distribution of POC and DOC in four reservoirs on the North Han River and the relationship with algal density. *J Korean Soc Water Qual*. 25:840–848. Korean
- Kim L-H, Choi E, Stenstrom MK. 2003. Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. *Chemosphere*. 50:53–61.
- Knoll LB, Vanni MJ, Renwick WH, Dittman EK, Gephart JA. 2013. Temperate reservoirs are large carbon sinks and small CO<sub>2</sub> sources: results from high-resolution carbon budgets. *Global Biogeochem Cy*. 27:52–64.
- [KMA] Korean Meteorological Administration. 2009. [cited 14 June 2014]. Available from: <http://www.kma.go.kr/weather/observation/currentweather.jsp>
- Kowalczevska-Madura K, Góldyn R, Dera M. 2015. Spatial and seasonal changes of phosphorus internal loading in two lakes with different trophy. *Ecol Eng*. 74:187–195.
- Lee J-Y, Kim J-K, Owen JS, Choi Y, Shin K, Jung S, Kim B. 2013. Variation in carbon and nitrogen stable isotopes in POM and zooplankton in a deep reservoir and relationship to hydrological characteristics. *J Freshwater Ecol*. 28:47–62.
- Liu E, Shen J, Yuan H, Zhang E, Du C. 2013. The spatio-temporal variations of sedimentary phosphorus in Taihu Lake and the implications for internal loading change and recent eutrophication. *Hydrobiologia*. 711:87–98.
- Marce R, Martínez EN, Armengol J, Caputo L, López P. 2006. Elemental ratios in sediments as indicators of ecological processes in Spanish reservoirs. *Limnetica*. 25:499–512.
- Martins G, Peixoto L, Brito AG, Nogueira R. 2014. Phosphorus–iron interaction in sediments: can an electrode minimize phosphorus release from sediments? *Rev Environ Sci Biotechnol*. 13:265–275.
- Michalak AM, Anderson EJ, Beletsky D, Boland S, Bosch NS, Bridgeman TB, Chaffin JD, Cho K, Confesor R, Daloğlu I. 2013. Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions. *P Natl Acad Sci*. 110:6448–6452.
- Morellón M, Valero-Garcés B, González-Sampériz P, Vegas-Vilarrúbia T, Rubio E, Rieradevall M, Delgado-Huertas A, Mata P, Romero O, Engstrom DR. 2011. Climate changes and human activities recorded in the sediments of Lake Estanya (NE Spain) during the Medieval Warm Period and Little Ice Age. *J Paleolimnol*. 46:423–452.
- Mushtaq B, Raina R, Yousuf A, Wanganeo A, Shafi N, Manhas A. 2015. Chemical characteristics of bottom sediments of Dal Lake Srinagar, Kashmir. *Development*. 1:1–7.
- Nikolai SJ, Dzialowski AR. 2014. Effects of internal phosphorus loading on nutrient limitation in a eutrophic reservoir. *Limnologia*. 49:33–41.
- Park J-H, Duan L, Kim B, Mitchell MJ, Shibata H. 2010. Potential effects of climate change and variability on watershed biogeochemical processes and water quality in Northeast Asia. *Environ Int*. 36:212–225.
- Perkins R, Underwood G. 2001. The potential for phosphorus release across the sediment–water interface in an eutrophic reservoir dosed with ferric sulphate. *Water Res*. 35:1399–1406.
- Reddy K, Fisher M, Ivanoff D. 1996. Resuspension and diffusive flux of nitrogen and phosphorus in a hypereutrophic lake. *J Environ Qual*. 25:363–371.
- SanClements MD, Fernandez IJ, Norton SA. 2009. Soil and sediment phosphorus fractions in a forested watershed at Acadia National Park, ME, USA. *Forest Ecol Manage*. 258:2318–2325.
- Seo A, Lee K, Kim B, Choung Y. 2014. Classifying plant species indicators of eutrophication in Korean lakes. *Paddy Water Environ*. 12:29–40.
- Seo JI, Nakamura F, Nakano D, Ichiyonagi H, Chun KW. 2008. Factors controlling the fluvial export of large woody debris, and its contribution to organic carbon budgets at watershed scales. *Water Resour Res*. 44. doi:10.1029/2008WR007165
- Shope CL, Bartsch S, Kim K, Kim B, Tenhunen J, Peiffer S, Park J-H, Ok YS, Fleckenstein J, Koellner T. 2013. A weighted, multi-method approach for accurate basin-wide streamflow estimation in an ungauged watershed. *J Hydrol*. 494:72–82.
- Søndergaard M, Jensen JP, Jeppesen E. 2003. Role of sediment and internal loading of phosphorus in shallow lakes. *Hydrobiologia*. 506:135–145.
- Stewart J, Tiessen H. 1987. Dynamics of soil organic phosphorus. *Biogeochemistry*. 4:41–60.
- Tamura H, Goto K, Yotsuyanagi T, Nagayama M. 1974. Spectrophotometric determination of iron (II) with 1, 10-phenanthroline in the presence of large amounts of iron (III). *Talanta*. 21:314–318.
- Tang W, Zhang H, Zhang W, Shan B, Zhu X, Song Z. 2015. Dynamics of heavy metals and phosphorus in the pore water of estuarine sediments following agricultural intensification in Chao Lake Valley. *Environ Sci Pollut Res*. 22:7948–7953.
- Teodoru CR, Del Giorgio PA, Prairie YT, St-Pierre A. 2013. Depositional fluxes and sources of particulate carbon and nitrogen in natural lakes and a young boreal reservoir in Northern Québec. *Biogeochemistry*. 113:323–339.
- Wan M, Shchukarev A, Lohmayer R, Planer-Friedrich B, Peiffer S. 2014. Occurrence of surface polysulfides during the interaction between ferric (hydr) oxides and aqueous sulfide. *Environ Sci Technol*. 48:5076–5084.
- Wang F, Chapman PM. 1999. Biological implications of sulfide in sediment—a review focusing on sediment toxicity. *Environ Toxicol Chem*. 18:2526–2532.
- Wang L, Liang T. 2015. Distribution characteristics of phosphorus in the sediments and overlying water of Poyang Lake. *PLoS One*. 10:e0125859.
- Wang S, Jin X, Pang Y, Zhao H, Zhou X, Wu F. 2005. Phosphorus fractions and phosphate sorption characteristics in relation to the sediment compositions of shallow lakes in the middle and lower

- reaches of Yangtze River region, China. *J Colloid Interface Sci.* 289:339–346.
- Wang S, Qian X, Han B-P, Luo L-C, Hamilton DP. 2012. Effects of local climate and hydrological conditions on the thermal regime of a reservoir at Tropic of Cancer, in southern China. *Water Res.* 46:2591–2604.
- [WAMIS] Water Management Information System. 2003. [cited 14 June 2014]. Available from: [http://www.wamis.go.kr/wkw/rf\\_dubrfobs.aspx](http://www.wamis.go.kr/wkw/rf_dubrfobs.aspx)
- Wersin P, Höhener P, Giovanoli R, Stumm W. 1991. Early diagenetic influences on iron transformations in a freshwater lake sediment. *Chem Geol.* 90:233–252.
- Wetzel RG. 2001. *Limnology: lake and river ecosystems*. 3<sup>rd</sup> ed. San Diego (CA): Academic Press.
- Williams WJ. 1979. *Handbook of anion determination*. Oxford (UK): Butterworth-Heinemann.
- Wipfli MS, Richardson JS, Naiman RJ. 2007. *Ecological linkages between headwaters and downstream ecosystems: transport of organic matter, invertebrates, and wood down headwater channels*. Wiley Online Library.
- [WCD] World Commission on Dams. 2000. *Dams and development: a new framework for decision-making*. London (UK): Earthscan.
- Xu Y, Schroth AW, Isles PD, Rizzo DM. 2015. Quantile regression improves models of lake eutrophication with implications for ecosystem-specific management. *Freshwater Biol.* 60:1841–1853.
- Yang Z, Wang L, Liang T, Huang M. 2015. Nitrogen distribution and ammonia release from the overlying water and sediments of Poyang Lake, China. *Environ Earth Sci.* 47:771–778.
- Yu F, Zou J, Hua Y, Zhang S, Liu G, Zhu D. 2015. Transformation of external sulphate and its effect on phosphorus mobilization in Lake Moshui, Wuhan, China. *Chemosphere.* 138:398–404.
- Zan F, Huo S, Xi B, Su J, Li X, Zhang J, Yeager KM. 2011. A 100 year sedimentary record of heavy metal pollution in a shallow eutrophic lake, Lake Chaohu, China. *J Environ Monit.* 13:2788–2797.
- Zhang R, Wu F, Liu C, Fu P, Li W, Wang L, Liao H, Guo J. 2008. Characteristics of organic phosphorus fractions in different trophic sediments of lakes from the middle and lower reaches of Yangtze River region and Southwestern Plateau, China. *Environ Pollut.* 152:366–372.