Do NH₃ and chemical oxygen demand induce continuous release of phosphorus from sediment in heavily polluted rivers?

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ABSTRACT

While phosphorus (P) is a vital element in freshwater systems, excessive P loads will induce eutrophication. Large inputs of various pollutants, including P, to rivers in semi-arid regions result in complex environmental problems. In this study, we investigate dissolved oxygen (DO), ammoniacal nitrogen (NH₃), chemical oxygen demand (COD_{Cr}), soluble reactive P (SRP) in surface water and pore water, and sediment P in the Niuwei River, within the Hai River Basin. From our results we developed and tested a theory for P release in semi-arid regions driven by DO. The results show that NH₃ and COD_{Cr} can cause variations in DO in surface water. The presence of pollutants at high concentrations caused seasonal hypoxia. Hypoxic river water induced adsorption and hydrolysis of NaOH-Pi and labile organic P (L-Po), which then resulted in increased SRP concentrations in pore water and surface water. Overall, our results illustrate that NH₃ and COD_{Cr} may be important for P adsorption and desorption and for management of water quality problems in rivers in semi-arid regions.

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1. Introduction

Eutrophication of freshwater systems, as one of the most serious environmental issues in semi-arid region, is mainly caused by phosphorus (P) (Carpenter, 2008; Pernet-Coudrier et al., 2012). Rapid socioeconomic development, huge increases in population, and the systematic damming of rivers induce deterioration of freshwater ecosystems (Li et al., 2012; Pernet-Coudrier et al., 2012; Shan et al., 2012; Taylor et al., 2015). Over the last 30 years, numerous nutrient management schemes have been initiated in China, with the aim of improving water quality. The Chinese government is very concerned about controlling pollution inputs, and so regulations and projects have been implemented, such as the Chinese National Water Pollution Control and Technology Management Project. Despite recent sustained efforts to improve water quality, eutrophication still persists in rivers in semi-arid regions, and the water quality has deteriorated to such a degree that it is not suitable for any use (Han et al., 2013). Although external P inputs to rivers have been decreasing, internal release of P from sediment provides

sufficient reactive P to sustain harmful algal blooms (Read et al., 2014). Studies that provide information about the mechanisms and drivers of P adsorption and desorption in fluvial sediment in semi-arid regions are therefore urgently needed (Kraal et al., 2013; Ahlgren et al., 2005).

Biogeochemical cycles are generally driven by reducing and oxidizing conditions (Nielsen et al., 2010). Excessive nutrient inputs will consume oxygen and induce hypoxia in the bottom waters, with the result that P is readily remobilized from sediments. This internal source of P will fuel high primary productivity and oxygen consumption; this is particularly relevant for the slow flowing rivers with numerous dams that are common in semi-arid regions of northern China (Gustafsson et al., 2012). Iron (Fe) and sulfur (S) may influence P adsorption and desorption. The reductive dissolution of Fe-oxides induces P release under seasonal hypoxia (Cowan et al., 1996; McManus et al., 1997). In summer, the lower oxygen levels in bottom water induce high rates of sulfate reduction, with the result that there are fewer iron oxides to bind P when sediment iron oxides are being converted to iron sulfides (Jensen et al., 1995; Rozan et al., 2002). In re-oxygenated conditions, the iron sulfides can be oxidized, at which point they create iron oxides that have the ability to sequester P (Dale et al., 2013). In addition, sulfur-oxidizing bacteria can accumulate P, which will be released from

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seasonally hypoxic sediment during summer (Schulz and Schulz, 2005). Recently, it was discovered that a filamentous bacterium from the *Desulfobulbaceae* family (cable bacteria) could control iron-P dynamics in sediments in a coastal hypoxic basin (Pfeffer et al., 2012; Seitaj et al., 2015; Sulu-Gambari et al., 2015).

The Hai River Basin (HRB) experiences severe water resource shortages, and water quality was seriously deteriorated. Excessive quantities of pollutants from agricultural activities and industrial development have been discharged into the system, to the degree that the river suffers from a mixture of pollutants at high concentrations. P biogeochemical cycling is much more complex in this type of river. Through long-term monitoring, we discovered that ammoniacal nitrogen (NH_3) and chemical oxygen demand (CODcr) were important components of the pollutant load in surface water. We also found that there were relationships between NH_3 , CODcr, and P. In this contribution we present field data from a tributary of the HRB, the Niuwei River, and demonstrate the link between seasonal changes in concentrations of NH_3 , CODcr, dissolved oxygen (DO), P in surface and pore water, and P fractions in sediment. The results from this study will be very significant for pollutant control, especially P, in rivers in semi-arid regions.

2. Materials and methods

2.1. Study area

The Niuwei River is the most polluted part of the Fuyang River and is contaminated by a wide range of pollutants. It flows through a fertile plain that easily supports intensive agriculture, mainly wheat, corn, and vegetables (Li et al., 2012). This region has a temperate continental monsoon climate and most of the rainfall falls during summer; precipitation in June, July, and August accounts for 70% of the annual precipitation (Chun et al., 2009). The water flows from south west to north east. There are dams and gates in this region that lead to fragmentation and instability of the river system. The Niuwei River was chosen for this study as it is representative of the conditions in the HRB in northern China.

2.2. Field sampling

The sampling sites were located on the main channel of the Niuwei River. In general, sampling sites should not be in dead water,

backwater, or discharge outfall areas, and should be, as far as possible, on straight sections of the river where the flow is gentle and the channel is wide. We selected five sampling sites, the locations of which are presented in Fig. 1. We collected the sample at the middle of every-month from Jan-2014 to Dec-2015, which continue 2 years. Five sample sites distribute along the Niuwei River. The S1 and S2 were at the urban area of Xingtai City and Ren County. S3 was located at the transition area between the city and suburban region, and S4 and S5 were at suburban district. As a transition site, sediment was also collected at S3 in this research. We collected the water samples (200 mL) with an organic glass sampler (WB-PM, Beijing Splitter Instrument Co., Ltd.) from the middle of the river. The samples were stored at 4 °C in a refrigerator in our vehicle and were immediately transported to the laboratory, where analyses were carried out within two days. DO concentrations were measured in situ with a portable device (YSI ProPlus).

Surface sediments (about 2 cm) were collected with PVC sampling tubes, the diameter and length were 6.3 and 60 cm. There were three subsampling sites at each sampling site. Two subsamples collected at the same site were pooled and homogenized to obtain a representative sample. One sediment sample was used for extracted the pore water sample. Sediment samples for P analysis were kept in sealed plastic bags at 0 °C during transport to the laboratory. Samples were freeze-dried at −50 °C (FD-1 freeze-dryer) on arrival at the laboratory. Dried samples were ground and passed through a 100-mesh sieve. Sediment sample for extracted pore water was deal as soon as possible. Quartered samples were taken as representative samples, and were stored in sealed plastic bags at room temperature until analysis. All the samples were collected from January 2014 to December 2015.

2.3. Sample analysis

2.3.1. SMT fractions

P fractions were determined as outlined in the Standards Measurements and Testing (SMT) protocol (Ruban et al., 2001a,b). Sediment P was classified into total P (TP), inorganic P (Pi), organic P (Po), P associated with Ca (HCl-Pi), and P bound to Fe, Al and Mn oxides and hydroxides (NaOH-Pi). To determine TP, 0.2 g dry sample calcined at 450 °C for 3 h. The cool ash was transferred to a centrifuge tube, to which 20 mL of 3.5 mol L^{−1} HCl was added. The tube shaken overnight (16 h) and then was centrifuged at 2000g for

Fig. 1. The sample sites in Niuwei River.

15 min. After centrifugation, the extract was collected for determination of TP. To measure Pi and Po, 0.2 g dry sample was put into a centrifuge tube, to which 20 mL of 1 mol L⁻¹ HCl was added. The tubes shaken overnight (16 h), and then were centrifuged at 2000g for 15 min. After centrifugation, the extract was collected for determination of Pi. The Po content was calculated as the difference between TP and Pi.

For determination of HCl-Pi and NaOH-Pi, 0.2 g dry sample were put into centrifuge tubes, to which 20 mL of 1 mol L⁻¹ NaOH were added. The tubes shaken overnight (16 h) and then centrifuged at 2000g for 15 min. After centrifugation, NaOH-Pi was extracted from the supernatant, and HCl-Pi was extracted from the residue. To determine NaOH-Pi, 10 mL of the centrifuged liquid was separated with a pipette, to which 4 mL of 3.5 mol L⁻¹ HCl was added. The tube shaken vigorously for 20 s, and allowed to stand overnight (16 h). A brown precipitate appeared and settled, and then was centrifuged at 200g for 15 min. NaOH-Pi was determined in the supernatant. The residue was washed with 12 mL of 1 mol L⁻¹ NaCl, and stirred for 5 min. It was then centrifuged at 2000g for 15 min, and the supernatant was discarded. Then, 20 mL of 1 mol L⁻¹ HCl was added to the tube and stirred overnight (16 h). After centrifugation at 2000g for 15 min, HCl-Pi was determined in the extract. All the P in the extract was measured by molybdate colorimetry (Aspila et al., 1976).

2.3.2. Fractionation of Po

Po was operationally defined into three fractions, including labile Po (L-Po), moderately labile Po (M-Po), and nonlabile Po (N-Po). To determine L-Po, duplicate samples of 1.0 g were placed into two 100 mL centrifuge tubes. To one tube, 50 mL of 0.5 mol L⁻¹ NaHCO₃ was added and the sample was placed horizontally on a reciprocating mechanical shaker for 16 h. The sample was centrifuged at 7000 rpm for 15 min and the supernatant was filtered into a 50-mL volumetric flask. To determine L-Pi, an aliquot containing between 2 and 40 µg of P was added to a 50-mL volumetric flask; five drops of *p*-nitrophenol indicator were added to the flask and the pH was adjusted with 2 mol L⁻¹ HCl until the indicator color just changed from pale yellow to colorless. Approximately 40 mL of deionized water was added to the flask, followed by 8 mL of reagent B. After 20 min, the P concentration was determined on a calibrated spectrophotometer at 880 nm. A blank containing the 0.5 mol L⁻¹ NaHCO₃ extracting solution was analyzed along with the sample. To determine total L-P in the extract, 0.5 g of K₂S₂O₈ was added with a calibrated scoop to a 25-mL volumetric flask. An appropriate aliquot of the extract was added into the flask, and then 3 mL of 2.5 mol L⁻¹ H₂SO₄ was added. The sample was digested on a hot plate at >150 °C for 20–30 min, until the vigorous boiling subsided. The sample was cooled and 5 mL of deionized water were added. After mixing, five drops of *p*-nitrophenol indicator were added to the flask and the pH was adjusted with 5 mol L⁻¹ NaOH. Approximately 10 mL of deionized water were added to the flask, followed by 4 mL of reagent B. After 20 min, the P concentrations were determined with a calibrated spectrophotometer at 880 nm. The difference between the total L-P by persulfate oxidation and L-Pi gives an estimate of L-Po. To determine the M-Po concentrations, 50 mL of 1 mol L⁻¹ HCl was added to the residue from the L-P extraction, and the sample was placed on a reciprocating mechanical shaker for 3 h. An aliquot of 1 mol L⁻¹ HCl was used to rinse the residue from the filter paper used in the L-P extraction. After 3 h, the sample was centrifuged at 7000 rpm for 15 min, and the supernatant was filtered into a 50-mL volumetric flask. The TP and Pi in the extract were determined as previously described. Po extracted in the 1 mol L⁻¹ HCl is considered part of the M-P fraction. The residue was rinsed from the HCl extraction with deionized water, centrifuged for 5 min, after which point the supernatant solution was discarded. Fifty milliliters of 0.5 mol L⁻¹ NaOH was added to

the residue, and the sample was shaken for 16 h. At the end of the extraction time, the sample was centrifuged at 7000 rpm for 15 min. The supernatant contains both M-Po (fulvic acid P) and N-Po (humic acid P). To separate these fractions, an aliquot of the NaOH extract was removed and acidified to pH 0.2 with concentrated HCl. The acidified sample was centrifuged at 7000 rpm for 15 min. The TP in both the NaOH extract and the acidified sample were determined as previously described. The TP in the acidified sample is a measure of fulvic acid P. Humic acid P was estimated by subtracting fulvic acid P from the TP measured in the NaOH extract. To determine highly-resistant, N-Po, the residue from the NaOH extraction was rinsed with deionized water, shaken for 5 min, and centrifuged, after which the supernatant solution was discarded. The residue was placed in a crucible and ashed at 550 °C for 1 h. The ash was dissolved by shaking in 1 mol L⁻¹ H₂SO₄ for 24 h, and P in solution was measured as previously described (Pierzynski, 2000).

The detail information about “SMT fractions” and “Fractionation of Po” were shown in support information.

2.3.3. Water sample analysis

To determine soluble reactive P (SRP) in surface water, water samples were filtered through a 0.45-µm synthetic fabric filter membrane. Concentrations of SRP were then measured using the molybdate colorimetry method (Wei, 2002). Concentrations of NH₃ were measured using the spectrophotometric blue method (Wei, 2002) after the water samples were filtered through a 0.45-µm synthetic fabric filter membrane. COD_{Cr} was determined by the colorimetry method (HACH DR2800) after digestion by COD chromate reagent (HACH DRB200, catalog number 21258-25). Samples of surface sediment (the top 2 cm) firstly picked out impurity, such as the plant debris, and then centrifuged at 5000 rpm for 10 min to extract the pore water and the supernatant was filtered through Whatman No. 41 quantitative paper into a 50-mL volumetric flask. Concentrations of SRP in pore water were then measured by the molybdate colorimetry method. The NH₃ and COD_{Cr} monitoring data for the HRB were processed by ArcGIS 10.0.

3. Results

3.1. Temporal and spatial variations of the different indexes in surface and pore water

The concentrations of pollutants showed a tendency to increase and then decrease between sampling sites. Concentrations of NH₃, COD_{Cr}, SRP in surface water, and SRP in pore water were higher at S2 than at S1, and then the concentrations decreased from S3 to S5. These pollutant concentrations exceeded the thresholds for Class V of the Environmental Quality Standards for Surface water (National Standard of the People's Republic of China, GB3838-2002). The average concentration of NH₃ in S1 to S5 was 6.95, 7.12, 6.79, 6.13 and 3.93 mg L⁻¹, respectively. The average concentration of COD_{Cr} in S1 to S5 was 69.75, 72.46, 66.42, 60.92 and 46.67 mg L⁻¹, respectively. The average concentration of SRP in surface water and in pore water were in S1 to S5 were 2.15, 2.41, 1.93, 1.85 and 1.15 mg L⁻¹ and 8.13, 8.24, 8.04, 7.88 and 7.00 mg L⁻¹, respectively. In contrast, DO concentrations first decreased and then increased, and minimum and maximum values were observed at S2 and S5, respectively. The average concentration of DO from S1 to S5 was 1.26, 1.07, 1.36, 1.64 and 2.02 mg L⁻¹, respectively.

We studied changes in the concentrations of the variables at site S3. DO concentrations were subject to seasonal variations, and declined in summer followed by re-oxygenation (increases) in fall and winter. For Jan to Dec, the concentration of DO was 1.75, 2.10, 2.35, 2.20, 1.95, 1.35, 0.65, 0.30, 0.30, 0.75, 1.15, 1.45 mg L⁻¹, respectively. NH₃, COD_{Cr}, SRP in surface water, and SRP in pore water

Fig. 2. Spatial (S1–S5: A) and temporal (S3: B) variation of DO, NH₃, CODcr, SRP in surface water and SRP in pore water in Niuwei River.

decreased in spring and then increased to their maximum values in summer, and then decreased again. For Jan to Dec, the concentration of NH₃ was 4.45, 3.80, 3.70, 4.15, 6.45, 7.00, 8.85, 9.35, 11.15, 8.45, 7.70, 6.40 mg L⁻¹, respectively. The concentration of CODcr was 66.0, 56.0, 49.5, 51.0, 56.5, 67.0, 76.0, 79.5, 84.0, 73.0, 70.5, 68.0 mg L⁻¹, respectively. The average concentration of SRP in surface water and in pore water were 1.45, 1.10, 0.95, 1.05, 1.25, 1.40, 2.00, 2.30, 3.70, 3.45, 2.70, 1.75 and 7.83, 7.73, 7.69, 7.79, 7.85, 8.09, 8.17, 8.28, 8.42, 8.29, 8.24, 8.13 mg L⁻¹, respectively. The pollutant concentrations at S3 exceeded the thresholds for Class V. The data are shown in Fig. 2 and SI Tables 1 and 2.

3.2. Phosphorus in surface sediments

Information about P fractions in sediment at S3 is presented in Figs. 3 and 4. The main component of Pi was NaOH-Pi, the concentration of which was 590.7 mg kg⁻¹, followed by HCl-Pi, the concentration of which was 424.3 mg kg⁻¹. Concentrations of Po were lowest (164.8 mg kg⁻¹). Po was divided into three parts, namely N-Po, M-Po, and L-Po, the concentrations of which were 126.7, 32.3, and 5.7 mg kg⁻¹, respectively.

Spatial variation in the different P components in surface sediments is presented in Fig. 4. The concentrations of the NaOH-Pi and Po fractions from the SMT method showed little variation from January to December. NaOH-Pi increased slightly from January to March, followed by a decrease, and then a further increase. The NaOH-Pi concentrations ranged from 587.85 to 593.10 mg kg⁻¹, with an average of 590.51 mg kg⁻¹. Concentrations of Po ranged from 160.40 to 167.75 mg kg⁻¹, and the average concentration was 164.71 mg kg⁻¹. Variations in the components of Po, M-Po and L-Po,

Fig. 3. Fractionation of surface sediment in S3 in Niuwei River.

followed the same pattern as concentrations of Po. Concentrations of M-Po and L-Po ranged from 30.00 to 33.70 mg kg⁻¹ and from 4.65 to 6.85 mg kg⁻¹, respectively. The average M-Po and L-Po concentrations were 32.20 and 5.67 mg kg⁻¹, respectively. As stable components of P, there were no obvious changes in both HCl-Pi and N-Po.

4. Discussion

Concentrations of NH₃, CODcr, and SRP, in surface water and pore water were higher in urban areas (S1 and S2) than in suburban

Fig. 4. Temporal variation of NaOH-Pi, HCl-Pi, Po (A) and Nonlabile-Po, Moderately labile-Po, labile-Po (B) in surface sediment in S3 in Niuwei River.

Table 1

Pearson correlation coefficients for physicochemical characteristics in the Niuwei River (n = 600).

	DO	NH ₃	CODcr	SRP-surface water	SRP-pore water
DO	1				
NH ₃		1			
CODcr			1		
SRP in surface water				1	
SRP in pore water					1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

Table 2

Pearson correlation coefficients for physicochemical characteristics at site 3 (n = 240).

	DO	NH ₃	CODcr	SRP-surface water	SRP-pore water	NaOH-Pi	HCl-Pi	N-Po	M-Po	L-Po
DO	1									
NH ₃		1								
CODcr			1							
SRP-surface water				1						
SRP-pore water					1					
NaOH-Pi						1				
HCl-Pi							1			
N-Po								1		
M-Po									1	
L-Po										1

N-Po: Nonlabile-Po; M-Po: Moderately labile-Po; L-Po: Labile-Po.

* Correlation is significant at the 0.05 level (2-tailed).

Fig. 5. The distribution of NH₃ and CODcr in surface sediments from river systems in Hai River Basin.

areas (S3, S4, and S5). There are many industries, such as paper and steel, in Xingtai City and Ren County that discharge large quantities of pollutants. A proportion of the wastewater and domestic sewage are discharged in their untreated forms into the river. Further, the self-purification capacity of the part of the river that flows through the city is reduced by the artificial river bank, which are smaller river curvature, little vegetation index, hardening of cement and little landscape heterogeneity, a simple littoral zone and lack of change in river morphology (Zhang et al., 2014). These factors mean that there is nitrogen (N) and P accumulation in the river water (Li et al., 2012). Although agriculture wastewater is discharged to the river, the presence of a more integrated littoral zone, which

has variety vegetation and high landscape heterogeneity, in that particular area means that the river has a higher self-purification ability (Zhang et al., 2014). Nutrient concentrations were therefore higher in suburban areas than in urban areas. In contrast, DO concentrations were higher in suburban areas than in urban areas, which reflects the different pollutants and variations in the river ecosystem. Pearson correlation analysis showed that there were negative relationships between DO and NH₃, CODcr, and SRP in surface water and pore water ($p < 0.01$, $R^2 = -0.537$, -0.432 , -0.371 , -0.299 , respectively) (Table 1). The pollutants, such as NH₃ and CODcr, consume the DO, so the higher pollutant concentrations will induce DO decline in the river water. The positive relationship

between the pollutants indicates a common origin and/or mutual transformations (such as SRP in surface water and SRP in pore water, $R^2 = 0.893$, $p < 0.01$).

Site S3 was chosen for an in-depth study of the relationships between the variables. Unlike lakes and estuaries, hypoxia and anoxia in river water are driven by catchment inflows and stratification (Sci'luna et al., 2015). Seasonal hypoxia in shallow rivers may be induced by pollution inputs, seasonal rainfall, and temperature (Wang et al., 2016). In the Niuwei River, the DO concentrations in surface water varied by $\pm 0.73 \text{ mg L}^{-1}$. The negative relationships between DO and both NH_3 and CODcr ($p < 0.01$, $R^2 = -0.952$, and -0.969 , respectively) also indicate that pollution may influence the DO contents. The negative relationship between DO and SRP ($p < 0.01$, $R^2 = -0.838$) in surface water indicates that DO may trigger release or adsorption of SRP. P recycling in sediments is enhanced under anoxic conditions in the absence of amorphous Fe^{3+} , which has a strong affinity for dissolved phosphate and promotes enhanced microbial phosphate release (Ingall et al., 1993; Steenbergh et al., 2011). Further, Fe^{3+} and Mn^{5+} oxides may be directly involved in the adsorption and hydrolysis of Po compounds, and may influence P release from sediment (Olsson et al., 2010; Huang and Zhang, 2012). The influence of DO on SRP in surface water is mainly through its influence on the P concentrations in sediment. Decreases in DO cause increases in the SRP concentrations in pore water ($p < 0.01$, $R^2 = -0.941$). Further examination showed that DO was positively related to NaOH-Pi, M-Po, and L-Po ($p < 0.01$, $R^2 = 0.812$, 0.679 , and 0.763 , respectively). Another important hint is the negative relationship between SRP in pore water and NaOH-Pi, M-Po, and L-Po ($p < 0.01$, $R^2 = -0.714$, -0.732 , and -0.764 , respectively). NaOH-Pi represents the P bound to Al, Fe, and Mn oxides or hydroxides, and Fe-P was the main form of P in the sediment (Ruban et al., 2001a). Fe-P and Al-P are also readily influenced by pH and the oxidation-reduction potential (Ruban et al., 1999) and can be released into pore water and surface water under reducing conditions. These results confirm that DO affects SRP concentrations in surface sediment through its influence on the Fe/Mn-Pi and L-Po in sediment. From the above examination of the river system, we obtained the following picture of the patterns of P release in this heavily polluted river. A range of pollutants at high concentrations caused seasonal hypoxia and low DO concentrations. The low DO levels induced increases in the SRP in pore water because of NaOH-Pi and L-Po adsorption and hydrolysis, which then caused increases in the SRP in surface water (Table 2).

P from sediment remains a significant internal pollutant source while external sources are gradually decreasing. Pollution from NH_3 and CODcr increases as economic and social development increase (Pernet-Coudrier et al., 2012). More than 50% of the rivers in the HRB exceeded the Class V water quality thresholds for NH_3 and CODcr (National Standard of the People's Republic of China, Environmental Quality Standards for Surface Water, GB3838-2002) (Fig. 5). The results of this study indicate that combined pollution will cause ongoing internal P release, which will then induce environmental problems, such as eutrophication, in rivers. We suggest that reductions in concentrations of NH_3 and CODcr may be critical for P control and management in heavily polluted rivers. It should be noted that the processes and mechanisms are complex, and biological and chemical processes need to be studied in detail (Kraal et al., 2013; Sulu-Gambari et al., 2015).

5. Conclusions

In this study, we tested and confirmed a P release theory for rivers in semi-arid regions driven by changes in DO. The results show that NH_3 and CODcr may induce variations in DO in surface water. From our examination of the trends in the data, we built

a conceptual model of the P release system. The pollution triggered seasonal hypoxia and low DO levels, which then induced increases in SRP concentrations in pore water and surface water because of NaOH-Pi and L-Po adsorption and hydrolysis. At the watershed scale, NH_3 and CODcr may be important for P control and management.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ecoleng.2017.02.003>.

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