Control of nutrients after discharge to lakes through wastewater

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Abstract Control of nutrients as nitrogen and phosphorus after discharge into lakes is necessary since it is difficult and costly to control within wastewater plants currently in China. This paper studied the cycling of phosphorus and nitrogen with water and sediments from two lakes in China. It is found that oxygen plays a critical role in regulating phosphorus and nitrogen cycling within water and sediments. Three different oxygenation methods including aeration, calcium peroxide and hydrogen peroxide were studied to control phosphorus and nitrogen in overlying water. In anoxic conditions, the P concentration in water increased from an average 14 µg/L to 115.2 µg/L for Xili Lake, and from an average 24 µg/L to 1,000 µg/L for Jinchun Lake. The concentration of ammonia increased under anoxic conditions, while the concentration of nitrate increased under oxic conditions. In anoxic conditions, the nitrate concentration decreased probably through denitrification. Both N and P accumulation processes can be controlled under the three treatments. The phosphorus removal efficiency from the water body was in the order of CaO2 addition > aeration > H2O2 addition, while controlling effectiveness for ammonia was in the order of aeration > CaO2 addition > H2O2 addition.

Keywords Aeration; calcium peroxide; hydrogen peroxide; internal nutrient cycling; nutrient control

Introduction Eutrophication has become a big problem for the water environment in China and over 80% lakes in China are now in eutrophic conditions. On the other hand, control of nutrients in wastewater plants before they are discharged to lakes is very difficult in the current period of time due to lack of funds. In China, only 30% of municipal wastewater has been treated for removal of organics, and less than 5% of wastewater plants are operated to remove nutrients such as nitrogen and phosphorus from wastewater before they are discharged into lakes. Consequently, control of nutrients after they are discharged to lakes becomes doubly urgent in China. This may offset the incomplete removal of nutrients in wastewater plants but also is helpful in controlling the lake eutrophication.

When discharged to lakes, nitrogen usually presents in four forms: ammonia, nitrate, nitrite and organics. Major transformation processes involve ammonification, nitrification and denitrification. The nutrient of phosphorus is relatively simple, most of the phosphorus presents in a particulate condition by attaching to clay particles, a minor part is soluble phosphorurate. Intensive studies reported that the internal transformations of nutrients mainly occur across the sediment/water interface in lakes, and are related to a number of factors that can alter the exchange balance: the capacity of sediments to retain nutrients, the conditions of the overlying water, e.g. dissolved oxygen, redox potential, pH, temperature, etc., and the biota involved (Redshaw et al., 1990; Burley et al., 2001). Among these factors, dissolved oxygen plays an important role in regulating the flux and transformation of both nitrogen and phosphorus across the sediment/water interface (Beutel, 2001; Hilda et al., 2003). This study is (1) to study the oxygen’s role in regulating internal nutrients cycling of phosphorus and nitrogen, (2) to examine the feasibility of using three different oxygenation methods to control the cycling of nutrients in overlying water.
methods, aeration, calcium peroxide and hydrogen peroxide, to control the subsequent accumulation of phosphorus and nitrogen in lake waters.

**Methods**

**Experiments**

Experimental water and sediments were taken from two lakes, one is Xili Lake located at Shenzhen in south China, another one is Jinchun Lake located at Beijing in north China. Sediment samples as shown in Table 1 were placed in the dark and stored at 4°C.

Polyethylene tubes with 15.4 cm internal diameter and 30 cm length were used for experiments. Well-mixed sediment samples were added into the tubes to 10 cm, then pre-aerated water samples were transferred into the tubes to 15 cm depth. One dissolved oxygen (DO) electrode and one pH electrode were inserted through a rubber stopper to monitor the change of DO and pH in the water column. Each tube has one sampling port drilled at heights of 5 cm above the sediment surface, which was sealed with a silicon rubber caulking.

In the experiments, water samples with 50–60 mL were obtained with a syringe periodically and immediately filtered by a 0.45 µm membrane filter (Pall, USA). The water samples were then acidified and analyzed for ammonia, nitrate, soluble reactive phosphorus (SRP), iron and manganese. From the 15th day of the experiments, the overlying water in each tube was oxygenated using three different methods so as to increase the DO levels in batch systems. To establish oxic conditions, one experimental tube was aerated by bubbling air through an aerator into the overlying water (5 cm above the sediment/water interface) for the following 10 days to obtain water column DO > 7.5 mg/L; the second tube was oxygenated by addition of CaO₂, 100 mg of CaO₂ were mixed into the sediments with a stainless steel spatula; this is equal to a maximum release of 7.87 mg/L of molecular oxygen; the other tube was oxygenated by H₂O₂ dosages, 156 mL H₂O₂ (30%), which is equal to a maximum oxygen release of 7.87 mg/L, was gradually added into the batch tube with a peristaltic pump. At the same time control tubes were maintained during the whole experimental period of time.

**Analyses**

For sediment samples, pretreatment was conducted with H₂SO₄ + Na₂S₂O₈ digestion, total P was determined with a modification of the molybdenum blue method (Murphy and Riley, 1962), total N was analyzed with the Kjeldahl method (APHA, 1995). The organic matter of the sediment sample was quantified from the loss of volatile matter on ignition at 550°C for 2 h in a muffle-furnace. A modified EPA Method 3050B (USEPA, 1996) and the ICP/MS (Agilent Hp4500 plus) method were used, respectively, to digest and analyze the iron and manganese in sediments. Sediment pH was measured by directly plugging a pH electrode (Orion–720A) into the pretreated sediments with the ratio of water to sediment as 1:2.5.

For water samples, dissolved oxygen was measured with an Oxi 330 meter and a Cellox 325 electrode (WTW, German). pH was measured *in situ* with a pHŠ-25 meter (Shanghai, China). DO and pH were recorded every day during the experimental period. Ammonia

**Table 1** Physico-chemical properties of sediments collected from Xili Lake and Jinchun Lake

<table>
<thead>
<tr>
<th>Sites</th>
<th>pH</th>
<th>Moisture % ww</th>
<th>Organic matter % ww</th>
<th>Total P mg/g</th>
<th>Total N mg/g</th>
<th>Fe mg/g</th>
<th>Mn mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xili Lake</td>
<td>6.92</td>
<td>62.14</td>
<td>12.44</td>
<td>1.49</td>
<td>4.34</td>
<td>2.07</td>
<td></td>
</tr>
<tr>
<td>Jinchun Lake</td>
<td>7.12</td>
<td>77.25</td>
<td>23.10</td>
<td>6.85</td>
<td>13.40</td>
<td>16.27</td>
<td>0.18</td>
</tr>
</tbody>
</table>

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was measured with the Nessler’s spectrophotometric method (APHA, 1995), nitrate was measured with ion chromatography (DX-100, USA, Dionex), SRP was determined with the ascorbic acid method (APHA, 1995), iron and manganese were measured directly with the ICP/MS (Agilent Hp4500 plus). All the measurements were made with triplicate samples.

Results and discussion
Control of phosphorus nutrient

Once the experiments were started, it was found that the DO level of the overlying water began to drop down. Within 3 days, the DO became less than 0.2 mg/L. Then the concentration of phosphorus nutrient in overlying water varied significantly. Figure 1 shows the releasing processes of phosphorus nutrient and control effectiveness during the experimental period in terms of SRP.

In oxic conditions, sediment cores from Xili Lake showed a little release of P to the overlying water. Once entered into anoxic conditions 3 days later, phosphorus in terms of SRP began to release at a much faster rate than that in oxic conditions. The concentration of SRP in the water column with sediment cores taken from Xili Lake increased from approximately 14 µg/L to 115.3 µg/L, and from an averaged 24 µg/L to 1,000 µg/L in the sediment cores taken from Jinchun Lake.

After treatment with 3 different aeration methods, the concentration of phosphorus in the water column changed in a very different way. In the test with samples of Xili Lake, SRP decreased to 30 µg/L after 10 days aeration treatment. While the concentrations of SRP in the overlying water columns with sediments from Jinchun Lake showed no apparent decrease compared with the anoxic control as 1,060 µg/L, and stabilized finally at high SRP concentration of 1,055 µg/L. In the anoxic control, phosphorus content remained high within the sequential 10 days of incubation. This may indicate that the phosphorus nutrient present in the sediment of Xili Lake is different from that in Jinchun Lake, thus resulting in different behaviors of release and control effectiveness.

For the peroxide-based aerations, both CaO₂ and H₂O₂ can decrease the phosphorus concentration in the water column, but CaO₂ is more effective than H₂O₂ in maintaining low SRP concentrations in the water column as shown in Figure 1. The CaO₂ reduced the overlying water SRP concentrations by up to 87.2% and 93.0% of SRP compared with the anoxic control, respectively, in the sediment cores taken from Jinchun Lake and Xili Lake. Relatively, addition of H₂O₂ decreased the phosphorus content in the overlying water only by 27.7% and 32.5% compared with the anoxic control.

Figure 1 Release and control of phosphorus content in waters
Control of nitrogen nutrient

Figure 2 presents the variation of ammonia and nitrate in experiments with the sediment taken from Xili Lake. At the beginning of the experiment, it was in oxic condition, both NH$_4^+$ and nitrate concentrations did not change much. When the experimental systems were gradually switched to anoxic conditions, concentration of ammonia in the water column increased sharply with time, and reached its highest at the end of the anoxic control. Ammonia is the predominant species (>77.6%) of dissolved inorganic nitrogen since nitrification cannot occur. NO$_3^-$ in the water column was consumed in anoxic conditions, and decreased to less than 0.138 mg N/L at the end of the anoxic condition.

After treatment with aeration, ammonium concentrations started to decline down to values lower than those found in anoxic conditions, while nitrate values increased. In the experiments, the nitrate levels increased from averaged 0.103 mg N/L on Day-15 to averaged 0.363 mg N/L on Day-26, whereas ammonia-N decreased greatly from averaged 0.492 mg N/L on Day-15 to less than 0.160 mg N/L on Day-26.

In the treatments with H$_2$O$_2$ addition, there is no apparent change of ammonia and nitrate during the 4 days after H$_2$O$_2$ addition, and only little change was observed during the whole period of treatment. While with the addition of CaO$_2$, there is a greater decline of ammonia occurring in the batch system than that in the H$_2$O$_2$ treatments, which indicates that CaO$_2$ addition either stops the release process of ammonia or favors the ammonia oxidizing bacteria.

Discussion

Anoxic conditions are generally considered as the stimulator for the release of P from sediments. Under oxic conditions, P is immobilized through the formation of a Fe(III)/PO$_4^{3-}$ complex, whereas under anoxic conditions P is released from the sediments by reduction of Fe(III) to Fe(II). In this study, it is found out that the phosphorus in sediments and bottom waters from Xili Lake was related to both iron and manganese in sediments, while the sediments from Jinchun Lake were not. Correlation studies demonstrated that P release was positively correlated to the Fe ($R_{P-Fe} = 0.800$) and Mn ($R_{P-Mn} = 0.772$) concentrations in the overlying water from Xili Lake (data were not shown). In contrast, in the experiments with cores taken from Jinchun Lake, there was no concurrent release of Fe, Mn and P found, but the correlation between phosphorus and organic matter is much more evident than that of Fe-P and Mn-P in sediments and overlying waters, indicating that the internal P cycling in Jinchun Lake was regulated by some other mechanisms.

One of the most important implications of these findings was the potential P release that could occur from the sediments if the lake were to experience a dissolved O$_2$ crash and also
the measures taken to control the internal P cycling. Since anoxic P fluxes greatly exceed oxic P fluxes, periods of extended anoxic conditions at the sediment–water interface could result in a tremendous P release into the water column from sediments. In redox-insensitive Jinchun Lake, providing O₂ to the water column only might not be enough to control the internal P cycling due to its high mobility of P in oxic conditions. Therefore some other oxygenation alternatives are needed to control the internal release of P.

Apparent reductions in water P content were found during the CaO₂ addition to the experimental cores with both sediments from Xili Lake and Jinchun Lake, this may suggest that Ca and PO₄³⁻ interaction probably will regulate the internal P cycling. Formation of Ca(OH)₂ during decomposition of CaO₂ in the water body caused precipitation of P as Ca₃(PO₄)₂. The O₂ produced in decomposition of CaO₂ oxidizes the dissolved Fe(II) and Mn(II) to suspended Fe(OH)₃ and Mnₓ(OH)ᵧ, which provides additional P adsorption sites. Based on the experimental results, it appears that calcium peroxide is much more efficient in decreasing phosphorus concentrations in the water column and inhibiting the release of phosphorus from both redox-sensitive and redox-insensitive sediments.

The behavior of nitrogen nutrient is similar to that of phosphorus but in a much different mechanism. There was little release of ammonia-N from sediments under oxic conditions, but substantial release of ammonia undertaken under anoxic conditions. Anoxic accumulation of ammonia is mainly caused by decomposition of organic matter in sediments. The release of inorganic N as NH₄⁺ is generally collective due to the low N requirement of anaerobic organisms (Esteves, 2001). Bacterial decomposition of organic matter in aquatic sediments is generally governed by the nature of the organic matter and the supply of electron acceptors such as NO₃⁻, thus nitrate content decreased substantially at the same time, which provides the evidence of denitrification processes in anoxic conditions.

With in situ aeration, ammonia accumulation ceased, and ammonia in the overlying water decreased with a concurrent increase in nitrate. This indicated that aeration provides O₂ in the batch systems, thus increasing the activity of aerobic bacteria, especially the activity of the ammonia oxidizing bacteria. While in the addition of H₂O₂ and CaO₂, there is less change of the concentration of ammonia and nitrate than those in the aeration treatments.

Aeration is a common strategy used to ameliorate anoxia conditions in natural water bodies, thus it can be used as a method to increase the DO levels at the sediment/water interface. Traditionally, aeration systems have used air as an oxygen source. It is very efficient in changing the DO status in the water and surface sediments, so the DO sensitive chemicals such as Fe²⁺, Mn²⁺ and HS⁻ will be oxidized and buried in the bottom deposits. H₂O₂ is an ecologically desirable pollution control agent since it yields only water and/oxygen upon decomposition. Thus, it has been used in increasingly greater quantities for environmental applications, such as the wastewater treatment and soil bioremediation, but fewer have been applied in natural aquatic systems so far. Calcium peroxide CaO₂ is one of the most versatile and safest to handle of the family of solid inorganic peroxide compounds which can be considered a “solid form” of hydrogen peroxide (Tieckelmann and Steele, 1991). The byproducts of calcium peroxide in water are lime, hydrated lime, and hydrogen peroxide, which will finally increase the O₂ levels and pH values in the water. In addition, CaO₂ is not very reactive towards water because of its insoluble nature (Tieckelmann and Steele, 1991).

**Conclusion**

P fluxes in Lake XiLi were redox-dependent, concurrent release of P was found in anoxic conditions; while P fluxes in Jinchun Lake are not regulated by redox conditions, it showed higher release of P in anoxic conditions than that in Lake XiLi. Anoxic conditions caused
the collection of ammonia and also resulted in denitrification of nitrate; oxic conditions stopped the collection of ammonia and transformation of ammonia to nitrate.

Aeration, H$_2$O$_2$ and CaO$_2$ addition are all efficient in regulating the internal cycling of nitrogen and phosphorus. The controlling efficiency for phosphorus was in the order of CaO$_2$ addition > aeration > H$_2$O$_2$ addition, while the controlling efficiency for ammonia was in the order of aeration > CaO$_2$ addition > H$_2$O$_2$ addition.

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References


