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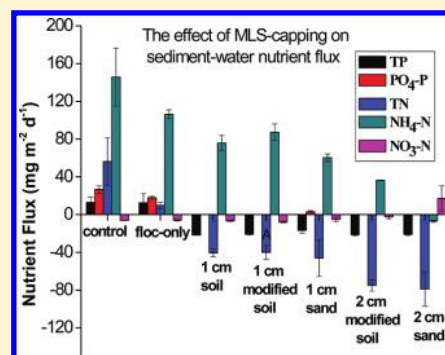
# Reducing the Recruitment of Sedimented Algae and Nutrient Release into the Overlying Water Using Modified Soil/Sand Flocculation-Capping in Eutrophic Lakes

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**ABSTRACT:** The effect of simultaneously removing algal blooms from water and reducing the resuspension and nutrient release from the sediment was studied using modified local soil/sand flocculation-capping (MLS-capping) in simulated water-sediment systems. Twenty one sediment cores in situ with overlying water containing algal blooms were collected from Meiliang Bay of Lake Taihu (China) in July 2011. The algal cells in the water were flocculated and sunk to the sediment using chitosan modified local soils, and the algal flocs were capped with modified and nonmodified soil/sand and then incubated at 25 °C for 20 days. In the MLS-capping treated systems, the TP concentration was reduced from 2.56 mg P L<sup>-1</sup> to 0.06–0.14 mg P L<sup>-1</sup> and TN from 14.66 mg N L<sup>-1</sup> to 6.03–9.56 mg N L<sup>-1</sup> throughout the experiment, whereas the sediment to water fluxes of TP, TN, PO<sub>4</sub>-P, and NH<sub>4</sub>-N were greatly reduced or reversed and the redox potential remarkably increased compared to the control system. A capping layer of 1 cm chitosan-modified sand decreased the resuspension of the sediment by a factor of 5 compared to the clay/soil/sediment systems and the overlying water kept clear even under constant stirring conditions (200 rpm). The study suggested that by using MLS-capping technology it is possible to quickly reduce the nutrient and turbidity of water by flocculating and capping the algal cells into the sediment, where the resuspension of algal flocs is physically reduced and the diffusion of nutrients from sediment to the overlying water chemically blocked by the MLS capping layers.



## INTRODUCTION

The mineral resource of phosphorus is becoming limited, affecting food security in many countries, and the world reserves could only last for about a hundred years.<sup>1</sup> Ironically, point and nonpoint sources of nutrients are polluting our aquatic environment. The lack of environmentally friendly and cost-effective innovative technologies is partly responsible for this broken biogeochemical cycle.<sup>2</sup> Eutrophication of freshwater bodies has promoted the growth of cyanobacteria as harmful algal blooms (Cyano-HABs).<sup>3</sup> Cyano-HABs deteriorate water quality, increase the turbidity of aquatic ecosystems, smother aquatic plants and thereby suppress important invertebrate and fish habitats. They threaten drinking water safety in many aquatic ecosystems, for example, Lake Erie in North America,<sup>4</sup> Lake Victoria in Africa,<sup>5</sup> and Lake Taihu in China.<sup>6</sup>

During the last decades great efforts have been made to control Cyano-HABs around the world. There are several strategies to control HABs, for example, mechanical, biological, chemical, and genetic measures.<sup>7</sup> These strategies involve removal of the HABs by light-shading,<sup>8</sup> flotation, filtration and pumping/sucking of algae,<sup>9</sup> circulation of epilimnion water,<sup>10</sup> chemical flocculation or algicides,<sup>4</sup> clay flocculation,<sup>11,12</sup> and biological controls using filter-feeding fish and zooplankton,<sup>13,14</sup> and using plant allelopathy or bacteria.<sup>15</sup> So far few technologies can be applied successfully at large scales in natural waters in an ecologically safe and cost-effective way, and

very few of the existing in situ methods can quickly and sustainably reduce or reuse the nutrients in addition to clearing up the algal blooms.

In order to simultaneously mitigate Cyano-HABs and eutrophication in natural shallow waters, Pan and colleagues developed a Modified Local Soil/Sand Induced Ecological Restoration technology (MLS-IER), where algal blooms together with the excessive nutrients in the cells are flocculated and sunk into the sediment by spraying chitosan modified local soil/sand suspension to the bloom water and subsequently convert the algae biomass into submerged vegetations in shallow lakes.<sup>16–22</sup> In 2006, the severe algal blooms in the entire Liaoyangyuan Bay (10 000 m<sup>2</sup>) in North Lake Taihu was cleared up using MLS-IER technology in one day.<sup>16</sup> Submerged vegetations in the entire bay were successfully restored four months later and the biodiversity index of zoobenthos and phytoplankton were increased compared with control area.<sup>16</sup> Comparing to chemical flocculants,<sup>23–26</sup> unpolluted local soils (not contaminated by heavy metals, fertilizers or other hazardous materials) or commercially available clean sands are not only cheap and easily accessible but also, most

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importantly, ecologically safe for the natural aquatic ecosystems. However, sands or soils by themselves do not have functions in algae removal or water quality improvement, and innovative technologies are essential to make them efficient for lake restoration. The ecological principle underlining the MLS-IER is that lakes can be switched from algae dominated alternative stable state to macro-vegetation dominated state after the water clarity is increased and the total nutrients load reduced below a critical level.<sup>27,28</sup> The improvement of water quality in shallow eutrophic lake is naturally very slow even if the external loads are under control.<sup>29</sup> Dissolved nutrients can be largely absorbed by the algal cells during the blooms. Thus, MLS-IER technology can potentially be used at very large scale to clear up severe Cyano-HABs, to reduce total nutrient levels and increase the water transparency so as to accelerate the ecological restoration in eutrophicated waters. However, such a positive effect may be quickly diminished by the resuspension of the algae flocs and the diffusion of nutrients from the sediment. Another concern for the MLS technology is the likelihood of exacerbation on the anoxic conditions in the sediment due to the decomposition of flocculated algae, which may not only increase the nutrient flux from sediment<sup>18</sup> but also depress the growth of submerged vegetation seeds.<sup>30</sup> In order to solve these problems, the MLS-capping technology (a multilayer sediment control strategy) was proposed to reduce the resuspension of flocculated algae and the release of internal nutrients from the sediment so that the growth of submerged vegetation in the MLS-capping treated shallow waters may facilitate a sustainable improvement of sediment–water environment.

Capping is a traditional way to block nutrients in sediments. While chemical capping agents may be a matter of concern from the safety viewpoint,<sup>31</sup> natural sands are known to be inert and ecologically safe for lakes and effective in preventing resuspension.<sup>32</sup> Many waters with sandy sediment are clearer than shallow waters with muddy sediment. Sandy sediment is also favorable for the growth of submerged vegetation.<sup>33</sup> The condition for turning algal biomass into submerged vegetation using MLS-IER is that the algae must be collected and transferred from water to the sediment and then decomposed into nutrients that are ready to be utilized by the submerged vegetation. The flocculated cyanobacteria cells tend to decompose under dark, anoxic, and high temperature conditions. Although a sublayer sediment may satisfy these conditions in warm seasons, anoxic sediment usually tends to release nutrients into water due to the reduction of iron or manganese oxides.<sup>34</sup> Clean sands or soils with low organic contents usually have a much higher redox potential than the polluted muddy sediment. If algal flocs can be put into the sublayer sediment that is capped with an aerobic top layer of soil/sand, the capping layer may play dual functions in reducing the mixing/resuspension and internal nutrients release. The improved top layer sediment–water environment can then become favorable for the restoration of macrophyte vegetation in shallow waters. To our knowledge, there are no previous studies on how the mixing/resuspension of flocculated algae and the diffusion of internal nutrients due to the decomposition of algal cells can be reduced or even reversed by using modified soil/sand and, if so, the mechanisms of the manipulation processes.

In this study, the effects of algal bloom removal and nutrient flux reduction from the sediment were studied using MLS flocculation-capping technology in simulated sediment–water

systems taken from Meiliang Bay, Lake Taihu (China). Column incubation experiment under controlled conditions was used to measure the nutrient fluxes from/to the sediment and changes of redox potential (ORP) across the sediment–water interfaces. A jar test was used to study the effect of resuspension prevention for different treatments of MLS-capping. The objective of the study is to explore the effect and mechanisms on the reduction of mixing/resuspension and nutrient diffusion from the sediment after the algal blooms were removed and transferred to the sediment using MLS technology.

## ■ EXPERIMENTAL SECTION

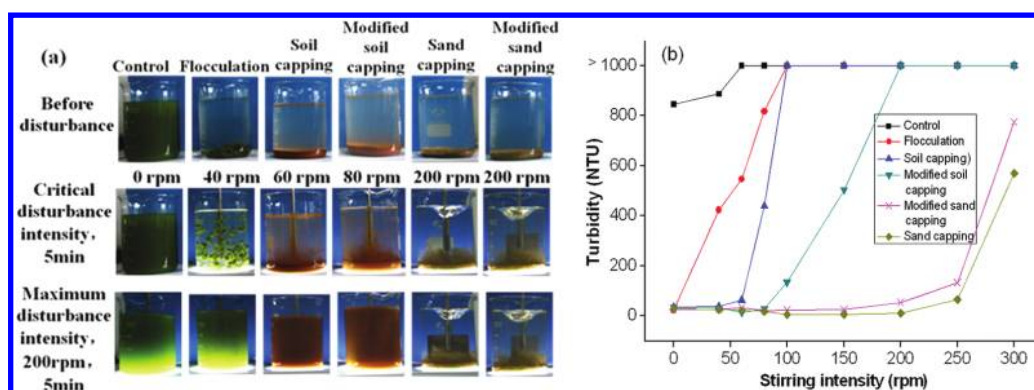
**Study Site.** The sampling sites (31°31.297'N, 120°09.364'E) were in Meiliang Bay, the northern part of Lake Taihu, China. The water depth was 1.8 m. This area has suffered annually from severe cyanobacterial blooms over the last years. After reduction of external nutrient loads in recent years, internal loads from sediment and degradation of algae become a significant source of nutrient in the area.<sup>35</sup>

**Resuspension Experiment.** The chitosan (solids, C<sub>56</sub>H<sub>103</sub>N<sub>9</sub>O<sub>39</sub>) was obtained from Qingdao Haisheng Bio-engineering Co. Ltd., Qingdao, China. The soil used here was collected from the bank of Meiliang Bay at Wuxi, and the sand was purchased from a local vendor. They were washed with distilled water and dried for 10 h at 90 °C. Soil used for flocculation was sieved through 180 meshes (74 μm) and those for capping were through 40 meshes (380 μm). Chitosan was dissolved by 0.5% acetate acid before modifying the soil or sand particles.

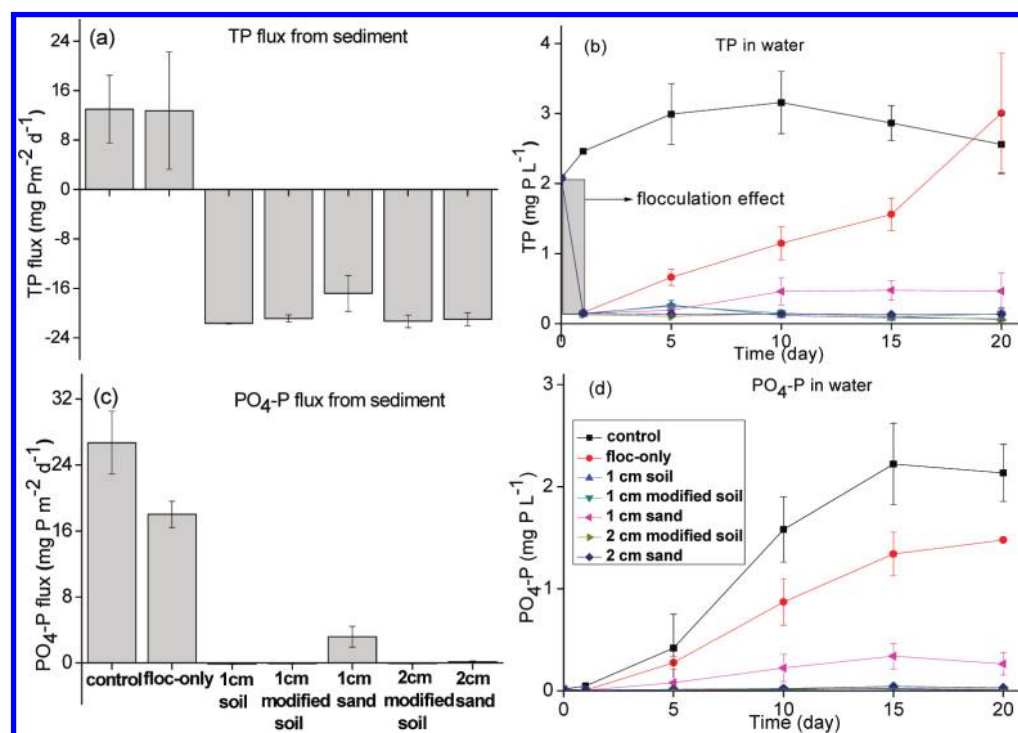
The resuspension experiment (the jar test) was conducted in six 500 mL beakers containing 450 mL bloom water (Chl-a 4876 μg/L) from Meiliang Bay, Lake Taihu. One beaker containing algal water only without adding anything was used as a control. Algal cells in the rest five test beakers were first flocculated using MLS (2 mg/L chitosan and 75 mg/L soil). Ten minutes after the sedimentation of algal flocs, 1 cm thick layer of unmodified soil, chitosan modified soil, unmodified sand, and chitosan modified sand were added, respectively, to cap the flocs. Two hours after the capping, the overlying water in the beakers was stirred (six-head stirrer ZR3-6, made in Shenzhen, China) at different speed (20–300 rpm) for 5 min. The stirrer was located at about 1 cm above the capping layer of the sediment. After the stirring, the overlying water 1 cm below the water surface was sampled and analyzed for turbidity (Hach 2100P portable turbidimeter) to estimate the resuspension effect.

**Sediment and Lake Water.** Twenty one plexiglass cylinders with a diameter of 8.4 cm and height of 50 cm were used as sampler and incubation vessels for the experiment. The lake water together with the top 20 cm sediment was sampled using the plexiglass sampler in July 2011. The overlying water of the sediment columns was siphoned off and then replaced gently with 1.2 L of surface water containing high concentration of algal cells (the water column was 22 cm deep in the cylinders). The concentrations for Chl-a (1.64 mg/L), TN (12.52 mg N L<sup>-1</sup>), TP (2.08 mg P L<sup>-1</sup>), PO<sub>4</sub>-P (0.015 mg P L<sup>-1</sup>), NO<sub>3</sub>-N (0.69 mg N L<sup>-1</sup>), and NH<sub>4</sub>-N (1.66 mg N L<sup>-1</sup>) in the surface water were measured before treatment.

**MLS-Capping Incubation Experiment.** After the algal water-sediment cylinders were prepared as mentioned above, the algal cells (except in three control cylinders, where neither flocculation nor capping were applied) were flocculated from the water and sunk down to the sediment using chitosan



**Figure 1.** The effect of MLS-capping on resuspension reduction (a) and the turbidity caused by different disturbance intensities (b), where 1000 NTU is the maximum limit of the instrument. The critical disturbance intensity means the disturbance intensity at which resuspension occurs.



**Figure 2.** Sediment to water flux of TP (a) and  $\text{PO}_4\text{-P}$  (c) and concentrations of TP (b) and  $\text{PO}_4\text{-P}$  (d) in the overlying water. Control represents no flocculation and no capping; flocc-only represents removing algal cells with MLS without capping; 1 cm soil represents flocculating algal cells with MLS and capping with 1 cm thick soil; 2 cm modified soil represents flocculating algal cells with MLS and capping with 2 cm thick chitosan modified soil.

modified local soil. Ten minutes after the sedimentation of algal flocs, 1 cm of unmodified soil, 1 cm chitosan modified soil, 1 cm sand, 2 cm chitosan modified soil, and 2 cm sand were added to cap the flocs, respectively (five capping treatments and 1 with flocculation treatment only, i.e., without capping). All the incubation experiments were conducted in triplicate at  $25 \pm 1^\circ\text{C}$  in the dark.

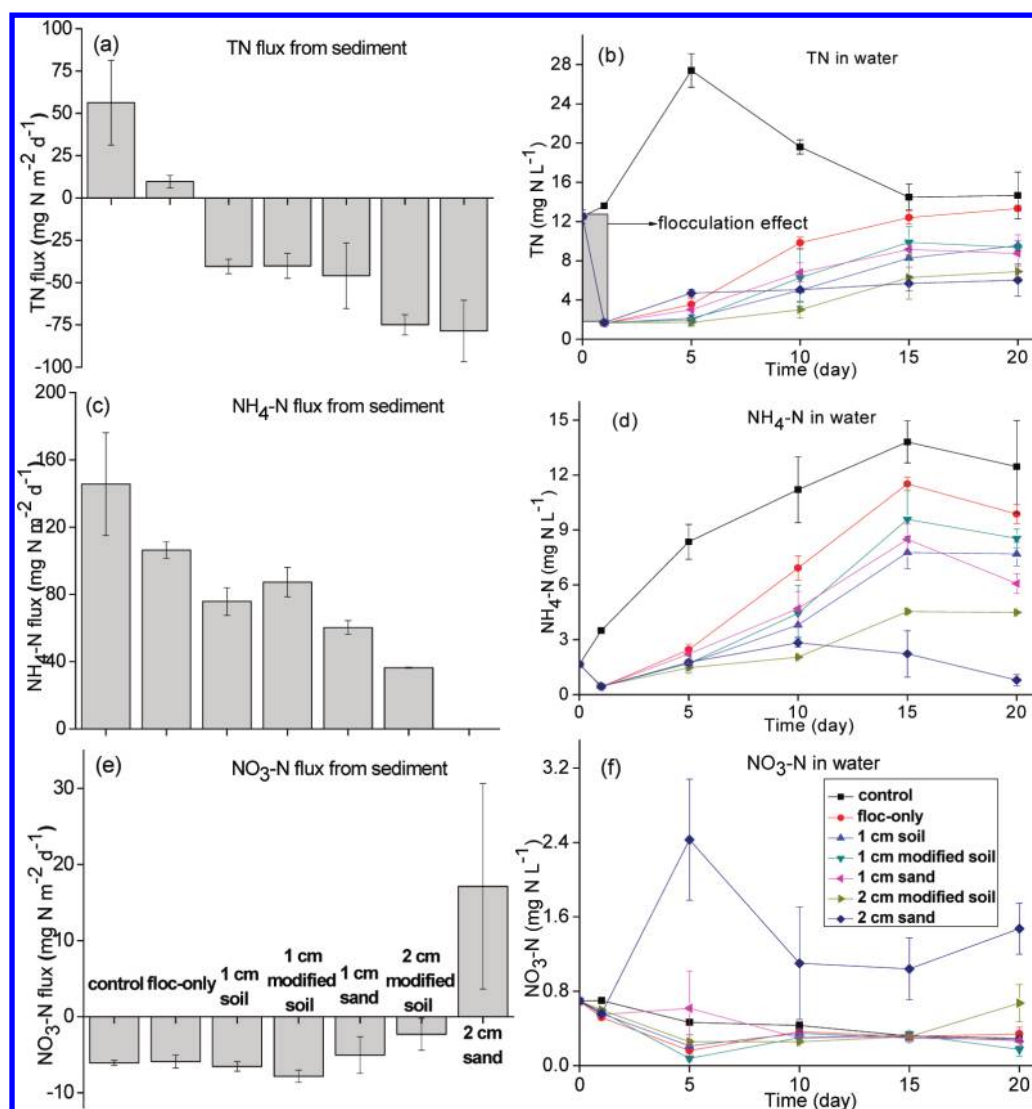
The overlying water samples (100 mL) in the incubation experiment were collected every 5 days until day 20. The water samples were collected 10 cm above the sediment–water interface using a syringe, and then 100 mL filtered lake water was added to maintain the total overlying water volume constant. Chl-a was extracted by acetone (90%) for 24 h at  $4^\circ\text{C}$  from algal cells collected with  $0.45\ \mu\text{m}$  membrane filters. Total nitrogen (TN) was determined using alkaline potassium persulphate digestion–ultraviolet spectrometer. Total phosphorus (TP) was determined using potassium persulfate

digestion–Mo–Sb–Vc colorimetric method and soluble reactive phosphate ( $\text{PO}_4\text{-P}$ ) by Mo–Sb–Vc colorimetric method. Ammonium ( $\text{NH}_4\text{-N}$ ) was measured by Nessler's colorimetric method and nitrate ( $\text{NO}_3\text{-N}$ ) by ultraviolet colorimetric method. The oxidation–reduction potential (ORP) was measured using an ORP meter (HANNA H19125). The concentrations of TP,  $\text{PO}_4\text{-P}$ , TN,  $\text{NH}_4\text{-N}$ , and  $\text{NO}_3\text{-N}$  in the incubated water columns were measured on day 1 after the flocculation and then every 5 days after the capping.

**Calculation of the Nutrient Flux at Sediment–Water Interfaces.** The average nutrient flux across the water–sediment interface was calculated according to following equation:

$$F_i = [V(c_n - c_0) + \sum_{j=1}^n V_{j-1}(c_{j-1} - c_a)] / (S \cdot t)$$





**Figure 3.** Sediment to water flux of TN (a),  $\text{NH}_4\text{-N}$  (c) and  $\text{NO}_3\text{-N}$  (e) and concentrations of TN (b),  $\text{NH}_4\text{-N}$  (d) and  $\text{NO}_3\text{-N}$  (f) in the overlying water.

where  $F_i$  is the average flux until day  $i$  ( $\text{mg m}^{-2} \text{d}^{-1}$ ),  $V$  is the volume of overlying water (L),  $c_n$  and  $c_{j-1}$  are the nutrient concentration ( $\text{mg L}^{-1}$ ) on day  $n$  and day  $j-1$ , respectively;  $c_0$  is the nutrient concentration before treatment ( $\text{mg L}^{-1}$ ),  $V_{j-1}$  is volume for sampling water (L),  $c_a$  is the nutrient concentration of the water for compensating sampled water ( $\text{mg L}^{-1}$ ),  $S$  is the area of the volume ( $\text{m}^2$ ),  $t$  is incubation time (day). All the fluxes presented in this paper were the accumulated results for 20 days.

**Statistical Analysis.** Duncan's multiple range test was conducted to determine significant differences among different treatments using SAS.<sup>36</sup> Due to the limited sample size (3), a significance was assumed when  $P < 0.05$ .<sup>37</sup>

## RESULTS

**Resuspension Reduction Using MLS-Capping.** The effect of resuspension reduction for different capping treatments was compared in Figure 1. There was no resuspension of flocs in all MLS treated systems if there was no disturbance in the water column (first row photos in Figure 1a). However, under disturbance conditions, the critical intensity of stirring that began to cause visual resuspension varied with different

capping treatment (second row photos in Figure 1a). The MLS only treated system without capping could only resist the lowest intensity of stirring (40 rpm), while this ability was increased five times (200 rpm) when the flocs were capped by 1 cm MLS-sand or sand alone. This effect on the reduction of resuspension was further demonstrated in the third row photos in Figure 1a, where the overlying water was still clear for the modified sand capping system while all the other systems became entirely resuspended under a stirring condition of 200 rpm. This effect was quantitatively confirmed by the measurement of turbidity in the overlying waters under different stirring conditions (Figure 1b). The maximum turbidity that the instrument can measure is 1000 NTU. Both MLS only and soil capping systems reached to the maximum turbidity ( $\geq 1000$  NTU) at about 70 rpm. However, in chitosan modified soil capping and modified-sand or sand capping systems, the maximum turbidity ( $\geq 1000$  NTU) was reached at about 190 and  $>350$  rpm, respectively (Figure 1b). These results showed that chitosan-modified soils remarkably increased the ability to resist resuspension compared to nonmodified soils, and chitosan modified sand or sand alone had the highest ability to reduce resuspension.

### Phosphorus Flux Across Sediment–Water Interfaces.

During the incubation experiment, a positive flux of TP from sediment to the overlying water (source) was observed for the control ( $13.01 \text{ mg P m}^{-2} \text{ d}^{-1}$ ) and the flocculation only ( $12.76 \text{ mg P m}^{-2} \text{ d}^{-1}$ ) systems (Figure 2a). However, the TP flux was entirely reversed into negative values for all the flocculation-capping treated systems, suggesting that MLS capping layer became the sink of TP (Figure 2a). This may be explained from the change of redox potential in the top layer of the sediment as discussed in the following sections. The TP concentrations in the overlying water were reduced by more than 94% (reduced from  $2.56 \text{ mg P L}^{-1}$  to less than  $0.14 \text{ mg P L}^{-1}$ ) in all flocculation-capping treated systems (except 1 cm sand capping) compared with the control system on day 20 (Figure 2b). Although TP concentration can be quickly reduced in the flocculation only system, it was gradually released back to the water within weeks without the capping layer (Figure 2b). The release of TP was entirely stopped with all capping treatments (Figure 2a, b).

The  $\text{PO}_4\text{-P}$  flux from sediment to water column was  $26.69 \text{ mg P m}^{-2} \text{ d}^{-1}$  (a source) for the control system (Figure 2c). This was reduced to  $18.01 \text{ mg P m}^{-2} \text{ d}^{-1}$  for the flocculation only system and further down to  $3.17 \text{ mg P m}^{-2} \text{ d}^{-1}$  for the flocculation-1 cm sand capping system and nearly zero for the other four flocculation-capping treated systems (Figure 2c). The  $\text{PO}_4\text{-P}$  concentration in the water column on day 20 was  $2.13 \text{ mg P L}^{-1}$  in the control. This was reduced to  $1.48 \text{ mg P L}^{-1}$  in the flocculation only system and below  $0.01 \text{ mg P L}^{-1}$  in the three flocculation-soil capping treated systems (Figure 2d). Sand capping appeared to be less effective than the soil capping on the P flux control.

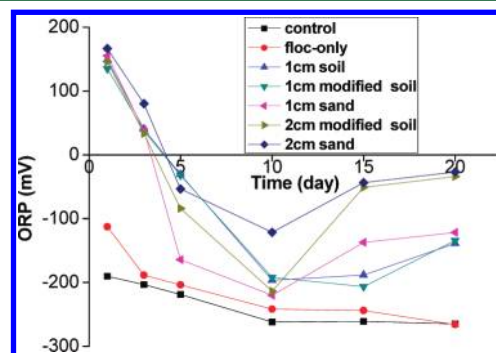
**Nitrogen Flux Across Sediment–Water Interfaces.** The TN flux from sediment to water column was  $56.31 \text{ mg N m}^{-2} \text{ d}^{-1}$  (a source) for the control system (Figure 3a), which was reduced to  $9.70 \text{ mg N m}^{-2} \text{ d}^{-1}$  for the flocculation only system and was further reversed to  $-40.47$ ,  $-40.11$ ,  $-46.01$ ,  $-74.97$ , and  $-78.67 \text{ mg N m}^{-2} \text{ d}^{-1}$  for the flocculation-1 cm soil, flocculation-1 cm modified soil, flocculation-1 cm sand, flocculation-2 cm modified soil, and flocculation-2 cm sand capping systems, respectively (Figure 3a). On day 20, the TN concentration was reduced from  $14.66 \text{ mg N L}^{-1}$  in the control system to  $6.03 \text{ mg N L}^{-1}$  in the flocculation-2 cm sand capping system (Figure 3b). The effect on TN concentration and flux reduction for 2 cm capping treated systems was systematically higher than that of 1 cm capping ( $P < 0.05$ ).

The  $\text{NH}_4\text{-N}$  flux from sediment to water gradually decreased in the order of control, flocculation only, flocculation-1 cm chitosan modified soil, flocculation-1 cm soil, flocculation-1 cm sand, flocculation-2 cm modified soil, and flocculation-2 cm sand capping (Figure 3c, d). The flux of  $\text{NH}_4\text{-N}$  was reversed into negative value in the flocculation-2 cm sand capping system. The  $\text{NH}_4\text{-N}$  concentration in the water was reduced from  $12.5 \text{ mg N L}^{-1}$  in the control to  $0.5 \text{ mg N L}^{-1}$  in the flocculation-2 cm sand capping system at the end of experiment. The effect of  $\text{NH}_4\text{-N}$  flux reduction was remarkably increased from 1 to 2 cm soil capping and the sand capping was more effective than the soil capping in terms of  $\text{NH}_4\text{-N}$  flux control.

In contrast to those of TP,  $\text{PO}_4\text{-P}$ , TN, and  $\text{NH}_4\text{-N}$ , the flocculation-capping treatment generally did not reduce the flux of  $\text{NO}_3\text{-N}$  and the concentration of  $\text{NO}_3\text{-N}$  in water (Figure 3e, f). The flux and concentration of  $\text{NO}_3\text{-N}$  in the control system were  $-6.08 \text{ mg N m}^{-2} \text{ d}^{-1}$  and  $0.29 \text{ mg N L}^{-1}$ , which

increased to  $17.14 \text{ mg N m}^{-2} \text{ d}^{-1}$  and  $1.47 \text{ mg N L}^{-1}$ , respectively, in the flocculation-2 cm sand capping system (Figure 3e, f). However, the chitosan modified soil capping reduced the  $\text{NO}_3\text{-N}$  flux and, subsequently, the  $\text{NO}_3\text{-N}$  flux from sediment to water was remarkably different between chitosan modified soil capping (negative flux) and that of sand (positive flux) (Figure 3e).

**Redox Potential Changes at the Water–Sediment Interfaces.** The flocculation only treatment slightly raised the ORP values in the sediment (especially during the first day) compared with the control, but the ORP of the two systems generally remained similar below  $-200 \text{ mV}$  throughout the experiment (Figure 4). For all the flocculation-capping treated



**Figure 4.** The ORP changes at the water–sediment interface after MLS-capping treatment.

systems, ORP values were increased to about  $+150 \text{ mV}$  on the first day and remained positive until 3 to 4 days (Figure 4). The ORP gradually decreased to the minimum of  $-100$  to  $-220 \text{ mV}$  in day 10 and then increased again for all the flocculation-capping treated systems (Figure 4). At the end of 20 days, the ORP value increased from  $-250 \text{ mV}$  in the control and flocculation only systems to about  $-130 \text{ mV}$  in 1 cm capping systems and further to  $-27 \text{ mV}$  in the 2 cm capping systems (Figure 4).

## DISCUSSION

**Modified Soil and Sand Capping for Resuspension Control.** The resuspension of algal flocs and the sediment can impair the improved water clarity achieved by MLS, especially in shallow waters that are subject to wind-induced turbulence. Results in Figure 1b showed that chitosan-modified soil exhibited a much higher ability to counteract resuspension, 3-fold greater than unmodified soil. However, modified and unmodified sands displayed no significant difference. This is because the netting-bridging function of the natural polymer chitosan is not only responsible for the flocculation of algae cells but also for other solid particles. However, it is mainly effective in bringing smaller and lighter particles together such as algae cells and fine soil particles.<sup>19</sup> The capacity of sand to resist resuspension comes mainly from the higher density and particle size, where chitosan plays a less role. The ability of antiresuspension by sand was 5 times higher than that of unmodified soil (Figure 1b), which agreed to other reports under field conditions.<sup>32</sup>

To increase the capacity of antiresuspension by a factor of 3–5 could be substantial in maintaining water clarity for triggering a positive ecological effect because both the biological and ecological processes in the water and sediment are directly

controlled by water clarity. Light is vital for submerged vegetations and for the biodiversity in aquatic ecosystems. Results in Figure 1 demonstrated that the overlying water could maintain clear even under constant stirring of 200 rpm when the flocs were capped with 1 cm modified sand or sand alone. Although the jar test method is necessary for quantitative comparison and screening of antiresuspension materials, its real effect in antiresuspension needs to be further studied under field conditions in the future. In practical engineering, the potential value of antiresuspension could be further improved by using larger sand granules for capping. However, large sands can be less effective in blocking the nutrient diffusion from the sediment. The idea of MLS-IER technology is to use the limited period of water and sediment improvement to trigger the restoration of submerged vegetation in shallow waters, which could, in turn, enhance the sustainable ability of antiresuspension.<sup>16</sup>

**The Effect of MLS-Capping on Nutrient Flux and Nutrient Levels in Water.** Although clay flocculation, as a temporary/emergency treatment, to mitigate HABs has been studied extensively over the last two decades,<sup>11,12</sup> little progress has been made on the resuspension of algal flocs and potential nutrient release from the sediment. With the idea of MLS-capping and ecological restoration, it is possible to reduce the total nutrient levels quickly in water and prevent the resuspension of the algae flocs and the nutrient release from the sediment. Figure 2b showed that MLS flocculation followed by 1–2 cm soil capping generally reduced TP to 0.06–0.14 mg P L<sup>-1</sup> and PO<sub>4</sub>-P to 0.005–0.01 mg P L<sup>-1</sup> throughout the tested period (removal rate >94%). This effect may be significant for eutrophication control, but may be still not enough to limit the algal bloom by one treatment. Sand capping was much less effective than soil capping in terms of P control, where TP was reduced to 0.13–0.46 mg P L<sup>-1</sup> and PO<sub>4</sub>-P to 0.027–0.26 mg P L<sup>-1</sup> (Figure 2b). Different soil-capping treatments did not show significant differences in terms of TP flux and TP concentration in water ( $P > 0.05$ ), indicating that 1 cm layer soil capping was effective in preventing TP flux from the sediment to the overlying water when most algal biomass in the water was transferred to the sediment under the capping layer (Figure 2a, b). The TP and PO<sub>4</sub>-P concentration are positively correlated to ORP, the effect was therefore attributed to the chemical blockage of P flux due to the increased ORP, where phosphorus tends to adsorb (become a sink) rather than desorb (a source) on/from the soil particles. Although sand capping appeared to be less effective in the chemical control on P flux than that of soil capping, the physical effect of antiresuspension of sand should be taken into account in practice where wind and wave could be substantial. It should be noted that, also we are discussing P levels after one treatment, the purpose of MLS-IER technology is to trigger ecological restoration of submerged vegetation by reducing algal concentration and nutrient levels, which should, in turn, play the major role in further reduction of TP level in a long-term sustainable way.

The local soil and sand are about 5 and 15 US\$/ton, respectively, which are much cheaper than chemical flocculants such as PAC (400 US\$/ton) and Phoslock (2500 US\$/ton). The cost of using chitosan in the field as concentration of 2 mg/L is about 0.04 US\$/m<sup>3</sup>. In shallow lakes like Lake Taihu, the cost of using MLS-IER to achieve multiple purposes of algal removal, water quality improvement, sediment improvement, and ecological restoration is about 0.2 US\$/m<sup>2</sup>. Although the

idea of MLS technology, from ecological safety and cost-effective viewpoint, is to use natural materials of soil, sand, and natural modifiers such as chitosan or proteins extracted from shellfish or plants for pollution control in natural waters,<sup>16–22</sup> it is also possible to modify the MLS materials with chemical or micro-organism components, especially in small waters where there may be less ecological and cost concerns. Many types of soil/sand/clay can become highly effective for fixation of phosphorus after they are modified with LaCl<sub>3</sub>.<sup>38</sup> If the capping material is modified by lanthanum and aluminum, the P flux control effect may be chemically further improved.<sup>23,25,26</sup> When microorganisms are embedded into the MLS materials, it may be easier for algae toxins to be biodegraded under the capping layer.<sup>39</sup> Further interdisciplinary studies are needed for algal bloom and eutrophication control, where soil or sand can be ideal carriers for various physical, ecological, biological, and chemical components.

The soil capping effect for nitrogen is more complicated. While the flocculation-soil capping treatment can entirely reverse the TN flux and largely reduce the NH<sub>4</sub>-N flux, it also significantly increases the NO<sub>3</sub>-N flux at the sediment–water interfaces especially for sand capping (Figure 3a, c, e). This may be due to the increased dissolved oxygen and ORP levels which cause nitrification.<sup>40</sup> This result implies that a thicker capping layer is not always encouraging despite of the concern of cost; one must also look into the effect of sediment–water flux of nutrients. In practice, we recommend to use 1 cm chitosan modified soil combined with sand capping, which can not only prevent the resuspension but also circumvent the possible NO<sub>3</sub>-N problem.

It should be noted that during the 20 days incubation experiment, the flocculated algae cells may still be largely preserved (not decomposed) in the sediment. Over longer time periods, and especially as the water temperature increases, more algal cells may be decomposed and more nutrients may be released. In the field, the resuspension induced by the wave and water current, or the burrowing of benthos may impair the effect of MLS-capping. The behavior of nutrient flux dynamics across the sediment–water interfaces needs further studies under field conditions.

#### The Effect of MLS-Capping on Redox Environment.

Unlike anaerobic sediment, the fresh surface soil or sand that is in constant contact with air and sunshine is aerobic by nature. It is not surprising that the ORP values of the top layer sediment can be quickly increased to become positive during the first few days after the capping. The decrease in ORP in the subsequent 10 days may be due to the redox stratification of heterotrophic processes that shifted vertically into the overlying cap.<sup>41,42</sup> The increase of ORP during days 10–20 may be due to the decrease of decomposition rate, which needs further studies. The remarkably raised ORP increased the adsorption of P in the capping layer and therefore prevent the diffusion of nutrients to the overlying water from the sublayer sediment. In practice, we suggest to use a sandwich soil–sand capping, which can chemically reduce the nutrient flux and physically prevent the resuspension of the sediment. The capping layer can only provide a temporary block to reduce the nutrient flux from the sediment. When the water transparency is sufficiently improved, the restoration of submerged vegetation may take over the long-term role in maintaining and improving the positive effect of MLS.

**Implications for Environmental and Ecological Engineering.** Excess phosphorus is polluting our aquatic



environment, while, ironically, mineable resources of this essential nutrient are becoming quickly limited on the earth.<sup>1,2</sup> On the other hand, the ecological restoration in natural waters depends on the reduction of excess nutrients from the water, which is naturally a very slow process.<sup>27,28</sup> There are very few safe and cost-effective technologies available to quickly rehabilitate natural water bodies once they are polluted. Technical innovation may be critical in repairing this broken biogeochemical cycle of nutrients.<sup>1,2</sup> Excess nutrients and algal blooms cause ecological problems when they stay in water or sediment that are exchangeable with water column, but not the net burial of nutrients that are not exchangeable with water. The MLS technology provides a safe and cost-effective principle to manipulate the nutrient distribution between water and sediment by transferring algal cells/flocs or adsorbed pollutants on solid particles into the sediment and seal them into the sublayer sediment.<sup>16</sup> The redistributed nutrients in the sediment can either stay outside the water column for certain period of time in deep waters, or be reused as a resource to restore a healthier ecological system dominated by submerged vegetation in shallow waters, where the nutrients can be further turned into marketable fish proteins through the reconstructed food web. Innovative studies may provide opportunities to repair the broken biogeochemical cycle.<sup>2</sup>

In practical engineering in field lakes, after the nutrient levels in water column are reduced, the control of resuspension and diffusion/release of nutrients from the sediment is crucial for the MLS technology. Here, after using MLS-capping, various nutrient release from the sediment can be reduced and the source of nutrients (TP, TN, PO<sub>4</sub>-P) changed into sink in the capping layer (see figure in TOC). In a limited and isolated water body, once the seed bank of algal blooms in the water column is mostly transferred and sealed into the sediment with the MLS-capping technology, the recruitment of algal blooms could be largely reduced when the inoculants are mostly buried, decomposed, and absorbed by the growth of submerged vegetations.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Gilbert, N. The disappearing nutrient. *Nature* **2009**, 461 (7265), 716–718.
- (2) Elser, J.; Bennet, E. A broken biogeochemical cycle. *Nature* **2011**, 478, 29–31.
- (3) Paerl, H. W.; Huisman, J. Blooms like it hot. *Science* **2008**, 320 (5872), 57–58.
- (4) Chorus, I.; Bartram, J. *Toxic Cyanobacterial in Water*; E&FN Spon: London, 1999.
- (5) Carmichael, W. W. Health effects of toxin-producing cyanobacteria: "The CyanoHABs". *Hum. Ecol. Risk Assess.* **2001**, 7 (5), 1393–1407.
- (6) Guo, L. Doing battle with the green monster of Taihu Lake. *Science* **2007**, 317 (5842), 1166–1166.
- (7) Anderson, D. M. Approaches to monitoring, control and management of harmful algal blooms (HABs). *Ocean Coast. Manage.* **2009**, 52 (7), 342–347.
- (8) Chen, X. C.; Kong, H. N.; He, S. B.; Wu, D. Y.; Li, C. J.; Huang, X. C. Reducing harmful algae in raw water by light-shading. *Process Biochem.* **2009**, 44 (3), 357–360.
- (9) Wiley, P. E.; Brenneman, K. J.; Jacobson, A. E. Improved algal harvesting using suspended air flotation. *Water Environ. Res.* **2009**, 81 (7), 702–708.
- (10) Hudnell, H. K.; Jones, C.; Labisi, B.; Lucero, V.; Hill, D. R.; Eilers, J. Freshwater harmful algal bloom (FHAB) suppression with solar powered circulation (SPC). *Harmful Algae* **2010**, 9 (2), 208–217.
- (11) Beaulieu, S. E.; Sengco, M. R.; Anderson, D. M. Using clay to control harmful algal blooms: Deposition and resuspension of clay/algal flocs. *Harmful Algae* **2005**, 4 (1), 123–138.
- (12) Sengco, M. R.; Anderson, D. M. Controlling harmful algal blooms through clay Flocculation. *J. Eukaryotic Microbiol.* **2004**, 51 (2), 169–172.
- (13) Jeppesen, E.; Jensen, J. P.; Sondergaard, M.; Fenger-Gron, M.; Bamm, M. E.; Sandby, K.; Moller, P. H.; Rasmussen, H. U. Impact of fish predation on cladoceran body weight distribution and zooplankton grazing in lakes during winter. *Freshwater Biol.* **2004**, 49 (4), 432–447.
- (14) Gulati, R. D.; van Donk, E. Lakes in the Netherlands, their origin, eutrophication and restoration: State-of-the-art review. *Hydrobiologia* **2002**, 478 (1–3), 73–106.
- (15) Wu, Y. H.; Liu, J. T.; Yang, L. Z.; Chen, H.; Zhang, S. Q.; Zhao, H. J.; Zhang, N. M. Allelopathic control of cyanobacterial blooms by periphyton biofilms. *Environ. Microbiol.* **2011**, 13 (3), 604–615.
- (16) Pan, G.; Yang, B.; Wang, D.; Chen, H.; Tian, B. H.; Zhang, M. L.; Yuan, X. Z.; Chen, J. A. In-lake algal bloom removal and submerged vegetation restoration using modified local soils. *Ecol. Eng.* **2011**, 37 (2), 302–308.
- (17) Pan, G.; Zhang, M. M.; Chen, H.; Zou, H.; Yan, H. Removal of cyanobacterial blooms in Taihu Lake using local soils. I. Equilibrium and kinetic screening on the flocculation of *Microcystis aeruginosa* using commercially available clays and minerals. *Environ. Pollut.* **2006**, 141 (2), 195–200.
- (18) Pan, G.; Zou, H.; Chen, H.; Yuan, X. Z. Removal of harmful cyanobacterial blooms in Taihu Lake using local soils. III. Factors affecting the removal efficiency and an in situ field experiment using chitosan-modified local soils. *Environ. Pollut.* **2006**, 141 (2), 206–212.
- (19) Zou, H.; Pan, G.; Chen, H.; Yuan, X. Z. Removal of cyanobacterial blooms in Taihu Lake using local soils. II. Effective removal of *Microcystis aeruginosa* using local soils and sediments modified by chitosan. *Environ. Pollut.* **2006**, 141 (2), 201–205.
- (20) Renner, R.; Eichenseher, T.; Thrall, L. Quick, cheap method for algae removal. *Environ. Sci. Technol.* **2006**, 40 (5), 1377.
- (21) Pan, G.; Chen, J.; Anderson, D. M. Modified local sands for the mitigation of harmful algal blooms. *Harmful Algae* **2011**, 10 (4), 381–387.
- (22) Chen, J.; Pan, G. Harmful algal blooms mitigation using clay/soil/sand modified with xanthan and calcium hydroxide. *J. Appl. Phycol.* **2011**, DOI: 10.1007/s10811-011-9751-7.
- (23) Robb, M.; Greenop, B.; Goss, Z.; Douglas, G.; Adeney, J. Application of Phoslock (TM), an innovative phosphorus binding clay, to two Western Australian waterways: Preliminary findings. *Hydrobiologia* **2003**, 494 (1–3), 237–243.
- (24) Egemose, S.; Reitzel, K.; Andersen, F. O.; Flindt, M. R. Chemical lake restoration products: Sediment stability and phosphorus dynamics. *Environ. Sci. Technol.* **2010**, 44 (3), 985–991.
- (25) de Vicente, I.; Huang, P.; Andersen, F. O.; Jensen, H. S. Phosphate adsorption by fresh and aged aluminum hydroxide. Consequences for lake restoration. *Environ. Sci. Technol.* **2008**, 42 (17), 6650–6655.
- (26) Reitzel, K.; Hansen, J.; Andersen, F. O.; Hansen, K. S.; Jensen, H. S. Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. *Environ. Sci. Technol.* **2005**, 39 (11), 4134–4140.



- (27) Scheffer, M.; Carpenter, S.; Foley, J. A.; Folke, C.; Walker, B. Catastrophic shifts in ecosystems. *Nature* **2001**, *413* (6856), 591–596.
- (28) van Nes, E. H.; Rip, W. J.; Scheffer, M. A theory for cyclic shifts between alternative states in shallow lakes. *Ecosystems* **2007**, *10* (1), 17–27.
- (29) Kagalogou, I.; Papastergiadou, E.; Leonardos, I. Long term changes in the eutrophication process in a shallow Mediterranean lake ecosystem of W. Greece: Response after the reduction of external load. *J. Environ. Manage.* **2008**, *87* (3), 497–506.
- (30) Wu, J.; Cheng, S. P.; Liang, W.; He, F.; Wu, Z. B. Effects of sediment anoxia and light on turion germination and early growth of *Potamogeton crispus*. *Hydrobiologia* **2009**, *628* (1), 111–119.
- (31) Parkyn, S. M.; Hickey, C. W.; Clearwater, S. J. Measuring sub-lethal effects on freshwater crayfish (*Paraneopros planifrons*) behaviour and physiology: Laboratory and in situ exposure to modified zeolite. *Hydrobiologia* **2011**, *661* (1), 37–53.
- (32) Danielsson, A.; Jonsson, A.; Rahm, L. Resuspension patterns in the Baltic proper. *J. Sea Res.* **2007**, *57* (4), 257–269.
- (33) Istvanovics, V.; Honti, M.; Kovacs, A.; Osztoics, A. Distribution of submerged macrophytes along environmental gradients in large, shallow Lake Balaton (Hungary). *Aquat. Bot.* **2008**, *88* (4), 317–330.
- (34) Wang, S. R.; Jin, X. C.; Bu, Q. Y.; Hao, L. X.; Wu, F. C. Effects of dissolved oxygen supply level on phosphorus release from lake sediments. *Colloids Surf., A* **2008**, *316* (1–3), 245–252.
- (35) Wang, H. J.; Lu, J. W.; Wang, W. D.; Huang, P. S.; Yin, C. Q. Spatio-temporal distribution of nitrogen in the undulating littoral zone of Lake Taihu, China. *Hydrobiologia* **2007**, *581*, 97–108.
- (36) Duncan, D. B. Multiple range and multiple F tests. *Biometrics* **1955**, *11*, 1–42.
- (37) Gibbs, M.; Oezkundakci, D. Effects of a modified zeolite on P and N processes and fluxes across the lake sediment-water interface using core incubations. *Hydrobiologia* **2011**, *661* (1), 21–35.
- (38) Yuan, X. Z.; Pan, G.; Chen, H.; Tian, B. H. Phosphorus fixation in lake sediments using LaCl<sub>3</sub>-modified clays. *Ecol. Eng.* **2009**, *35* (11), 1599–1602.
- (39) Yan, H.; Pan, G.; Zou, H.; Li, X. L.; Chen, H. Effective removal of microcystins using carbon nanotubes embedded with bacteria. *Chin. Sci. Bull.* **2004**, *49* (16), 1694–1698.
- (40) Strauss, E. A.; Richardson, W. B.; Bartsch, L. A.; Cavanaugh, J. C.; Bruesewitz, D. A.; Imker, H.; Heinz, J. A.; Soballe, D. M. Nitrification in the Upper Mississippi River: Patterns, controls, and contribution to the NO<sub>3</sub>-budget. *J. N. Am. Benthol. Soc.* **2004**, *23* (1), 1–14.
- (41) Vopel, K.; Gibbs, M.; Hickey, C. W.; Quinn, J. Modification of sediment-water solute exchange by sediment-capping materials: Effects on O<sub>2</sub> and pH. *Mar. Freshwater Res.* **2008**, *59* (12), 1101–1110.
- (42) Himmelheber, D. W.; Pennell, K. D.; Hughes, J. B. Natural attenuation processes during in situ capping. *Environ. Sci. Technol.* **2007**, *41* (15), 5306–5313.