Lead adsorption capacities of different components in natural surface coatings

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Abstract: Pb adsorption capacities of Fe oxide, Mn oxide and organic materials in natural surface coatings (biofilms and associated minerals) collected in three lakes, two ponds and a river in Jilin Province, China and Cayuga Lake in US were studied. A novel extraction technique was employed to remove one or more component(s) from the surface coatings. Pb adsorption to surface coatings before and after extraction was performed to determine the adsorptive properties of the extracted component(s). The statistical analysis of observed Pb adsorption was carried out using nonlinear least squares fitting (NLSF) to estimate the Pb adsorption capacity of each component of surface coatings. For each body of water, the estimated Pb adsorption capacity of Mn oxide (mol Pb/mol Mn) was significantly higher than that of Fe oxide (mol Pb/mol Fe). The value of estimated adsorption capacities of organic materials with the unit mol Pb per kg COD was similar to or less than that of Fe oxides with the unit mol Pb per mol Fe. Comparison of components of surface coatings in different waters showed that the estimated Pb adsorption capacities of components in surface coatings developed in different natural waters were different, especially for Mn oxides.

Keywords: surface coatings; iron oxide; manganese oxide; organic material

Introduction

Pb and other heavy metals in the aquatic environments have promoted great interest in their transport and fate for their toxicity, bioaccumulation and lack of degradation. The cycling of these metals in aquatic environments has been attributed to their binding or adsorption to surfaces of solid phases and complexation with the ligands in the water (Turekian, 1977; Muller, 1990; Giusti, 1995). Many researches have been made in developing models to describe trace metal adsorption to homogeneous surfaces (Humbert, 1990; Schindler, 1991; Westall, 1995). Metal oxides, especially iron and manganese oxides, and organic materials are very important components in the solid phases for their capacities of adsorbing heavy metals (Sigg, 1985; Tessier, 1987; Nelson, 1995). The relative significance of bio- vs. abiotic factors as controls for trace metal cycling is expected to be influenced by conditions in aquatic environment (e.g. pH, temperature, ionic strength and metal speciation in the water) (Muller, 1990; Giusti, 1993) and the nature of the heavy metal itself as well (Lion, 1982; Lusso, 1981). Additionally, interactions between constituents could alter the metal adsorption properties of these constituents in a heterogeneous matrix (Tipping, 1982; Honeyman, 1988). For example, microorganisms could alter the deposition of metal oxides through either passive or active processes (Lion, 1988; Ito, 1996). As for Pb adsorption, a number of laboratory studies have indicated that Pb is predominantly associated with ferrimanganese coatings (Whitney, 1975; Lion, 1982). However, significant fraction of Pb have also been reported to be associated with organic materials in natural aquatic environments (Brendin, 1972; Cooper, 1974).

As surface coatings play very important roles in the cycling of heavy metals and other pollutants, some studies have been carried out on their adsorption or binding property of pollutants (Nelson, 1995; Headley, 1998; Gray, 2001). The role of the components of natural surface coatings in controlling Pb adsorption has been investigated by Nelson et al. (Nelson, 1999a; 2002) using an adsorption additive model. The technique of selective extraction followed by Pb adsorption and statistical analyses was employed by Dong et al. (Dong, 2000) to evaluate the relative contributions of metal oxides and organic material to total observed Pb adsorption by the surface coating materials. The purpose of the study reported here is to focus on the Pb adsorption capacity of each component in surface coatings developed in different natural waters. As Pb adsorption to Al oxides and other components in surface coatings was negligible (Dong, 2000; Nelson, 1999a), only Fe oxides, Mn oxides and organic materials were studied here. The same technique described above was employed here to determine the Pb adsorption parameters of each component. The resulted Pb adsorption capacities of Fe oxide, Mn oxide and organic material in surface coatings were compared between each other in each body of water. The adsorption capacity of each component was also compared among surface coatings developed in different waters and the surrogate materials used in additive model by Nelson et al. (Nelson, 1999a; 2002).

1 Materials and methods

1.1 Development and characterization of natural surface coatings

Three lakes, one river and two ponds (Jingyuwan Lake, Nandu Lake, Songhua Lake, Songhua River and two ponds in Xianghai wetland) in Jilin Province, China and Cayuga Lake in U.S. were chosen as the aquatic environments to develop natural surface coatings. Nandu Lake is an eutrophic lake located in Changchun City with significant Mn deposition (Xu, 1999). Songhua Lake is an oligotrophic lake with a lithotrophic bottom while Jingyuwan Lake is a mesotrophic lake. The site selected to collect surface coatings in Songhua River located at the downstream of Jilin City. The ponds are located in Xianghai wetland and Pond I is a mesotrophic reedy pond while pond II is an eutrophic pond. Cayuga Lake is a large deep lake with mesotrophic conditions located in central New York State, U.S. (Nelson, 1999a).

At each aquatic field sites, glass microscope slides (5.0 x 7.5 x...
0.1 cm) were fixed on polyethylene racks and submerged in the water at a depth of about 30 cm for a period of 2 weeks (four weeks for Gayung Lake). Prior to placement in the water, glass slides and racks were pre-cleaned with detergent, soaked for 24 h in soap solution, acid washed for 24 h in 15% HNO₃, and then rinsed in distilled-deionized water (ddH₂O), followed by a second 24 h acid wash and a final rinse in ddH₂O. In each case, visible surface coatings were present on the glass slides after development.

After exposure in the field, the glass slides (submerged in water) with attached surface coatings were transported to the laboratory for microscopic examination, extraction and measurement of Pb binding.

1.2 Extraction of natural surface coatings

Extracted with 0.02 mol/L hydroxylamine hydrochloride (NH₂OH·HCl) and 0.01 mol/L HNO₃ for 20 min was used to remove manganese oxides, 0.4 mol/L sodium dithionite (Na₂S₂O₄) for 30 min at pH 6.0 to remove iron and manganese oxides, and 10% oxalic acid for 60 h to remove most of the metal oxides and some of the organic material (Dong, 2000; 2001). The extractions were taken in 100 mm petri dishes.

Organic material in unextracted and extracted surface coatings was quantified by measuring the chemical oxygen demand (COD) using a modification of Standard Method # 5220 B (APHA, 1995; Dong, 2001).

1.3 Measurement of Pb adsorption to surface coatings

Pb adsorption to unextracted and extracted surface coatings were measured in solutions with defined metal speciation and initial Pb concentrations ranging from 0.2 to 2.0 μmol/L. The Pb adsorption solutions were prepared by dilution of 1000 μg/mL Pb(NO₃)₂, reference solutions using a minimal mineral solution (MMS) solution with ionic strength adjusted to 0.05 mol/L with NaNO₃ (Table 1). Pb speciation in the solutions at pH 6.0 was calculated using MINTEQ (Westall, 1976) at Pb(II) = 6.0 × 10⁻⁵ mol/L. The calculations showed that free Pb(II) ions would comprise 99% of the total dissolved Pb with only 6% PbSO₄ and 15% Pb(OH)₂. Two slides from each treatment were placed in polyethylene racks after rinsed by MMS solution without Pb for 2.5 h and submerged into each of five 800-ml solutions with five different Pb concentrations (six different concentrations for pond surface coatings). These solutions were contained in 1 L beakers under a condition of 25 ± 1°C. The solutions were stirred continuously with magnetic stirrors for 24 h, maintaining the pH at 6.0 ± 0.1 using 0.01 mol/L HNO₃ and NaOH. After equilibrium, slides with surface coatings were extracted into 25 ml of 15% HNO₃ for 24 h. Pb in equilibrium solutions were measured by GFAAS. Total extractable Fe, Mn and Pb in the acid extracts were analyzed by ICP-AES to determine the concentrations of metal oxides and Pb adsorbed in the surface coatings after Pb adsorption. These measurements of metal oxides in surface coatings were carried out after Pb adsorption to avoid the effect of the dissolution of these oxides.

<table>
<thead>
<tr>
<th>Component or species</th>
<th>Concentration, μmol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂·H₂O</td>
<td>200</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>140</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>910</td>
</tr>
<tr>
<td>KNO₃</td>
<td>150</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>10</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>5</td>
</tr>
</tbody>
</table>

Notes: ionic strength adjusted to 0.05 mol/L with NaNO₃; pH = 6.0

1.4 Statistical analyses

As none of the extraction techniques removed only one component (ppb) from the surface coatings without partly extracting at least one of the other components as well, accurate determination of Pb associated with each individual component (by difference before and after extraction) was required. Consideration of contributions from the partial fractions of other components removed from the slides. Here the Pb adsorption data of extracted and unextracted surface coatings were analyzed by nonlinear least squares fitting (National Laboratory). The model used for the analysis considered total adsorption by surface coating at a given Pb concentration (C_m, μmolPb/m²) to be the sum of contributions from three constituents (Fe, Mn oxides and COD): 

\[ C_m = \sum \Gamma_i + \Gamma_{Fe} + \Gamma_{Mn} + \Gamma_{COD} \]  

(1) where C_m is the surface concentrations of each component (μmol Pb or mg Pb/m²) and the \( \Gamma_i \) terms are adsorption on a per unit quantity of material basis (e.g., 1 μmol Pb/100 μmol Fe), \( \Gamma_i \) for each component was expressed as a Langmuir adsorption isotherm: 

\[ \Gamma_i = \frac{C_m}{\Gamma_{i, max} + \frac{C_m}{\Gamma_{i, max}}} \]  

(2) where \( \Gamma_i \) is the adsorption of Pb by component \( i \) per unit surface area, \( \Gamma_{i, max} \) is the maximum adsorption of Pb by component \( i \), K is the Langmuir equilibrium coefficient and [Pb] is the concentration of Pb. Adsorption to each component is expressed per unit nominal surface area of the glass slides containing the surface coating, not the total surface area of the adsorbing phase.

For each body of water, the data sets consisted of Pb adsorption data for unextracted surface coatings plus surface coatings extracted with each of the three extractants were fitted using multiple data sets fitting. Fitting function was the combination of Eqs. (1) and (2), and \( \Gamma_{i, max} \) and K were set as shared parameters. Before fitting was carried out, four sets of \( C_m \) were inputted and set as not variable while \( \Gamma_{i, max} \) and K were set as variable, > 0, and initialized based on the assumption that each component had the same adsorption capacity. After this, iterations were performed until \( X^2 \) is not reduced (the fitting converged) or \( X^2 \) did not change in 4 iterations (the fitting did not converge), where \( X^2 \) was used to represent the derivations of the theoretical curves from the experimental data.

2 Results and discussion

2.1 Character of unextracted and extracted surface coatings

Natural surface coatings developed on glass slides in all the aquatic environments consisted of assemblages of microorganisms in a biofilm matrix associated with mineral deposits. All the mineral deposits were similar in appearance to fine particles. The surface coatings in Jiangyutuo Lake and in Xianhu Lake were similar. The color of both surface coatings and water was sage green and organisms on the surface coatings were mostly algae with some algae. Surface coatings developed in Songzhuan Lake were green in color and relatively thinner. The domination organisms on the surface coatings were green algae and diatoms. In Songhua River, the surface coatings were light gray in color, and most part of the glass slides were covered by filamentous microorganisms. Surface coatings developed in wetland pond I were very thin and were green in color. Pond II surface coatings were white in color with white mineral deposits and white filamentous fungal.
biomass. Surface coatings in Cayuga Lake contained large numbers of diatoms, green and red algae, bacterial cells and filamentous cyanobacteria and inosal monolayers (Dong, 2000).

The components of unextracted and extracted surface coatings are all listed in Table 2. It can be seen from Table 2 that although the content of components of unextracted surface coatings developed in different waters varied remarkably, surface coatings developed in each body of water were consistent from slide to slide (Fe and Mn concentrations and COD varied less than 10%), allowing the use of different slides for characterizations and for measurement of Pb adsorption.

<table>
<thead>
<tr>
<th>Waters</th>
<th>Surface oxide</th>
<th>Extracted</th>
<th>(\text{NH}_4)OH-(\text{HCl})</th>
<th>Na(_2)S(_2)O(_3)</th>
<th>Oxalic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Not extracted</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jinyuan Lake</td>
<td>Fe oxide</td>
<td>1817 ± 68</td>
<td>1803 ± 159</td>
<td>103 ± 90</td>
<td>266 ± 27</td>
</tr>
<tr>
<td></td>
<td>Mn oxide</td>
<td>512 ± 35</td>
<td>26 ± 3.9</td>
<td>9.2 ± 2.3</td>
<td>35 ± 3.1</td>
</tr>
<tr>
<td></td>
<td>Organic material</td>
<td>1551 ± 4</td>
<td>1537 ± 6</td>
<td>1395 ± 41</td>
<td>1311 ± 37</td>
</tr>
<tr>
<td>Nannya Lake</td>
<td>Fe oxide</td>
<td>735 ± 46</td>
<td>706 ± 58</td>
<td>164 ± 21</td>
<td>65 ± 5.6</td>
</tr>
<tr>
<td></td>
<td>Mn oxide</td>
<td>283 ± 25</td>
<td>9.1 ± 1.3</td>
<td>0.7 ± 0.2</td>
<td>BB(^a)</td>
</tr>
<tr>
<td></td>
<td>Organic material</td>
<td>1348 ± 51</td>
<td>1033 ± 159</td>
<td>1021 ± 84</td>
<td>1047 ± 104</td>
</tr>
<tr>
<td>Soudusha Lake</td>
<td>Fe oxide</td>
<td>185 ± 11</td>
<td>182 ± 10</td>
<td>64 ± 4.7</td>
<td>54 ± 3.4</td>
</tr>
<tr>
<td></td>
<td>Mn oxide</td>
<td>223 ± 2.2</td>
<td>3.4 ± 0.7</td>
<td>BB(^a)</td>
<td>BB(^a)</td>
</tr>
<tr>
<td></td>
<td>Organic material</td>
<td>257 ± 25</td>
<td>256 ± 19.2</td>
<td>296 ± 69</td>
<td>686 ± 99</td>
</tr>
<tr>
<td>Soughshu River</td>
<td>Fe oxide</td>
<td>1385 ± 100</td>
<td>1379 ± 165</td>
<td>231 ± 44</td>
<td>73 ± 11</td>
</tr>
<tr>
<td></td>
<td>Mn oxide</td>
<td>212 ± 21</td>
<td>29 ± 8.1</td>
<td>3 ± 1.0</td>
<td>BB(^a)</td>
</tr>
<tr>
<td></td>
<td>Organic material</td>
<td>1426 ± 5.7</td>
<td>1146 ± 58</td>
<td>884 ± 20</td>
<td>1350 ± 205</td>
</tr>
<tr>
<td>Pond I</td>
<td>Fe oxide</td>
<td>31 ± 2.6</td>
<td>30 ± 2.1</td>
<td>5.2 ± 0.7</td>
<td>4.7 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>Mn oxide</td>
<td>7.2 ± 0.6</td>
<td>BB(^a)</td>
<td>BB(^a)</td>
<td>BB(^a)</td>
</tr>
<tr>
<td></td>
<td>Organic material</td>
<td>118 ± 0.6</td>
<td>109 ± 0.6</td>
<td>78 ± 0.6</td>
<td>44 ± 2.7</td>
</tr>
<tr>
<td>Pond II</td>
<td>Fe oxide</td>
<td>882 ± 72</td>
<td>863 ± 57</td>
<td>419 ± 18</td>
<td>76 ± 13.3</td>
</tr>
<tr>
<td></td>
<td>Mn oxide</td>
<td>50 ± 5.6</td>
<td>4.7 ± 0.6</td>
<td>3.3 ± 0.4</td>
<td>2.3 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>Organic material</td>
<td>1454 ± 35</td>
<td>1330 ± 124</td>
<td>993 ± 20</td>
<td>1211 ± 26</td>
</tr>
<tr>
<td>Cayuga Lake</td>
<td>Fe oxide</td>
<td>353 ± 19</td>
<td>302 ± 25</td>
<td>60 ± 1.4</td>
<td>15 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>Mn oxide</td>
<td>22 ± 0.3</td>
<td>6.3 ± 0.7</td>
<td>1.7 ± 0.1</td>
<td>BB(^a)</td>
</tr>
<tr>
<td></td>
<td>Organic material</td>
<td>484 ± 29</td>
<td>330 ± 54</td>
<td>470 ± 25</td>
<td>88 ± 3.0</td>
</tr>
</tbody>
</table>

Notes: ° Unextracted Fe or Mn/ mg/m² for metal oxides and mg COD/m² for organic material; mean (n = 10) ± one standard deviation for metal oxides and mean (n = 2) ± one deviation for organic material; 1. Below detection limit

The extraction efficiencies of each extractant for surface coatings collected in different waters were different. \(\text{NH}_4\)OH-\(\text{HCl}\) reagents removed most of Mn from the surface coatings with a relative little effect on Fe and the organic materials. Na\(_2\)S\(_2\)O\(_3\) removed most of Fe and almost all of Mn. Oxalic acid removed most of Fe and Mn, but the organic materials removed were not very significant for surface coatings collected in some bodies of water. This may be due to the remaining of the oxalic acid, which increased the COD value of the extracted surface coatings. Nonetheless, different extraction reagents did extract different components selectively, allowing the use of Pb adsorption isotherms of surface coatings treated with different extractant to determine the contribution of each component to total Pb adsorption using the statistical analyses method.

2.2 Pb adsorption to unextracted and extracted surface coatings

The experiment data and the curves fitted for Pb adsorption to extracted and unextracted surface coatings by nonlinear least squares fitting (NSLF) in these aquatic environments are all shown in Fig. 1. The estimated Langmuir parameters for each component of different surface coatings are listed in Table 3 and the correlation coefficients (R) of the NSLF are also listed.

It can be seen from Fig. 1 that Pb adsorption to the surface coatings at pH 0.0 in MMS solution followed Langmuir adsorption isotherms. On the other hand, the Pb concentrations in the equilibrium solutions reduced remarkably from the initial concentrations, especially for unextracted surface coatings and surface coatings extracted by the \(\text{NH}_4\)OH-\(\text{HCl}\) reagents. This indicated that there were significant Pb adsorptions to the surface coatings. The surface coatings extracted with \(\text{NH}_4\)OH-\(\text{HCl}\), Na\(_2\)S\(_2\)O\(_3\) and oxalic acid significantly reduced the adsorption of Pb, especially for surface coatings collected in Jinyuan Lake, Nannya Lake and Pond 1.

The symbols of the experiment data of Pb adsorption to surface coatings with each treatment in all the waters were very close to the curves fitted (Fig. 1). The values of R in Table 3 also showed that the experiment data fitted the equation with the estimated R² and, very well. This might suggest that the methods employed here were capable of getting the adsorption capacities of components in surface coatings and the resulted parameters were fairly reliable.

2.3 Comparison of Pb adsorption capacity of each component

Extensive study on the estimated Pb adsorption property of each component on a per quantity of material basis was carried out here. In Fig. 2, Pb adsorption capacity is compared among the three components of surface coatings in each body of water; while in Fig. 3, Pb adsorption capacity of each component is compared among surface coatings in these waters and surrogate materials used in the additive model by Nelson et al. (Nelson, 1999a; 2002) for each of the three components. Pb adsorption isotherms for pure laboratory surrogate materials were determined under the same defined condition as that described for surface coatings on glass slides.
Table 3 Estimated Langmuir parameters for Pb adsorption to the three components in surface coatings developed in different waters using NLSF

<table>
<thead>
<tr>
<th>Waters</th>
<th>Parameters</th>
<th>( \Gamma_{\text{PM}}^0 )</th>
<th>( \Gamma_{\text{PM}}^V )</th>
<th>( \Gamma_{\text{PM}}^M )</th>
<th>( K_v )</th>
<th>( K_m )</th>
<th>( K_{\text{est}} )</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jinginganet Lake</td>
<td>Estimate</td>
<td>0.064</td>
<td>0.521</td>
<td>0.034</td>
<td>6.37</td>
<td>12.1</td>
<td>2.36</td>
<td>0.9971</td>
</tr>
<tr>
<td></td>
<td>Fit error</td>
<td>0.011</td>
<td>0.026</td>
<td>0.016</td>
<td>3.52</td>
<td>2.6</td>
<td>2.96</td>
<td>0.9959</td>
</tr>
<tr>
<td>Nanhui Lake</td>
<td>Estimate</td>
<td>0.053</td>
<td>0.207</td>
<td>0.034</td>
<td>4.56</td>
<td>42.3</td>
<td>3.31</td>
<td>0.9964</td>
</tr>
<tr>
<td></td>
<td>Fit error</td>
<td>0.012</td>
<td>0.044</td>
<td>0.005</td>
<td>2.78</td>
<td>8.6</td>
<td>1.29</td>
<td>0.9968</td>
</tr>
<tr>
<td>Songhua Lake</td>
<td>Estimate</td>
<td>0.193</td>
<td>0.729</td>
<td>0.102</td>
<td>3.24</td>
<td>31.0</td>
<td>0.29</td>
<td>0.9964</td>
</tr>
<tr>
<td></td>
<td>Fit error</td>
<td>0.019</td>
<td>0.074</td>
<td>0.122</td>
<td>1.37</td>
<td>14.5</td>
<td>0.43</td>
<td>0.9988</td>
</tr>
<tr>
<td>Songfluan River</td>
<td>Estimate</td>
<td>0.063</td>
<td>0.113</td>
<td>0.020</td>
<td>3.52</td>
<td>25.2</td>
<td>6.58</td>
<td>0.9988</td>
</tr>
<tr>
<td></td>
<td>Fit error</td>
<td>0.013</td>
<td>0.021</td>
<td>0.004</td>
<td>1.27</td>
<td>15.6</td>
<td>3.40</td>
<td>0.9995</td>
</tr>
<tr>
<td>Pond I</td>
<td>Estimate</td>
<td>0.330</td>
<td>1.060</td>
<td>0.058</td>
<td>0.47</td>
<td>21.1</td>
<td>4.45</td>
<td>0.9995</td>
</tr>
<tr>
<td></td>
<td>Fit error</td>
<td>0.383</td>
<td>0.066</td>
<td>0.007</td>
<td>0.66</td>
<td>5.0</td>
<td>1.37</td>
<td>0.9993</td>
</tr>
<tr>
<td>Pond II</td>
<td>Estimate</td>
<td>0.055</td>
<td>0.243</td>
<td>0.029</td>
<td>4.19</td>
<td>348.0</td>
<td>15.90</td>
<td>0.9993</td>
</tr>
<tr>
<td></td>
<td>Fit error</td>
<td>0.018</td>
<td>0.049</td>
<td>0.003</td>
<td>2.90</td>
<td>332.3</td>
<td>5.11</td>
<td>0.9993</td>
</tr>
<tr>
<td>Cayuga Lake</td>
<td>Estimate</td>
<td>0.118</td>
<td>0.959</td>
<td>0.039</td>
<td>0.24</td>
<td>250.5</td>
<td>1.44</td>
<td>0.9995</td>
</tr>
<tr>
<td></td>
<td>Fit error</td>
<td>0.524</td>
<td>0.100</td>
<td>0.021</td>
<td>1.40</td>
<td>108.4</td>
<td>1.52</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

Notes: Unit: \( \Gamma_{\text{PM}}^0 \): mol Pb/mol Fe; \( \Gamma_{\text{PM}}^V \): mol Pb/ml Mn; \( \Gamma_{\text{PM}}^M \): mol Pb/kg COD; \( K_v \): L/mol mol

Fig. 1 Pb adsorption to unexposed surface coatings (■) and surface coatings extracted with NH₄OH·HCl (○), Na₂S₂O₃ (▲) and oxalic acid (●); error bars indicate ± one deviation (n = 2)

The estimated Pb adsorption capacity of Mn oxide based on mol Pb per mol Mn was significantly higher than that of Fe oxide based on mol Pb per mol Fe for all of these surface coatings (Fig. 2). Many researchers concerning heavy metals adsorption to natural and artificial metal oxides also showed that the adsorption capacity of Mn oxides was higher than that of Fe oxides (McKenzie, 1980; Gray, 2001; Trivedi, 2001; Nelson, 2002). This difference was due to the structures of the oxides; the surface area of Mn oxide was significantly larger than that of Fe oxide (Nelson, 2002). The tendency for Mn to bind metals has been explained, at least in part, by the complex mineralogical structure of Mn oxides and wide range of zero point of charge (Chao, 1976). The difference between Pb adsorption capacities of Mn oxides and Fe oxides varied remarkably. This difference was greatest in Cayuga Lake, in which the adsorption capacity of Mn oxide is nearly two orders of magnitude greater than that of Fe oxide, and the smallest in Songhua River in which the adsorption capacity of Mn oxide was only about three times greater than that of Fe oxide. But if this comparison was carried out at lower equilibrium Pb concentration (e.g., < 0.05 µmol/L), the Pb adsorption capacities of Mn oxides based on mol Pb adsorbed by per mol metal were much greater than those of Fe oxides in all the waters investigated here. Considering the low trace metal concentration in the natural aquatic environment, the role of Mn oxides in binding Pb would be very significant in natural waters.

Pb adsorption to organic phases based on mol Pb adsorbed by per
kg COD in each body of water is also shown in Fig. 2. It shows that the number of moles of Pb adsorbed by Fe oxides on a per mol Fe basis was larger than or similar to that of Pb adsorbed by organic materials on a per kg COD basis. Considering that the surface concentrations of Fe oxides (μmol Fe/m²) and organic materials (mg COD/m²) on surface coatings were not very different from each other, it can be deduced that the Pb adsorption contribution of Fe oxides to total Pb adsorption would be similar to or larger than that of organic phase (Dong, 2002a; 2002b).

For Pb adsorption to Fe oxides in different surface coatings, the estimated adsorption capacity (mol Pb/mol Fe) based on Eqn 14 and 15, was similar in surface coatings collected in Jingyuetan Lake, Nanhui Lake, Songhua Lake, and the two wetland ponds (Fig. 3a). Fe oxides in Songhua Lake surface coatings were special for the relatively higher Pb adsorption capacity which was about 3 to 4 times greater than that of Fe oxides in surface coatings in the other five bodies of water mentioned above. This might be owing to the lithoid bottom of the lake, therefore the sediment have little effect on the surface coatings. Another reason might be that the algae were the domination organisms on the surface coatings, which might conducive to the formation of Fe oxides with high Pb adsorption activity (Richardson, 1988; Emmenegger, 2001). The amorphous Fe oxide used in the adsorption additive model was prepared by precipitation of Fe(II) by addition of NaOH to Fe(NO₃)₃ solution to reach a pH of 8.0 (amorphous Fe oxide 1, Nelson, 1999a) or 7.5 (amorphous Fe oxide 2, Nelson, 2002) in MMS media. The Pb
absorption capacity of amorphous Fe oxide \((\Gamma_{\text{Fe}} = 0.050 \text{ mol Pb/mol Fe and } K = 1.3 \text{ L/mol})\) was only higher than that of the Fe oxides in surface coatings developed in Cayuga Lake, and was about half of the adsorption capacity of the Fe oxides in surface coatings collected in five waters discussed above. This suggested that it might be under estimated to use this kind of amorphous Fe oxide as the surrogate material of the Fe oxides in natural surface coatings. This may explain why the additive model under estimated Pb adsorption by surface coatings developed in natural waters especially in the well, in which Fe oxides compose the majority of the components of the surface coatings (Nelson, 1999a). The adsorption capacity of amorphous Fe oxide \((\Gamma_{\text{Fe}} = 0.050 \text{ mol Pb/mol Fe and } K = 3.1 \text{ L/mol})\) was similar to that of the Fe oxide in surface coatings in the five bodies of water.

The estimated Pb adsorption capacities of Mn oxides (mol Pb/mol Mn) were different in different surface coatings and followed the order: Cayuga Lake and Pond I > Songhua Lake > Jingyuetan Lake > Pond II and Nanhua Lake > Songhua River (Fig. 3b). The highest adsorption capacity (Cayuga Lake and Pond I) was about one order of magnitude than the lowest one (Songhua River). The results of adsorption of Pb to two kinds of surrogate Mn oxides, biogenic Mn oxides and fresh abiotic Mn oxide, are also included in Fig. 3b. The biogenic Mn oxides were prepared via biologically catalyzed oxidation of Mn (II) by the bacterium Leptothrix discophora SS-1 (Nelson, 1999a; 1999b) and the fresh abiotic Mn oxide was prepared by oxidation of Mn (II) with K2MnO4 and NaOH at 90°C (Murry, 1974; Nelson, 1999b). The adsorption capacity of the biogenic Mn oxide was similar to the estimated adsorption capacities of the Mn oxides in surface coatings collected in Songhua Lake and Jingyuetan Lake, while the adsorption property of the abiotic Mn oxide and the Mn oxides in surface coatings collected in Pond II, Nanhua Lake and Songhua River was similar. Considering the trophic conditions of the waters, this might show that the biogenic Mn oxides were probably surrogate for Mn oxides of surface coatings developed in oligotrophic and mesotrophic aquatic environments and the fresh abiotic Mn oxide was suitable to surrogate Mn oxides of surface coatings developed in eutrophic aquatic environments. This might be explained as follows: the biogenic Mn oxides have higher adsorption capacities compared with abiotic oxides while the oligotrophic conditions are in favor of the formation of biogenic Mn oxides because of the high dissolved oxygen level.

For organic materials, the estimated Pb adsorption capacities were similar to each other in all the waters examined here, especially when Pb concentration was larger than 0.5 \(\mu\text{mol/L}\) (Fig. 3c). Specifically, the estimated Pb adsorption capacities of organic phases in surface coatings developed in Jingyuetan Lake and Nanhua Lake were almost the same. Meanwhile, the organic compounds in the surface coatings developed in the two lakes were also alike as described above. Only the adsorption capacities of organic phases in surface coatings developed in the two wetland ponds were slightly higher than the capacities of organic phases in the other surface coatings. The curve of the surrogate organic materials used for the additive model shown in Fig. 3c was the combined isotherms of cells including a kind of diatom, a kind of green alga and two kinds of bacteria and the extracellular polymer of \(B. \text{ cepacia} \) (Nelson, 1999a).

The Pb adsorption capacities of surrogate materials were lower (approx. 1/2—1/4) than the estimated capacities of organic materials on the surface coatings, which might be due to that the adsorption contributions of some surface coating components in addition to the adsorbed metals and organic materials, such as clay minerals, were contributed to the organic phases. Another explanation was that there might be some organic ligands with relatively higher Pb adsorption capacities associated with the surface coatings developed in natural waters (Muller, 1990).

3 Conclusions

In all the waters studied, the estimated Pb adsorption capacities of Mn oxides were significantly higher than those of Fe oxides based on the number of moles of Pb adsorbed by per mole metal, especially at lower Pb concentration. The number of moles of Pb adsorbed by Fe oxides containing one mole Fe was similar to or larger than that adsorbed by organic materials containing one kilogram COD. This proved that metal oxides played an important role in determining Pb adsorption to surface coatings.

For different waters, the estimated Pb adsorption capacities of components in surface coatings were affected by the waters in which the films were collected, especially for Mn oxides. The adsorption capacities of surrogate materials used in additive model fitted the estimated Pb adsorption capacity of components only in some bodies of natural water. Therefore, it was not suitable to use a single surrogate material to substitute for the component of surface coatings developed in any kind of natural waters, especially for Mn oxides.

References:


and ferromanganese oxides on nickel sorption by stream periphyton [J].
Environ Pollut., 112(1); 61—71.

Beadle J V, Glendening J, Kuhlau J et al., 1998. Rates of sorption and
partitioning of contaminants in river biofilms [J]. Environ Sci Technol., 32
(24); 3968—3973.

Sci Technol., 22(8); 862—871.

characteristics of estuarine particulate matter: Evaluation of contributions of Fe/Mn oxide
and organic surface coatings [J]. Environ Sci Technol., 16(10); 660—
666.

microbial biofilms in nature and engineered systems [J]. CRC Crit Rev
Environ Control., 17(4); 273—306.

distribution in the presence of suspended cells: Application to iron
deposition onto a biofilm surface [J]. Wat Res., 30(10); 2413—2423.

Lama S N, Bryan G W., 1981. A statistical assessment of the form of trace metals
in mineralized extraneous sediments employing chemical extractants [J]. Sci Total
Environ., 17; 165—196.

McKerrow R M., 1980. The adsorption of lead and other heavy metals on oxides of
manganese and iron [J]. Aust J Soil Res., 18(1); 61—73.

comparison between adsorption experiments and field measurement [J].
Aquatic Sci., 52; 75—92.

Murry J W., 1974. The surface chemistry of hydrous manganese dioxide [J]. J
Colloid Interface Sci., 46(3); 357—371.

simulated aquatic environment: Effects of bacterial biofilms and iron oxide
[J]. Water Res., 29(8); 1934—1944.

Nelson Y M, Liao L W, Shuler M L et al., 1999b. Lead binding to metal oxide
and organic phases of natural aquatic coating [J]. Limnol Oceanogr., 44
(7); 1715—1729.

oxides by leptothrix discophora SS-1 in a chemically defined growth medium
and evaluation of their Pb adsorption characteristics [J]. Appl Environ
Microbiol., 65(1); 175—180.

mechanisms of lead adsorption by biogenic manganese (hydr)oxide, iron
(hyd)oxide, and their mixtures [J]. Environ Sci Technol., 36(3); 421—425.

Richardson L L, Aguilera G, Nealeson K H., 1988. Manganese oxidation in pH and
O2 microenvironments produced by phytoplankton [J]. Limnol Oceanogr.,
33; 352—363.

Scheidler P W., 1991. The regulation of heavy metal concentrations in natural
aquatic systems [M]. Heavy metals in the environment [Vernet J. P. ed.].
Amsterdam, the Netherlands: Elsevier; 95—123.

Sigg L., 1985. Metal transfer mechanisms in lakes: the role of settling particles
[M]. Chemical processes in lakes (Stumm W ed.). New York: John
Wiley: 283—310.

Tessier A, Campbell P G C., 1987. Partitioning of trace metals in sediments
relationships with bioavailability [J]. Hydrobiologia., 149; 43—52.

Tipping E, Cooke D., 1982. The effects of adsorbed humic substances on the
surface charge of goethite in freshwater [J]. Geochim Cosmochim Acta.,
46; 75—80.

Trivelli P, Axe L., 2001. Predicting divalent metal sorption to hydrous Al, Fe,
and Mn oxides [J]. Environ Sci Technol., 33(9); 1779—1784.

41; 1139—1144.

with heterogeneous environmental sorbents. 1. Complexation of Cu(II)
by leonardite humic acid as a function of pH and NaClO4 concentration [J].
Environ Sci Technol., 29(4); 951—959.

Department of Civil Engineering, Cambridge; Massachusetts Institute of
Technology.

Whitney P R., 1975. Relationship of manganese-iron oxides and associated heavy
metals to grain size in stream sediments [J]. J Geochim Explor., 4; 251—
263.

Xu B, Wang C, Bi S et al., 1999. Eutrophication and ecological consequences of
Xadu Lake, Changchun [M]. Changchun, China; Jilin Science &
Technology Press.

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