Pb scavenging from a freshwater lake by Mn oxides in heterogeneous surface coating materials

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Abstract

Selective extraction techniques were used to assay the importance of specific solid phases in Pb binding by heterogeneous surface coating materials (biofilms) in Cayuga Lake, NY. Hydroxylamine hydrochloride (NH\textsubscript{2}OH\cdot HCl) was used to extract easily reducible Mn oxides, and sodium dithionite (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4}) was used to extract Mn and Fe oxides in two sets of biofilm samples retrieved from the lake. Pb remaining after extraction was removed by extraction with 10\% HNO\textsubscript{3}, determined by analysis of Pb\textsuperscript{208} using a sector field mass spectrometer with an inductively coupled plasma ion source (ICP-MS), and compared to the total extractable Pb. The results indicate that the greatest contribution to total Pb binding to the heterogeneous surface coating materials was from Mn oxides. Pb adsorption capacity of Mn oxides exceeded that of Fe oxides on a molar basis by approximately an order of magnitude. The high reactivity observed for natural Mn oxides indicates that they are biogenic in origin, consistent with expectations based on the relative biotic and abiotic rates of Mn(II) oxidation under circumneutral conditions. Collectively, these results confirm expectations based on prior observations of adsorption of added Pb by Cayuga Lake biofilms before and after selective extraction, and also confirm predictions for Pb phase association in the lake based on the behavior of laboratory surrogates for adsorptive surfaces.

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1. Introduction

The adsorption reaction of toxic trace metals controls their aqueous phase concentration, and residence time in many natural and engineered aquatic systems [1–5]. Considerable prior research has been devoted to understanding the respective role of the components of heterogeneous surface materials in the scavenging of trace metals. Some investigators have suggested particulate organic materials dominate trace metal binding [6,7] while others have indicated that trace metal adsorption to mineral phases is more significant [8,9]. Among possible inorganic adsorbents, Fe oxides have received prominent consideration because of the global abundance of Fe (vs. Mn) and because of the relatively high specific surface area of iron oxide mineral phases. However, recent laboratory and field data suggest that Pb binding by biogenic Mn oxides significantly exceeds that of even amorphous iron hydroxides and that biogenic Mn oxides may serve as the major adsorbent for Pb in some freshwater systems [10–14]. A rate law, based on laboratory investigations of the Mn-oxidizing bacterium \textit{Leptothrix discophora} SS1, indicates that the kinetics of formation of Mn(III/IV) oxide are likely to be controlled by biological catalysis (vs. abiotic oxidation) under the circumneutral pH conditions common in

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many aquatic systems [15]. Thus, the presence of highly reactive biogenic Mn oxides in aquatic environments is a reasonable expectation.

Sequential extraction is a valuable analytical tool that has been used to discern the importance of alternative reactive surfaces in the binding of trace metals, to distinguish between intra- and extracellular metals, and to assay for metal bioavailability [16–20]. However, this procedure may potentially introduce analytical errors through a variety of processes [21] including readsoption of extracted metals [22], solubilization of non-target solid phases, and/or incomplete solubilization of the phase selected for extraction [23]. Nevertheless, some recent evidence suggests that extraction methods can provide geochemically relevant information despite their analytical flaws. Dong et al. [12] used adsorption of Pb onto heterogeneous surface coatings before and after selective extraction to obtain isotherms for naturally occurring Fe oxides that agreed closely with those independently determined by Nelson et al. [24] for Pb adsorption to amorphous Fe oxide in the laboratory. Similarly, the extraction results of Dong et al. [12] indicated a dominant role for Pb scavenging by Mn oxides that was consistent with independent predictions based on the adsorption behavior of amorphous Fe oxides and biogenic Mn oxides obtained by Nelson et al. [10] and subsequently by Wilson et al. [13].

A caveat applies to the agreement noted above between the surface component reactivity predicted by Nelson et al. [10] and Wilson et al. [13] based on the Pb adsorption laboratory behavior of well-characterized surfaces and the component reactivity predicted by Dong et al. [12] based on Pb adsorption by natural materials before and after selective extraction. All of these results were determined in the laboratory under the same set of chemically defined solution conditions. All of the results also came from the adsorption of added Pb at levels (0.2–2.0 μM) likely to exceed those in uncontaminated aquatic environments. Use of chemically defined conditions by these investigators removed variations in adsorption caused by the presence of metal-binding ligands, competing metals, or pH variability in natural systems and greatly facilitated their ability to interpret results. However, the presence of different solution conditions in natural systems creates uncertainty with respect to whether the importance of biogenic Mn oxides predicted by the laboratory studies is consistent with the phase-specific Pb scavenging that actually occurs in the field. One of the non-trivial hurdles to determining natural trace metal levels is access to the requisite analytical sensitivity necessary for analysis of low ambient concentrations. In this research, we use selective extractions to measure natural levels of Pb associated with Fe and Mn oxides; analytical sensitivity was achieved through the use of sector field mass spectrometer with an inductively coupled plasma ion source for analysis of Pb. The extent (or lack) of agreement of actual Pb association with extracted solid phases with that predicted in the prior research under defined solution conditions is expected to contribute to our understanding of the extent to which results from laboratory studies can be extrapolated to field conditions.

2. Materials and methods

2.1. Sampling of natural heterogeneous surface coatings

Cayuga Lake in central New York State (USA) was chosen as the field site for collection of samples because of prior characterization of heterogeneous surface coatings by the investigators at this site [10,12,13]. Surface coatings (biofilms) developed on glass microscope slides (75 × 50 × 1 mm) held in polypropylene racks (Fluoroware, Chaska, MN, USA) that were submerged in the lake at a depth of approximately 30 cm for a period of 3 weeks. Two sets of slides were used in this study. “Set 1” and “Set 2” were submerged in the lake in November and December of 2001, respectively. Prior to placement in the lake, the glass slides and racks were precleaned with detergent, soaked for 24 h in soap solution, acid washed for 24 h in 10% HNO₃ (trace metal grade, Fisher Scientific, Pittsburgh, PA), and then rinsed in distilled-deionized water (ddH₂O), followed by a second 24 h acid wash and a final rinse in ddH₂O.

After retrieval from the lake, glass slides with attached biofilms were transported within 1 h to the laboratory (submerged in lake water) for chemical characterization and measurement of Pb binding. Biofilms obtained in the manner described above have been shown to be relatively consistent from slide to slide (Fe and Mn concentrations varied by less than 5%) [10,12], allowing the use of different slides for determination of total extractable metals and for residual metals after selective extractions.

2.2. Determination of total extractable metals in natural biofilms

Metal concentrations (Fe, Mn, Pb) in the biofilms (before and after selective extractions) were measured by extracting with 25 mL of 10% HNO₃ (trace metal grade, Fisher Scientific, Pittsburgh, PA, USA) for 24 h. The extracts were analyzed for Fe and Mn by graphite furnace atomic absorption spectrometry using a Perkin Elmer (Norwalk, CT, USA) AAAnalyst 100 equipped with an HGA 800 graphite furnace and an AS-72 autosampler. Concentration of Pb in acid extracts was determined by analysis of Pb²⁰⁸ using a sector field mass spectrometer with an inductively coupled plasma ion source (ICP-MS) (Element 2, Finnigan MAT, Bremen,
Germany). Measured Pb concentrations in the extracts ranged between 0.5 and 10 ppb. The method of standard additions was used in the ICP-MS analyses to ensure that any potential matrix effects caused by the extractant solutions on instrument response were accounted for. The ratio of Pb$^{206}$/Pb$^{208}$ in the samples confirmed that the Pb signal did not originate from another element and the absence of analytic interference. Controls consisting of clean slides and petri dishes exposed to the extraction reagents and processed in a manner identical with samples resulted in Pb signal no more than 2.3% of that for the total extractable Pb and were used to correct observed Pb concentrations.

### 2.3. Selective extraction techniques

Biofilm-coated slides were extracted in 25 mL of reagent in 150 mm plastic petri dishes using two extraction techniques. Extraction with 0.01 M NH$_2$OH·HCl + 0.01 M HNO$_3$ for 30 min at 25°C was used for solubilization of Mn oxides and associated Pb. Extraction with 25 mL of 0.4 M Na$_2$S$_2$O$_4$ for 40 min at pH 6.0 was used to dissolve Mn plus Fe oxides and associated Pb. This extractant was prepared immediately before use to avoid any reduction of S$_2$O$_4^{2-}$. The extractions were performed on separate slides from each sample set, rather than in sequence. After exposure to the selective extraction reagent, the residual unextracted metals in the surface coatings were removed by extraction with 10% HNO$_3$. The residual Pb remaining after extraction with 0.01 M NH$_2$OH·HCl + 0.01 M HNO$_3$ plus the Pb in the extractant equaled 94% and 107% of the total extractable Pb in Sets 1 and 2, respectively. This was considered an acceptable confirmation of mass balance given that the total extractable Pb and the Pb in the extract plus residual were based on analyses of different slides in each sample set.

### 3. Results and discussion

Surface coatings that developed on glass slides after 3 weeks immersion in Cayuga Lake consisted of assemblies of microorganisms in a biofilm matrix and associated mineral deposits. The biological composition of Cayuga Lake biofilms is described more extensively elsewhere [10]. Microscopic observation after staining with Prussian Blue and Leukoberelin Blue has revealed strong associations between Fe and Mn mineral deposits and organic materials [10,12].

Surface concentrations of Fe and Mn and Pb solubilized with 10% HNO$_3$ (defined as 100% of total extractable) and with each selective extractant are shown in Table 1. The extractant reagents employed were intended to selectively remove specific adsorbing phases without removing other components. Hydroxylamine hydrochloride (NH$_2$OH·HCl) was used to extract easily reducible Mn oxides, and sodium dithionite

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Fe oxides</th>
<th>Mn oxides</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface concentration ($\mu$mol/m$^2$)</td>
<td>Removal(%)</td>
<td>Surface concentration ($\mu$mol/m$^2$)</td>
</tr>
<tr>
<td>Set 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% HNO$_3$ (total acid extractable)</td>
<td>161.90±1.71</td>
<td>100</td>
<td>31.27±1.04</td>
</tr>
<tr>
<td>0.01 M NH$_2$OH·HCl + 0.01 M HNO$_3$ 30 min</td>
<td>29.40±2.45</td>
<td>18</td>
<td>27.54±0.13</td>
</tr>
<tr>
<td>0.4 M Na$_2$S$_2$O$_4$ 40 min</td>
<td>125.51±0.49</td>
<td>78</td>
<td>29.00±0.09</td>
</tr>
<tr>
<td>Set 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% HNO$_3$ (total acid extractable)</td>
<td>155.78±8.17</td>
<td>100</td>
<td>9.13±0.21</td>
</tr>
<tr>
<td>0.01 M NH$_2$OH·HCl + 0.01 M HNO$_3$ 30 min</td>
<td>31.19±3.27</td>
<td>20</td>
<td>7.68±0.15</td>
</tr>
<tr>
<td>0.4 M Na$_2$S$_2$O$_4$ 40 min</td>
<td>111.91±1.02</td>
<td>72</td>
<td>8.53±0.02</td>
</tr>
</tbody>
</table>

$^a$Values indicate average± one standard deviation of replicate slides from each set.

$^b$Values shown for NH$_2$OH·HCl+HNO$_3$ and Na$_2$S$_2$O$_4$ are the extracted amount per m$^2$ of slide surface area based on analysis of the residual metals (remaining after exposure to the extractant solution) as extracted with 10% HNO$_3$. 

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(Na$_2$S$_2$O$_4$) was used to extract Mn and Fe oxides. These selective extraction techniques were used to permit comparison of the results with those of Dong et al. [12] who measured Pb adsorption to Cayuga Lake surface coatings before and after extraction. NH$_2$OH · HCl removed 84–88% of the biofilm Mn, but also removed 18–20% of the Fe (Table 1). Extraction with Na$_2$S$_2$O$_4$ removed 72–78% and 93% of the Fe and Mn, respectively. The extraction efficiencies obtained in this study were similar to those previously observed by Dong et al. [12].

A major fraction of the total extractable Pb in the surface coatings (58–73%) was solubilized after the slides were extracted with NH$_2$OH · HCl to remove Mn oxides. Virtually all of the extractable Pb (90–91%) was solubilized after extraction with Na$_2$S$_2$O$_4$ to remove Mn plus Fe oxides.

Although it is possible that each extractant also removed additional components from the natural coating materials besides the target materials [12,25], as a first approximation, the amount of Pb adsorbed to Fe and Mn oxides in the heterogeneous surface coating materials can be estimated if it is assumed that the amount of Pb solubilized by each selective extraction technique was bound to Fe and Mn oxides removed by the extraction. This assumption requires that each extraction technique did not remove a significant amount of any other surface component (such as organic material) which can adsorb significant amount of Pb [12,25] or the Pb associated with other surface components. The results from each extraction could therefore be expressed in the following form:

$$\Gamma = a \text{Pb}_{\text{Mn}} + b \text{Pb}_{\text{Fe}}.$$  

where, $\Gamma$ represents total amount of Pb removed by the individual extraction (µmol/m$^2$ slide surface); Pb$_{\text{Mn}}$ and Pb$_{\text{Fe}}$ are amount of Pb bound to the Mn oxide and Fe oxide extracted (µmol/m$^2$); $a$ and $b$ are percentage of total extractable Mn and Fe removed by the individual extraction. Based on the data in Table 1, Pb$_{\text{Mn}}$ and Pb$_{\text{Fe}}$ were obtained by solving two equations based on the separate results of the two extractions for each set of natural biofilms (Table 2). The resulting values reflect the relative association of surface-bound Pb with Mn and Fe oxides. The Pb adsorption capacities of Mn oxide ($I_{\mu\text{mol Pb/mol Mn oxide}}$) and Fe oxide ($I_{\mu\text{mol Pb/mol Fe oxide}}$) were also estimated using Pb$_{\text{Mn}}$ and Pb$_{\text{Fe}}$ divided by total amount of Mn oxide and Fe oxide in the natural biofilms (µmol/m$^2$), respectively (shown in Table 2).

The calculated values of Pb$_{\text{Mn}}$ and Pb$_{\text{Fe}}$ indicate that the greatest contribution to total Pb binding to the heterogeneous surface coating materials was from Mn oxides. The estimated Pb adsorption capacities of Mn and Fe oxides were similar to each other between Sets 1 and 2 for both Mn oxide and Fe oxide as would be expected for adsorbents exposed to approximately the same lake surface water concentration of dissolved Pb. The consistency of adsorption capacity was observed although there was a different ratio of Mn oxide/Fe oxide in two sets of natural biofilms. The Mn/Fe ratio was lower in the second sample set and we speculate that this decrease resulted from a decrease in lake water temperature (which unfortunately was not monitored at the sample site), since the rate of biological oxidation of Mn(II) is well described by the Arrhenius equation at temperatures below 35°C [15].

Pb adsorption to Mn oxide on a molar basis ($I_{\mu\text{mol Pb/mol Mn oxide}}$) was almost an order of magnitude greater than that to Fe oxide ($I_{\mu\text{mol Pb/mol Fe oxide}}$). This result agrees closely with that obtained from laboratory Pb adsorption experiments using natural biofilms before and after selective extractions [12]. This result also strongly suggests that the Mn oxides in the surface coatings were biogenic in origin since Mn oxides formed by abiotic processes (including amorphous freshly oxidized Mn oxides) do not exhibit a Pb adsorption capacity that approaches that of the biologically formed Mn (III/IV) solid phase [26].

The results from the present study are consistent with prior research in which adsorption of added Pb by both well-characterized surrogate solid phases, and natural coating materials (before and after selective extraction) revealed that Fe and Mn oxides play a major role in Pb scavenging in Cayuga Lake. A salient, and important, difference is that the current research reveals the ambient low levels of Pb that are adsorbed under the chemical conditions existent in the Lake. Further, the results confirm that Pb association with Mn solid phases matches or exceeds Pb binding to Fe surfaces in this lake. Although the fraction of total surface-bound Pb associated with Mn in other freshwater systems will vary depending upon surface composition, the results confirm that the Pb adsorption capacity of Mn oxides exceeds that of Fe oxides on a molar basis by approximately an order of magnitude. Thus, the reactivity of Mn oxides with respect to Pb adsorption compensates for the lower abundance of Mn vs. Fe. The high reactivity observed

| Table 2: Estimation of Pb adsorption to Fe, Mn oxides in natural biofilms developed in Cayuga Lake |
| Set 1 | Set 2 |
| Pb adsorption to Mn oxide ($I_{\mu\text{mol Pb/mol Mn oxide}}$) (µmol/m$^2$) | 0.22 | 0.052 |
| Pb adsorption to Fe oxide ($I_{\mu\text{mol Pb/mol Fe oxide}}$) (µmol/m$^2$) | 0.070 | 0.046 |
| Pb adsorption capacity of Mn oxide ($I_{\mu\text{mol Pb/Mn oxide}}$) | $7 \times 10^3$ | $6 \times 10^3$ |
| Pb adsorption capacity of Fe oxide ($I_{\mu\text{mol Pb/Mn oxide}}$) | $4 \times 10^2$ | $3 \times 10^2$ |
for natural Mn oxides strongly suggests that they are biogenic in origin, consistent with expectations based on the relative biotic and abiotic rates of Mn(II) oxidation under circumneutral conditions [15]. Collectively, the results for Pb mineral phase association observed in this research confirm predictions based on laboratory studies [10,12,13] and provide closure between Pb adsorption experiments carried out in chemically defined laboratory conditions and the adsorptive behavior of Pb in the field.

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