Characterizing Zinc Speciation in Soils from a Smelter-Affected Boreal Forest Ecosystem

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SUPPLEMENTAL INFORMATION

AREA MAP WITH SITE PHOTOS, ZINC XAS STANDARDS, SYNTHESIS METHODS, LOADINGS, X-RAY DIFFRACTION, AND ZINC µXANES

6 Figures
1 Table
9 Pages
A.1. Soil sampling locations

Fig. S1. Sampling sites used in characterizing Zn speciation in relation to the smelter/processing facility (Yellow). Group I (Orange) and Group II (Green) soils are indicated with picture representations defining each classification. Aerial photo provided by University of Saskatchewan Department of Soil Science Soil Survey of Flin Flon, MB.
Fig. S2. Site 3, a Group I soil pocket on exposed bedrock highly susceptible to erosion during spring snow melt and rainfall events.
Fig. S3. Site 2 located in valley between exposed bedrock slopes. Soil is vegetated by an invasive metal tolerant grass species.
A.2. Precipitate standards

A Zn co-precipitated hydroxyl Interlayer Material (Zn-Al-HIM) was synthesized as per Scheinost et al. (2002). After synthesis, the resulting Zn-Al-HIM coprecipitate was washed to remove any unreacted Zn$^{2+}$.

The Zn-Al-LDH precipitate standard was prepared under a N$_2$ atmosphere with a 3:1 Zn:Al ratio using Zn(NO$_3$)$_2$ and Al(NO$_3$)$_3$ (Ajat et al., 2008). The precipitate was formed at pH 7 while adding the reactant solutions under mixing conditions; the resulting solution was heated for 18 hours at 70 °C (Ajat et al., 2008). The precipitate was then vacuum filtered and triple washed with D.I. water.

$\alpha$-Zn(OH)$_2$ was synthesized as per Waychunas et al. (2002); under a N$_2$ atmosphere the pH of a 0.55 M Zn(NO$_3$)$_2$ (pH 3.0) solution was slowly increased to 6.5 with CO$_2$ free 1.0 M NaOH while stirring. The solution was then aged for 24-hrs at room temperature under N$_2$ atmospheric conditions, the resultant precipitate was then vacuum filtered and triple rinsed with D.I. water to remove entrained (Zn$^{2+}$) and dissolved nitrate.

The synthesis of ZnCO$_3$ was performed as per Zhang et al. (2004). Briefly, a 1:1 of 0.05 M Zn(NO$_3$)$_2$ and 0.05 M K$_2$CO$_3$ solutions are mixed under vigorous stirring conditions at room temperature. The resulting precipitate was stirred for 1hr and then left still for 24 hrs, the ZnCO$_3$ precipitate was vacuum filtered and triple washed with D.I. water removing any unreacted Zn$^{2+}$. The precipitate was dried, ground, and placed in a sealed container for storage until XAS measurements were collected.

Zn oxide and Zn phosphate where purchased as reagent grade dry precipitates from Fisher Scientific Canada.

A.2. Sorption standards

Adsorption standards were prepared with mineral suspensions of 0.5g/L that were sparged with N$_2$ in a 0.1 M NaNO$_3$ background electrolyte. Initial pH was lowered to pH 5 to ensure that carbonate was removed from the system. Zinc was added (as Zn(NO$_3$)$_2$) for a final concentration of 1 mM; after Zn addition the pH was slowly titrated to pH 6.5 under N$_2$. The bottles were sealed, shaken for 48hr, filtered and the solid residue was washed with 0.1 M NaNO$_3$ to displace entrained Zn. A list of the loadings of the adsorption standards and surface areas of the sorbent phases can be found below (Table S1).
The MnO₂ sorbent is a birnessite mineral previously synthesized and characterized (Hardie et al., 2009) and provided by Dr. J. Dynes. The goethite sorbent was provided by Dr. Peak and has been previously characterized (Zhang, G.Y. and D. Peak, 2007). The SiO₂ mineral used as a reference material is an amorphous silica gel, accounting for the high surface area listed in Table S1.

**Table S1. Loadings of Zn adsorption reference standards**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Surface Area</th>
<th>Loading</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>63</td>
<td>47</td>
<td>3100</td>
</tr>
<tr>
<td>Fe(O)OH</td>
<td>63</td>
<td>39</td>
<td>2600</td>
</tr>
<tr>
<td>Na-Montmorillonite</td>
<td>-</td>
<td>16</td>
<td>1100</td>
</tr>
<tr>
<td>SiO₂</td>
<td>860</td>
<td>42</td>
<td>2800</td>
</tr>
</tbody>
</table>

**A.3. Mineral standards**

Zinc minerals (franklinite, sphalerite, and willimite) were supplied from the University Of Saskatchewan Department Of Geology. All materials had identical EXAFS and XANES features noted in previously reported mineral standards from other sources (Manceau et al., 2000; Scheinost et al., 2002; Jacquat et al., 2009a). Zinc standards spectra can be found in Fig. 1.

**References**


Figure. S4. X-ray diffraction pattern of Group I soil (Site 7) with phase identification indicating the soil and contaminant mineralogy.
Figure S5. X-ray diffraction pattern of Group II soil (Site 4) with phase identification indicating the soil and contaminant mineralogy.
Figure. S6. Zn μXANES collected during XRF mapping of Group I (Left) and Group II (Right) soils.