Quantitative Zinc Speciation in Soil with XAFS Spectroscopy: Evaluation of Iterative Transformation Factor Analysis

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Abstract

We employed a combination of selective sequential extractions and bulk XAFS spectroscopy, and extracted spectral XAFS components and their concentrations by iterative transformation factor analysis (ITFA), in order to determine the Zn speciation in a melter-contaminated, acidic soil. We compared the speciation by ITFA with one we performed earlier using principal component analysis and linear combination fit. ITFA identified 4 different species, two different franklinite-type phases (Zn-Fe spinels), sphalerite (Zn sulfide) and Zn oxalate, the latter forming as a precipitate during chemical extraction with oxalate solution. The second spinel-type phase could be extracted with the help of ITFA, although no appropriate reference sample was available. Spinel 1 and 2 have Zn-O distances of 1.96 and 1.99 Å, and Zn-Fe distances of 3.53 and 3.46 Å, respectively. The results from ITFA gave much better fits of experimental spectra and are better in line with elemental mapping and XAFS microspectroscopy. The major advantage of investigating XAFS data with ITFA is the possibility to derive all species even when part of the references are not available.

1. Introduction

Speciation of metals in contaminated soils is a prerequisite for predicting the environmental risks and to develop efficient and cost-effective remediation measures. While XAFS is the method of choice for providing molecular information on chemical forms, several coexisting species can be resolved only by the additional help of micro-spectroscopies, chemical and physical separation methods, and statistical methods [1–6]. Recently we have employed a combination of selective sequential extractions followed by XAFS spectroscopy, and have identified the spectral contributions by principal component analysis, target transforms and linear combination fits [7]. Another statistical method, ITFA, has been applied recently to derive the structure of two coexisting aqueous U(VI)-protocatechuic acid complexes [8]. This approach has the advantage that reference spectra of pure species can be substituted for by knowledge of the relative distribution of species in mixtures. That is, if the concentrations of at least some of the species are known from speciation modeling (or any other source like complementary spectroscopies), the spectra of the pure species can be calculated even when only spectra of species mixtures are available. The intention of the present paper was to investigate, whether this approach can be applied to decipher metal speciation in soils. As a model case, we investigated the Zn K-edge XAFS spectra collected from selective sequential extraction residuals of a contaminated soil [7].

2. Experimental

A topsoil sample was collected near the former zinc smelter in Palmetron, Pennsylvania [6]. This sample was ground, and subjected to increasingly aggressive extraction procedures [9]. After each of 6 extraction step, the removed zinc concentration was determined by atomic absorption spectrometry, and an XAFS spectrum was collected (fluorescence mode with Lytle detector at beamline X-11A, NSLS) [7]. The resulting 7 spectra (untreated soil sample and sample after each of 6 extraction steps) were investigated by ITFA [8, 10]. First, abstract Eigenvectors were derived from the set of XAFS spectra by principal component analysis. These Eigenvectors were used to estimate the number of species present (see below). Second, a Varimax rotation was applied to get qualitative concentrations of the factors. Third, additional information was used to derive real concentrations and real factors (i.e. the XAFS spectra of the pure species and their relative contributions) by iterative target transform.

3. Results and Discussion

Figure 1 (top) shows the first four Eigenvectors derived from XAFS spectra of the soil samples before and after 6 extraction steps. The amplitudes decline from vector 1 to 4. While vectors 1 to 3 still contain information similar to XAFS oscillations, vector 4 contains experimental noise only. Thus, the Eigenvectors suggest the presence of three species in all samples. From our previous investigations we knew that franklinite, sphalerite and zinc oxalate are the major Zn species of these samples [6, 7]. Therefore, by adding the spectra of these species to those of the soil samples, we would have expected to observe again three significant Eigenvectors only. However, Figure 1 (bottom) shows a fourth significant Eigenvector. Since we know the relative concentrations of three species in three of the spectra (the 3 reference spectra), we can now calculate the relative concentrations of all four species in the 10 samples by iterative target transform (Fig. 2). Finally, the real factors, i.e., the XAFS spectra of all four species, were derived (Fig. 3). Factor 2 is identical to the franklinite reference sample, factor 3 to the sphalerite sample, and factor 1 to the Zn oxalate reference. Factor 4 represents the fourth, unknown species. The spectral features (Fig. 3) and the fit results (Table I) suggest that factor 4 represents a second franklinite phase, which is distinguished from the franklinite reference by a larger Zn-O distance and a smaller Zn-Fe distance. The larger Zn-O distance may be due to Zn in both tetrahedral and octahedral coordination, which is not unusual for spinel structures. Furthermore, the difference in Zn-Fe distances may indicate different elemental composition, e.g. varying fractions of Zn, Fe and Mn in the structure.

In spite of their structural differences, the dissolution behavior of franklinite 1 and 2 is similar (Fig. 4). In the untreated soil sample, about 80% of the total zinc is in the two franklinite phases. During step 5, which is an oxalate solution step intended to dissolve weakly crystalline Fe oxides, a substantial amount of
Quantitative Zinc Speciation in Soil with XAFS Spectroscopy

Fig. 1. First 4 Eigenvectors of XAFS spectra of the 7 soil samples (top), and of the XAFS spectra of 7 soils samples plus franklinite, sphalerite and Zn oxalate (bottom).

Fig. 2. Relative concentrations of the four species determined by ITFA.

Table I. XAFS fit results of factors 2 and 4.

<table>
<thead>
<tr>
<th>Factor</th>
<th>CN</th>
<th>R (Å)</th>
<th>σ² (Å²)</th>
<th>ΔE0</th>
<th>σ_E0 (Å)</th>
<th>σ_{E0} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>O</td>
<td>1.98</td>
<td>0.002</td>
<td>13.0</td>
<td>3.53</td>
<td>0.007</td>
</tr>
<tr>
<td>4</td>
<td>Fe</td>
<td>1.99</td>
<td>0.010</td>
<td>11.9</td>
<td>3.48</td>
<td>0.008</td>
</tr>
<tr>
<td>Franklinite</td>
<td>XRD</td>
<td>4.0</td>
<td>1.99</td>
<td>12.0</td>
<td>3.50</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Fig. 3. Real spectral factors derived by ITFA, corresponding to the experimental XAFS spectra of franklinite (f2), sphalerite (f3) and Zn oxalate (f1). Factor 4 corresponds to the XAFS spectrum of the previously undetected species, a franklinite-like mineral.

Fig. 4. Absolute species distribution (cumulative) of the untreated soil sample (step 0) and after each of the selective sequential extraction steps (1 to 6).

Both franklinite phases is dissolved, but most of the dissolved Zn re-precipitates as Zn oxalate. The larger part of this Zn oxalate, and a smaller part of franklinite dissolves during step 6, a step intended to dissolve crystalline Fe oxides. None of these steps dissolves a significant amount of sphalerite, which hosts about 10% of total Zn (in the untreated sample). This is much less than the 30% derived by linear combination fits [7]. An amount of 10% is more consistent with the observations by XAFS microspectroscopy [6]. Furthermore, the reconstruction of the experimental spectra has significantly improved, giving another indication that the ITFA approach is superior to the approach employing principal component analysis, target transform and linear combination fits.

The problem of properly identifying aqueous and exchange-ably sorbed Zn cations is evident from the fact, that ITFA assigns about 10% of Zn oxalate to the untreated soil sample. Step 1 employing a 1M NH4NO3 solution, removed 7% of Zn indicating that this amount is aqueous Zn$^{2+}$ and/or Zn bound to cation exchange sites instead. The single O shell of aqueous Zn is a spectral feature also present in Zn oxalate, therefore making the discrimination by ITFA impossible.

In conclusion, we believe that ITFA has a great potential to improve the interpretation of XAFS of complex mixtures, since this statistical method depends less on a complete spectral database.
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References