Studies of Cu(II) in soil by X-ray absorption spectroscopy

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Frenkel, A. I. and Korshin, G. V. 2001. **Studies of Cu(II) in soil by X-ray absorption spectroscopy**. Can. J. Soil Sci. **81**: 271–276. Based on original data for copper, this paper evaluates the use and advantages of **X-ray absorption fine structure** (**XAFS**) in studies of heavy metals in soils. The structural parameters of the Cu^{2+} target were quantified for soil exposed to copper and the same soil eluted with 0.1 M HCl. Experimental data were obtained using synchrotron sources of second and third generations. **X-ray absorption near edge structure** (**XANES**) indicated that the copper in both samples is likely to be predominantly bound by oxygen-containing functional groups. **Extended X-ray absorption fine structure** (**EXAFS**) analysis showed that the equatorial Cu-O distances were similar to those seen for Cu^{2+}-humic complexes in aqueous solutions, but the axial distances for both samples were longer than in water. In the axial direction, this may indicate a type of ligation dissimilar to that in solutions. The magnitude of the mean square deviation of the axial Cu-O distance in the 0.1 M HCl eluted sample indicated a stronger bond compared with that in the sample containing both extractable and tightly bound copper. The results indicate that careful examination of structural data for sequentially eluted soils in combination with the development of new radiation sources to improve the sensitivity and quality of the data are likely to improve insight into the nature of interactions between heavy metals and soil.

Key words: Soil, copper, humic, speciation, extended X-ray absorption fine structure, X-ray absorption near edge structure

Frenkel, A. I. et Korshin, G. V. 2001. **Analyse du Cu(II) du sol par spectroscopie d'absorption aux rayons X**. Can. J. Soil Sci. **81**: 271–276. L'article que voici évalue l'utilité et les avantages de la XAFS dans l'étude des métaux lourds du sol à partir de données sur le cuivre. On a quantifié les paramètres structuraux des ions Cu^{2+} dans des échantillons de sol exposé au cuivre et du même sol, mais élué avec du HCl 0,1 M. Les données ont été recueillies au moyen de synchrotrons de deuxième et de troisième génération. La XANES révèle que le cuivre décelé dans les deux échantillons est sans doute essentiellement lié à des groupes fonctionnels renfermant de l'oxygène. L'examen par EXAFS révèle que la distance équatoriale entre les atomes d'oxygène et de cuivre est semblable à celle notée pour les complexes de substances humiques et d'ions Cu^{2+} en solution aqueuse, mais la distance axiale est plus grande dans les deux échantillons que dans l'eau. Dans le sens axial, pareil résultat pourrait indiquer l'existence d'une ligature différente de celle observée dans les solutions. Par son ordre de grandeur, la variance de la distance axiale Cu-O dans l'échantillon élué au HCl 0,1 M indique l'existence d'un lien plus solide que dans l'échantillon renfermant du cuivre extractible et du cuivre très lié. On en conclut qu'un examen attentif des données structurelles sur les sols élués de façon séquentielle et de nouvelles sources de rayonnement augmenteraient la sensibilité et la qualité des données, ce qui devrait nous en apprendre davantage sur la nature des interactions entre les métaux lourds et le sol.

Mots clés: Sol, cuivre, humique, espèces chimiques, EXAFS, XANES

X-Ray Absorption Fine Structure spectroscopy is an advanced structural technique based on the use of high intensity synchrotron radiation to measure the X-ray absorption coefficient of a material as a function of the X-ray energy. The interpretation of XAFS spectra provides quantitative information regarding the short-range atomic structure around the target element in the sample.

The fine structure in the XAFS spectrum originates from the oscillatory nature of the wave function of the photoelectron ejected from the target atom in the photoabsorption process. The fine structure in the absorption coefficient starts at ca. 40 eV and extends ca. 1000 eV past the absorption edge. For these energies, single and multiple scatterings of the photoelectron by its nearest neighbors define the behavior of the X-ray absorption coefficient, which, due to its nature, contains the information about the identity and coordination numbers of the surrounding atoms, as well as about relevant distances and their disorders. The method of XAFS, which studies the absorption coefficient in the discussed range of energies, is called Extended X-Ray Absorption Fine Structure (EXAFS). The X-ray absorption near edge structure (XANES) spectroscopy is an allied but independent method that examines the data in the energy region from the Fermi level up to 40 eV past the absorption edge. The spectral data for this region contain information about the electronic structure and bonding geometry of the system.

Since the EXAFS signal inherently contains information about the *local* (up to 5–8 Å around the target) chemical environment, this method is particularly powerful in combination with other structural techniques, notably X-ray diffraction. The latter method provides information about the *average* structure of the system, while EXAFS helps ascertain the dynamic or static local deviations from the average structure and thus characterizes the local chemical order (as in the case of alloys). If the average structure is known a priori, the theoretical EXAFS signal can be constructed based on ab initio calculations [e.g., using computer code FEFF (Zabinsky et al. 1995)]. The unknown structural parameters can be elucidated with a very high precision by fitting the theoretical predictions to the data. Using the EXAFS analysis routines, the interatomic distances currently can be determined with accuracy ± 0.01 Å or better. In some cases, the local structure can be qualitatively described for up to four or five coordination shells around the target atom (Frenkel et al. 1993, 1994; Nashner et al. 1997).

The interpretation of XANES is more complex than that of EXAFS and is based on both multiple scattering expansion and the electronic density of states. Full multiple scattering calculations are essential in the XANES data analysis, but until recently, simulation and interpretation of XANES for arbitrary systems, notably for those with hydrogen atoms, have been either unavailable or very difficult. Latest progress in ab initio modeling of XANES has made it possible to use EXAFS and XANES data in a complementary fashion to establish the geometry of the metal-binding sites in **humic species** (**HS**) and quantify their non-uniformity (Frenkel and Korshin 1999). This recent development offers new possibilities to obtain structural information for samples with very low metal concentrations, for which the EXAFS signal is too weak to be reliably processed. For example, XANES measurements were recently carried out for solutions with Cu concentrations as low as 4.2×10^{-5} M (Frenkel and Korshin 1999). Nevertheless, investigation of non-contaminated environmental samples requires the detection limits for target elements to be lowered by several orders of magnitude. This necessitates the use of the third generation of X-ray synchrotron sources. Recent experimental data show that their use gives reliable EXAFS data for copper concentration as low as 2×10^{-5} M (Mosselmans et al. 1999), while the detection limit for XANES may be much lower.

This and other recent publications (e.g., Davies et al. 1997; Manceau et al. 1996; Sery et al. 1996; Hesterberg et al. 1997) that describe the use of EXAFS/XANES to probe the state of heavy metals in soils, sediments and minerals, demonstrate the enormous, unrealized potential of these methods in environmental research. In this article, we will demonstrate, using soil contaminated with Cu as an example, how information about the chemical state of a metal and its bonding geometry can be obtained via the application of state-of-the-art instrumentation and analysis techniques.

MATERIALS AND METHODS

A 5-cm-thick layer of topsoil taken from a residential area in Seattle, WA, was homogenized and freeze-dried. 40 g of the freeze-dried sample was then exposed to 100 mL of 0.01 M copper sulfate solution for 24 h, then centrifuged and decanted. The solid phase so obtained was again homogenized, freeze-dried and used in XAFS measurements as sample 1. It was then eluted three times with 100 mL of deionized water, 100 mL of 0.1 M HCl at the pH values of 4 and 1, respectively. Between each elution, the sample was centrifuged, decanted, homogenized and freeze-dried. The suspension obtained by exposing the pre-treated soil to HCl at pH 1 was filtered through a 0.45-μm filter. The solid phase retained by this filter was designated as sample 2. Metal concentrations in the samples were measured using a Jobin-Yvon Ultratrace JY-138 inductively coupled spectrometer. The concentrations of copper in the original soil, sample 1 and sample 2 were 16, 135 and 47 mg kg^{-1}, respectively.

X-ray absorption measurements for sample 1 were carried out at the University of Illinois/Lucent Technologies X16-C beamline of the National Synchrotron Light Source at Brookhaven National Laboratory, Upton, NY. Sample 2 was measured at the UNICAT 33-ID beamline at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. In both cases, the X-ray energy varied from 200 eV below to 800 eV above the absorption K edge of Cu (E_K = 8979 eV). The data were obtained in the fluorescence mode. The pre-edge and near-edge regions of the data (-30 eV $< E-E_K <$ 40 eV) were acquired with a 0.5 eV energy increment. The EXAFS data in the range 40 eV $< E–E_K <$ 800 eV were acquired with a 2 eV increment. Up to six measurements were averaged for the same sample to improve the signal-to-noise ratio. To correct for the small energy shifts between the scans, all data sets were aligned vs. their absolute energy and interpolated to the same 0.25 eV-increment grid before the averaging. Cu metal foil was measured in the transmission mode simultaneously with all other samples and was used as the reference for the alignment of energies. In addition, the XANES data of Cu metal foil, Cu_2O and CuO were used as the references of the Cu(0), Cu(I) and Cu(II) oxidation states, respectively.

DATA ANALYSIS AND RESULTS

XANES data

Only Cu K-edge region XANES data corresponding to the $1s \rightarrow 4p$ transitions located between 8979 and 8995 eV will be discussed in this paper. The XANES spectra and their first derivatives for the reference materials (Cu metal, Cu_2O, CuO) and samples 1 and 2 are shown in Figs. 1 and 2, respectively. For samples 1 and 2, the major maximum of the absorption coefficient, or zero of its first derivative (feature C) is located at the energy very close to that observed for copper (II) oxide (Fig. 2). This indicates that, despite the potential presence of reducing species in the samples, no noticeable change of the oxidation state of copper occurred following the contact of the Cu(II)-containing solution with the soil. The first derivative XANES spectra of samples 1 and 2 have two prominent maxima denoted as A and B. The amplitudes of these maxima in the derivative XANES spectra of sample 1 were smaller than for sample 2. The separation between features A and B was virtually the same for the both samples. These features in the derivatized XANES spectra resemble those observed for Cu-HS complexes (Frenkel and Korshin 1999). In the latter case, the splitting of the corresponding derivative XANES spectra was attributed to the tetragonal distortion of the CuO_6 octahedron (Garcia et al. 1989; Palladino et al. 1993). We will present more discussion on this matter in the following sections.

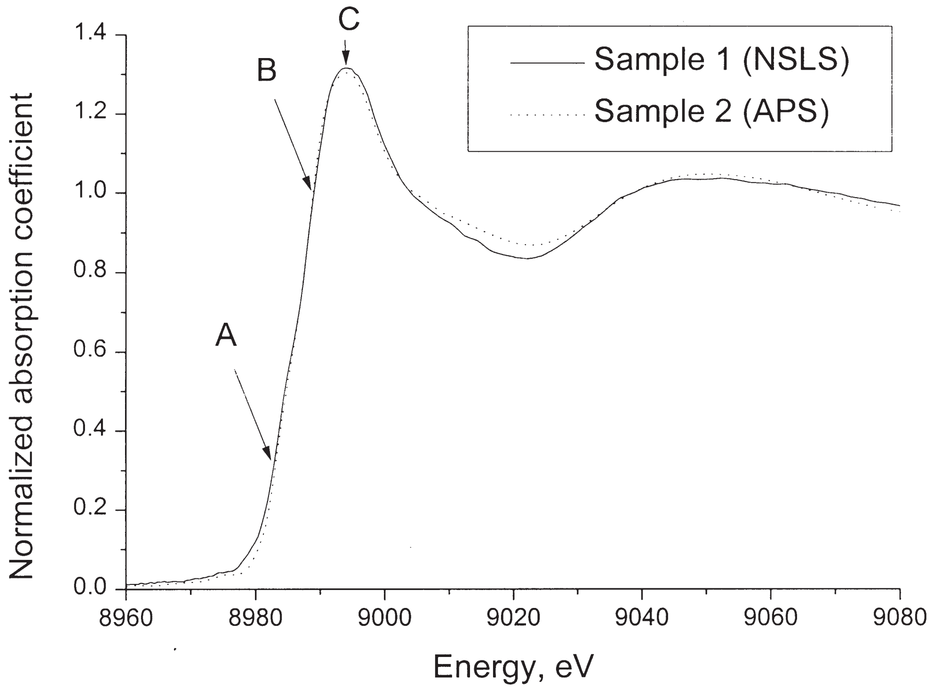

Fig. 1. The edge-step normalized Cu K-edge X-ray absorption coefficient measured in samples 1 and 2.

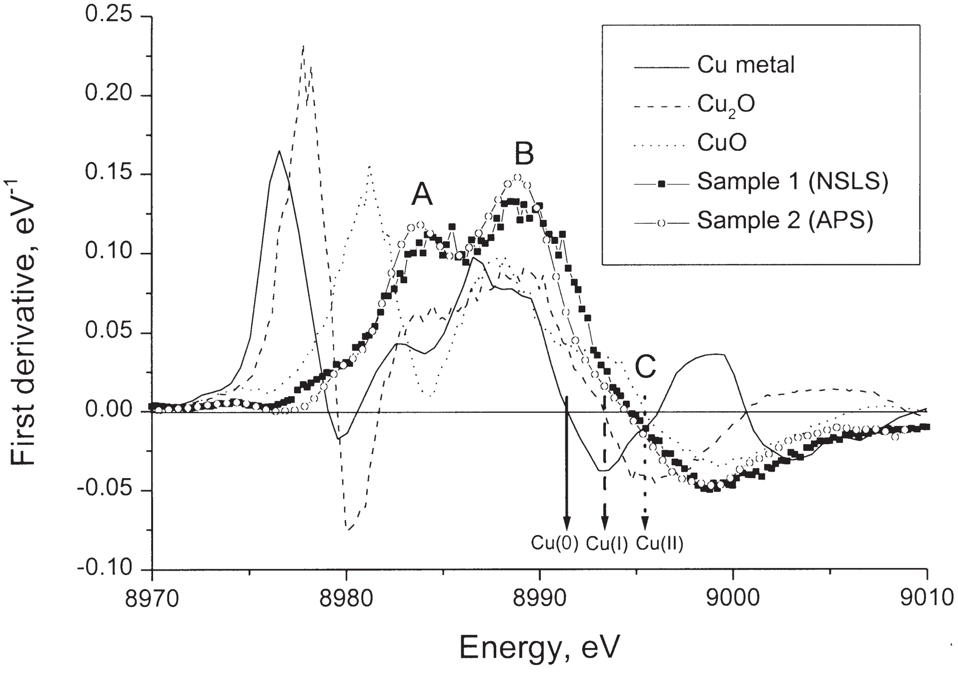

Fig. 2. The first derivative of the Cu K-edge absorption coefficients measured in Cu metal foil, Cu_2O, CuO, and samples 1 and 2.

EXAFS Data Processing: Background Removal

To extract the contribution from atoms surrounding the central radiation-absorbing atom, an isolated-atom smooth background function $\mu_0(k)$, where k is the photoelectron wave number, is subtracted from the experimental absorption coefficient $\mu(k)$, and the resultant signal is normalized by the absorption edge step:

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\Delta\mu_0(0)} \tag{1}$$

The background of all the data was removed using an AUTOBK program (Newville et al. 1993) utilizing the energy reference E_0 located in the middle of the edge jump. The

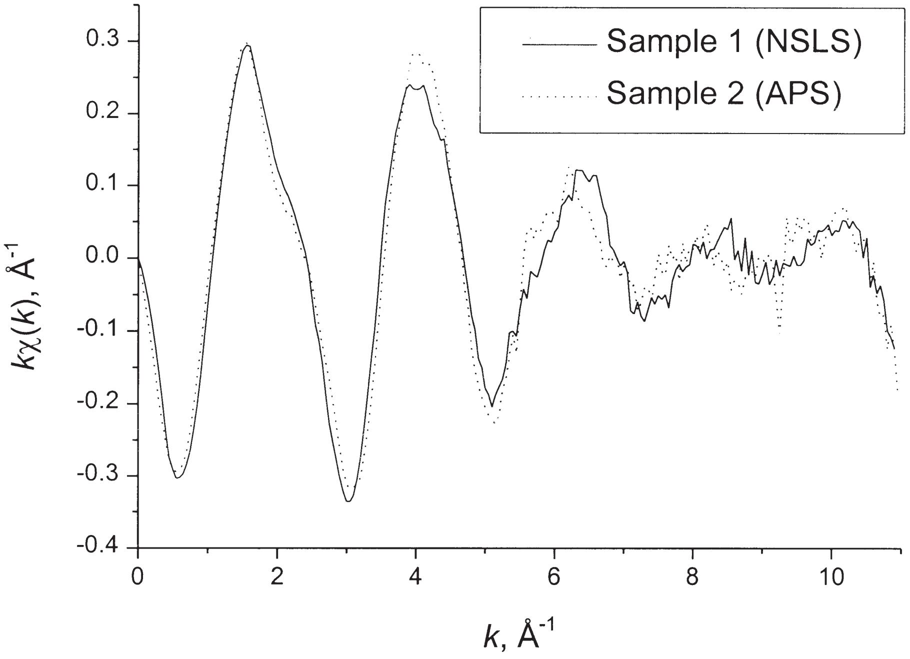

Fig. 3. EXAFS $k\chi(k)$ for samples 1 and 2.

resultant experimental EXAFS signals $k\chi(k)$ for the both samples are shown in Fig. 3.

EXAFS Data Analysis and the Model

In the single-electron single-scattering approximation, the edge-step normalized EXAFS signal $\chi(k)$ generated by a given shell of atoms could be written as:

$$\chi(k) = \frac{NS_0^2}{kR^2} f(k) \exp\left(-2k^2\sigma^2\right) \sin\left(2kr + \delta(k)\right) \qquad (2)$$

where N is the coordination number of the shell of same atomic species located approximately at the same distance from the central atom, R is the average distance to the shell, σ^2 is the mean square deviation of this distance (i.e., both static and dynamic disorder), S_0^2 is the many-body factor introduced to account for the shake-up and shake-off effects of the passive electrons. Terms $f(k)$ and $\delta(k)$ represent the photoelectron backscattering amplitude and phase shifts, respectively. The magnitude of the Fourier transform (FT) of $k\chi(k)$ in the r-space gives a qualitative representation of the effective radial pair distribution function [uncorrected for the $\delta(k)$ phase shift] of nearest neighbors to Cu (Fig. 4).

By visually inspecting this figure, one notices substantial differences between the experimental data for the soil samples. To interpret them, it is necessary to establish the most plausible model of the inner complexation shell of the copper in the samples. Due to the complexity of the structure and composition of soils, the copper speciation can be affected by the formation of complexes with oxygen-, sulfur- and nitrogen-containing functional groups belonging to soil humic species, presence of hydroxo-, carbonate and mixed complexes, adsorption on interfaces and precipitation of solid phases. In all these cases, except complexation via sulfur and nitrogen-containing functional groups and precipitation of Cu sulfides, the inner complexation shell of the target can be represented by the CuO_6 octahedron (Palladino et al. 1993). Since the samples were never subjected to reducing conditions, the presence of sulfides in them is unlikely. As for the nitrogen-containing groups, our preliminary experiments showed that their presence can be indicated by a pre-edge structure located in the derivative XANES spectra in the range 8976 to 8980 eV (Frenkel and Korshin 1999). This feature was not prominent in the spectra of samples 1 and 2 (Fig. 2). Based on this, we conclude that the properties of the inner complexation shell for the systems studied can be discussed based on the CuO_6 model.

The maximum of the first peak of sample 1, corresponding to the Cu-O pair distance, is shifted to the shorter distances compared with that of sample 2. This could be explained by either shortening of the mean Cu-O distance in the CuO_6 octahedron in sample 1 relative to sample 2, or by different mechanisms of Cu-ligand interactions in the two samples. Consistent data analysis allowed separating these two scenarios. The FEFF7 ab initio code (Zabinsky et al. 1995) was used to generate the $f(k)$ and $\delta(k)$ functions for the absorbing atom in the model. The experimental EXAFS spectra were fitted with the theoretical EXAFS function (Eq. 2) using the UWXAFS package, which provides a nonlinear least-squares fitting. During the fitting procedure, the corrections to the reference energy, Cu-O distances for the equatorial and axial oxygens (ΔR) and mean square disorders of the distances (σ^2) were varied independently until the best fit was achieved. The estimates of the errors in the parameters were also calculated. Thus, both the changes in

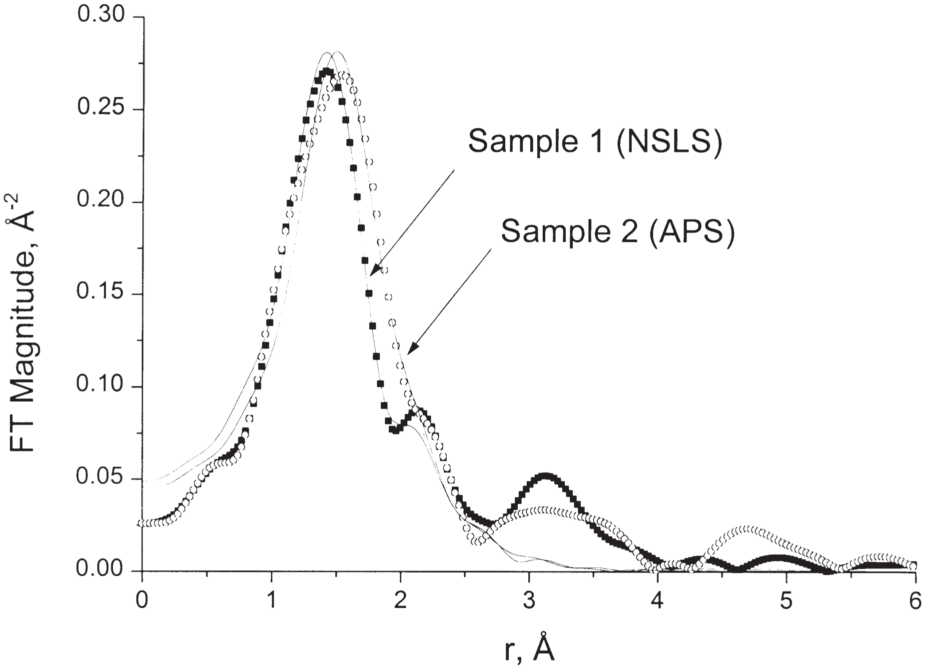

Fig. 4. Fourier transform magnitudes of the $k\chi(k)$ data (symbols) and FEFF7 theory (solid) for samples 1 and 2.

the Cu-O bond distances and their disorders were allowed in the local structure refinement.

The fitting was performed in the *r*-space between 1 and 2.5 Å by Fourier transforming both the experimental data and FEFF theoretical function (Fig. 4). The *k*-weighting factor and the Hanning window function defined between 2.5 and 9.5 Å^{-1} were used in Fourier transforms. The number of relevant independent data points N_{idp} in the data was calculated with Eq. 3 (Stern 1993):

$$N_{idp} = \frac{2\Delta k \Delta r}{\pi} + 2 \tag{3}$$

where Δk and Δr are the data ranges in *k*- and *r*-spaces, respectively. To reduce the number of fit variables, which should be smaller than N_{idp}, the many-body factor S_0^2 was fixed at 0.9, which is the middle of its most probable variation range (0.8 to 1.0). The number of variables was 5, while the number of relevant independent data points was 8.

RESULTS AND DISCUSSION

The best fit results for both soil samples are given in Table 1. The bond lengths for the CuO_6 octahedron for both samples are similar within the experimental uncertainties. The calculated equatorial Cu-O distances are similar to those seen for Cu^{2+}-humic complexes in aqueous solution (Korshin et al. 1998). At the same time, EXAFS analysis indicates the axial distances for both soil samples are notably longer than in dissolved complexes of copper (II) with humic species (2.57 to 2.59 and 2.10 to 2.14 Å, respectively). Although this result needs to be further ascertained, it may indicate that for the axial direction a type of ligation dissimilar to that in solutions may be predominant. The disorder factors, σ^2, of the equatorial Cu-O bonds in samples 1 and 2 are small and similar. In contrast, there is a significant change of the axial disorder factor in the eluted sample (Table 1). Specifically, the axial disorder factor of this bond in sample 2 ($\sigma^2 = 0.007$ Å^2) is almost an order of magnitude less than in sample 1 ($\sigma^2 = 0.05$ Å^2).

Such a difference between the parameters of the axial Cu-O bond length disorder between the two samples is consistent with the observation made in the XANES data. As mentioned above, the amplitudes of the features A and B (Fig. 2) are greater for sample 2 while the energy separation between them is the same for the both samples. Our previous results (Frenkel and Korshin 1999) verified quantitatively that these features in the first derivative spectra of XANES originate in the polarized nature of synchrotron radiation. Namely, a long (axial) Cu-O bond would give rise to a shoulder in the absorption coefficient (and the concomitant feature A in the first derivative) in the $1s - 4p$ transition region while a short (equatorial) bond would be characterized by a higher-energy peak (and the concomitant feature B in the first derivative) in this energy range. The energy separation between the two features is, therefore, related to the bond length difference between the axial and equatorial Cu-O bonds, and their amplitudes are affected by the Debye-Waller factors of these bonds. Our XANES results, therefore, indicate that the average disorder of the axial and equatorial Cu-O bonds is smaller in sample 2 than in sample 1, and their respective bond lengths are similar, in agreement with the EXAFS results.

The smaller magnitude of the mean square deviation of the axial Cu-O distance in the eluted sample indicated a stronger bond compared with that in the sample containing

Table 1. Structural characteristics of copper-oxygen bonds in samples 1 and 2

	r (Å)		σ^2 (Å^2)	
Sample	Equatorial	Axial	Equatorial	Axial
1	1.93 ± 0.02	2.59 ± 0.13	0.0056 ± 0.0009	0.05 ± 0.06
2	1.97 ± 0.02	2.57 ± 0.04	0.0063 ± 0.0013	0.007 ± 0.006

both extractable and tightly-bound copper. Indeed, the force constant of the effective pair potential and the mean square deviation of the average bond length are inversely proportional to each other (Frenkel and Rehr 1993). Although the chemistry of these bonds cannot be ascertained based solely on the structural data and more work needs to be done to clarify the nature of relevant functionalities and conformations, this result clearly supports the notion that the tightly bound fractions of heavy metals in soils interact more strongly with the matrix compared with the extractable metal. It is somewhat surprising that, at least for copper (II), the relevant difference manifests itself solely through the disorder along the axial bond. This result will have to be confirmed in more extensive experiments with soils containing varying metal loads.

CONCLUSIONS

Using the EXAFS and XANES techniques, we evaluated the nature of the first complexation shell of copper in soil and found indications pointing to the structural differences between the extractable and bound metal. The present work utilized new experimental possibilities, which have become available with construction of the 3rd generation synchrotron sources, to study the structural parameters of the target at fairly low concentration. Although the metal concentrations in the samples explored in this work were in the range of 40 to 150 mg kg^{-1}, there is little doubt that, using the third generation sources such as Advanced Photon Source at Argonne National Laboratory, high quality XAFS data can be obtained for target concentration as low as 1 to 10 mg kg^{-1} or less. However, it is recognized that the true potential of XAFS spectroscopy in studies of metals and other elements of interest in soils and other complex environmental samples has not been realized and much work in this direction lies ahead.

ACKNOWLEDGMENTS

The authors are grateful to the UNICAT staff at the Advanced Photon Source, Drs. P. Zschack, H. Hong, P. Jemian, J. Karapetrova, and to Drs. S. Bare and G. Mickelson (UOP) for their help in synchrotron measurements. A.I. Frenkel acknowledges support by DOE grant DEFG02-96ER45439 through Materials Research Laboratory at the University of Illinois at Urbana–Champaign. G.V. Korshin acknowledges support from US Environmental Protection Agency (Grant #R826645). The UNICAT facility at the Advanced Photon Source (APS) is supported by the University of Illinois at Urbana-Champaign, Materials Research Laboratory (US DOE, the State of Illinois-IBHE-HECA, and the NSF), the Oak Ridge National Laboratory (US DOE under contract with Lockheed Martin Energy Research), the National Institute of Standards and Technology (US Department of Commerce) and UOP LLC. The APS is supported by the US DOE, BES, OER under contract No. W-31-109-ENG-38.

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