

Influence of different drying conditions on Cu speciation in stream sediment, coastal sea sediment, and soil

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1 Introduction

An element in sediments and soil substances of the earth surface occurs in various physicochemical forms. The toxicity and bio-availability of elements change largely with their chemical forms. Although many speciation techniques have been proposed, a sequential extraction procedure has been most widely used to elucidate speciation of an element in sediments and soil substances. However, there is one reference material (BCR-701) available to quality control of speciation studies only for six elements (Cr, Ni, Cu, Zn, Cd and Pb). Thus, the provision of various kinds of reference materials and reference values for many elements obtained by speciation study would be beneficial for speciation study.

Thus, we require a wide range of geochemical reference materials such as stream sediment, marine sediment, lake sediment, and soil for the speciation study. To prepare such reference materials, we must know whether the initial chemical form in collected samples is preserved during the manufacturing process of geochemical reference materials. Therefore, in this study we elucidate the influence of different drying conditions on metal speciation in sediment samples because the process would have the largest impact on metal species in sediments and soils. Ohta and Kubota [1] have confirmed the validity of Cu speciation obtained by the sequential extraction using XANES spectroscopy. Thus, we focus on Cu speciation in stream sediment, coastal sea sediment and soil.

2 Sample materials

We collected stream sediment associated with Cu mine, muddy clay-rich coastal sea sediment deposited at anoxic estuarine condition, and Kuroboku soil (andosol) originated from volcanic ash and rich in organic materials. Collected samples were stored in polyethylene bags at 4°C, freeze-dried in the laboratory, and stored in refrigerator. Duplicated samples were stored in polyethylene bags, air-dried in the laboratory for 14-21 days at room temperature, and stored at ambient temperature without direct sunlight. Soil sample was sieved with a 2 mm screen. Other samples were sieved with a 0.18 mm screen. A sequential extraction procedure was applied to these samples in 2011 and 2013. We have confirmed that metal speciation in these samples change insignificantly by different drying conditions and storage period. However, sequential extraction procedure is

indirect speciation analysis: each chemical form in a material is destructively extracted using a chemical reagent. Thus, we identify and quantify chemical forms in these materials using X-ray absorption near edge structure (XANES) spectroscopy in 2015.

3 Experimental methods

The Cu in stream sediment, inner bay sediment, and soil were extracted using the sequential extraction procedure, which has been standardized by the Community Bureau of Reference (BCR) [2]. Table 1 summarizes the procedure used in this study. The BCR protocol extracts the elements in carbonate minerals or those weakly adsorbed on materials at step 1. Elements bound to Fe hydroxide and Mn oxide are extracted at step 2. Metal sulfides and elements bound to organic matter were extracted at step 3. The residual crystalline phases were decomposed at step 4. The concentration of Cu extracted at each stage was determined by ICP-AES.

Table 1: Outline of the sequential extraction procedure

Step	Extractant
1	CH ₃ COOH (0.11 mol/L), 16 h
2	NH ₂ OH·HCl (0.5 mol/L), 16 h
3	H ₂ O ₂ (8.8 mol/L), 1h at 20–30 °C and 1h at 85 °C, followed by CH ₃ COONH ₄ (1 mol/L), 16 h
4	HF-HNO ₃ -HClO ₄ , 3h 120°C

As for XANES spectroscopy, the residues after each step of the BCR extraction was filtrated through a 0.45 µm cellulose acetate membrane filter and freeze dried. The samples were stored in a refrigerator until XAFS analysis. The samples untreated with the BCR were enclosed in a polyethylene resin. As model compounds, several kinds of Cu compounds (e.g., sulfate salt and aqueous solution), metal doped Fe hydroxide (FeOOH), metal doped Mn dioxide (MnO₂), metal doped humic acid (HA), and sulfide ores, were also prepared. The Cu K-edge XANES spectra were recorded in a fluoresce mode at the BL-12C of KEK-PF. The fluorescence X-ray was measured by a 19 element pure-Ge SSD.

4 Results and discussion

Figure 1 shows the distributions of Cu concentrations in stream sediment, soil, and coastal sea sediment samples for the four fractions obtained by the BCR

protocol. The high proportion of Cu in stream sediment samples was extracted at step 1 (45 % of the total Cu), and at step 2 (30 % of the total Cu) and at step 3 (20 % of the total Cu). In soil samples, an extremely high proportion of Cu (70 % of the total Cu) was extracted at step 3 and the rest was mostly associated with the residual fraction (step 4). A significant amount of Cu was extracted at step 2 (35 % of the total Cu) and step 3 (50 % of the total Cu) for coastal sea sediment samples. Interestingly, there are no significant differences of Cu speciation determined by the BCR protocol between air-dried sample and freeze-dried one.

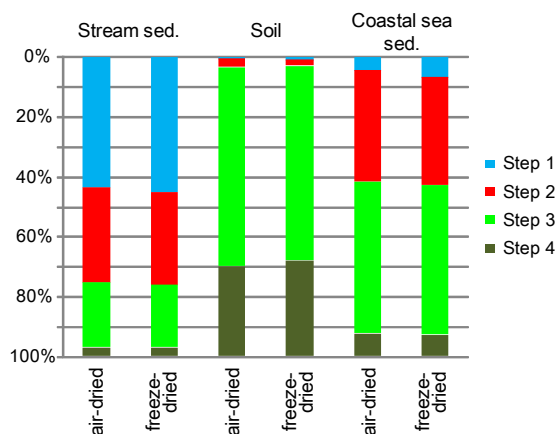


Fig. 1: Distribution of Cu concentrations in stream sediments, soil, and coastal sea sediments determined by the BCR protocol.

XANES spectra of Cu in the untreated stream sediment samples are shown Figure 2. XANES spectra of Cu in stream sediment do not differ considerably among the air-dried sample and the freeze-dried one. The features of XANES spectra of untreated sample were reasonably reproduced by the linear combination fitting (LCF) using five components of CuSO_4 , Cu-bearing FeOOH, Cu-bearing HA, JCu-1 (chalcopyrite), and the final residual phase (the residue after step 3 extraction). The CuSO_4 (20–25 % of the total Cu) is assumed to be an oxidation product of chalcopyrite and expected to be extracted at step 1. The percentages of Cu-bearing FeOOH (15–20 % of the total Cu) indicate the percentages of Cu bound to Fe hydroxides, which were extracted at step 2 extraction of the BCR protocol. Cu-bearing humic acid (<10 %) and JCu-1 (35 %) are used as a substitute for Cu bound to organic materials and metal sulfide ores, which are the target phases of the step 3 extraction. However, the estimated proportions of these compounds do not correspond to the BCR results perfectly.

Even though stream sediments were collected from downstream of Cu mine, XANES analysis suggests that the percentage of chalcopyrite to total Cu is only 35 % (Fig. 2). Furthermore, XANES spectra of the sample do not change significantly with the different drying methods. These facts suggest that chemical form of Cu in the river system has already been oxidized well: it has been kept in a steady state. We assume that oxidized chalcopyrite in

stream sediments have been altered partly to CuSO_4 and reacted with Fe hydroxide and humic substances.

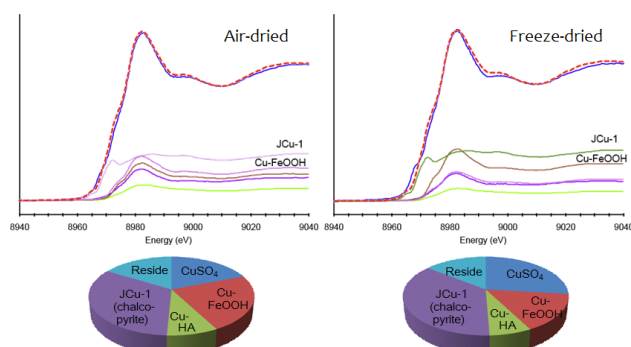


Fig. 2: LCF of XANES spectra of stream sediments derived from Hitachi Cu mine.

XANES spectra of Cu in soil samples untreated with the BCR protocol and their LCF results are shown in Figure 3. As with the case of stream sediment samples, XANES spectra of Cu in soil substances do not differ significantly between the air-dried sample and freeze-dried one. The features of XANES spectra of untreated samples were fitted by Cu-bearing HA (55 % of the total Cu), Cu sulfide (JCu-1) (5% of the total Cu), and the final residue (the residue after step 3) (40 % of the total Cu). The presence of Cu-bearing FeOOH was negligible in XANES spectra. The estimated proportions of step 3 (Cu-bearing HA and JCu-1) and step 4 (the residue after step 3) are similar to the concentration ratios of Cu extracted by the BCR protocol. The high proportions of Cu-bearing HA are reasonable because soil samples are rich in organic materials.

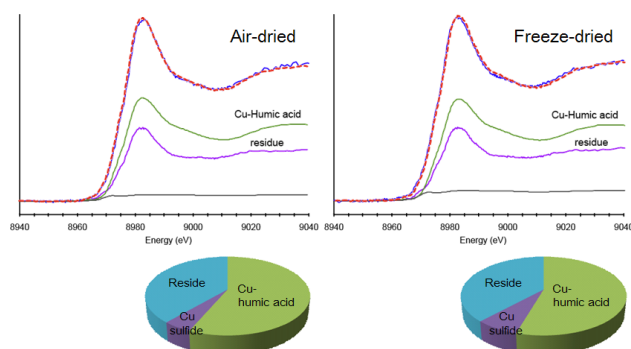


Fig. 3: LCF of XANES spectra of Kuroboku soil.

In contrast, XANES spectra of Cu in the coastal sea sediments collected from Tokyo Bay differ significantly among air-dried sample and freeze-dried one (Fig. 4), nevertheless there are no significant differences of the distribution of Cu concentrations determined by the BCR protocol (Fig. 1). XANES spectrum of the air-dried sample rather resembles that of stream sediment samples, However, XANES spectrum of freeze-dried sample shows the distinct shoulder peak at the lower energy side of the main peak and smaller main peak than that of air-dried sample.

LCF results show that Cu-bearing HA and Cu sulfide (JCu-1) are the most dominant species in air-dried sample and freeze-dried one, respectively (Fig. 4). A significant amount of Cu sulfide (77 % of the total Cu) in the freeze-dried sample indicates that authigenic Cu sulfide was formed in the inner bay sediment under the anoxic condition. However, the proportion of Cu sulfide (23 % of the total Cu) in the air-dried sediment is considerably smaller than those in the freeze-dried one. It is possible that authigenic Cu sulfide in sediments has been considerably oxidized during the air-dried period (14-21 days). The activity of aerobic microorganisms in samples may have accelerated the oxidation reaction of Cu sulfide in the drying process. The high proportion of Cu-bearing HA (70%) in XANES spectra of the air-dried sample indicates that Cu released in the fluid in the oxidation process of Cu sulfide has selectively bound with organic matters.

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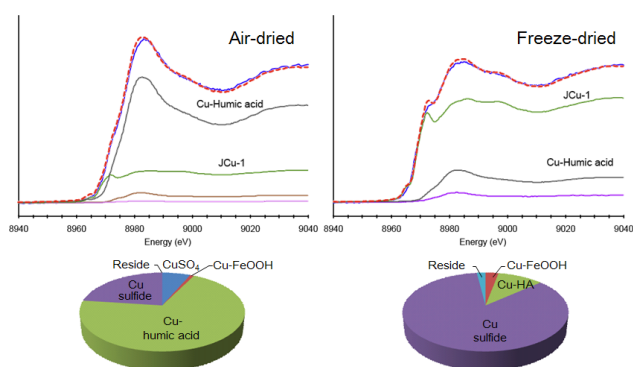


Fig. 4: LCF of XANES spectra of coastal sea sediments derived from the Tokyo Bay.

5 Summary

We examined the differences of Cu species in the air-dried sample and the freeze-dried one using the sequential extraction procedure (the BCR protocol) and XANES spectroscopy. Stream sediments associated with Cu mine and volcanic soil substances enriched in organic matter are abundant in reducing compounds of chalcopyrite and organic matters, respectively. However, there are no significant differences of Cu speciation in the air-dried sample and the freeze-dried one. In contrast, coastal sea sediment having an anoxic face has the different results from stream sediment and soil. XANES analysis revealed that authigenic Cu sulfide precipitate occurs abundantly in the freeze-dried sample, but it has been considerably oxidized in the air-dried sample. Curiously, there are no meaningful differences of Cu speciation obtained by the BCR protocol.

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References