Influence of different drying conditions on Cu and Zn speciation in sediment and soil substances

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Geological Survey of Japan, AIST provides nationwide geochemical maps of 53 elements using stream and marine sediments for environmental assessment on the earth's surface. However, toxicity and bioavailability of elements in materials change according to their chemical species. Therefore, elemental speciation would be informative to conduct more appropriate risk assessment in an environment. To perform reliable speciation analysis, we must know whether the initial chemical form in collected samples is preserved. Thus, we examine the influence of drying and storage procedures on metal speciation in sediment and soils.

We collected stream sediment associated with Cu mine, inner bay sediment, and Kuroboku soil (andosol) in 2010. Collected samples were stored in polyethylene bags at 4°C, freeze-dried in the laboratory, and stored in refrigerator. Duplicated samples are stored in polyethylene bags, air-dried in the laboratory at 25°C for 14-21 days, and stored at ambient temperature without direct sunlight. As a preliminary study, a sequential extraction (SEP) 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, SEP is indirect speciation analysis: each chemical form in a material is destructively extracted using a chemical reagent. Thus, we identify and quantify directly chemical forms in these materials using X-ray absorption near edge structure (XANES) spectroscopy in 2015. XANES spectra of Cu and Zn in stream sediment and soil do not differ considerably among air-dried and freeze dried samples. Even though stream sediments were collected from downstream of Cu mine, the percentage of chalcopyrite to total Cu is less than 20%. In contrast, XANES spectra of Cu and Zn in the inner bay sediments differ significantly among air-dried and freeze-dried samples. The proportion of metal sulfide in air-dried inner bay sediment is considerably smaller than those in freeze-dried sediment. Because inner bay sediment has anoxic faces, authigenic (possibly biogenic) metal sulfide may be totally oxidized during the air-dried procedure. We consider the inconsistency of metal speciation obtained by SEP and XANES spectroscopy in the presentation.