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Chemical and mineralogical characterization of arsenic, lead, chromium, and cadmium in a metal-contaminated Histosol

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ABSTRACT

The chemical and mineralogical forms of As, Pb, Cr, and Cd were studied in a metal-contaminated organic soil (Histosol) that received runoff and seepage water from a site that was once occupied by a lead smelter. Soil samples were collected from different depth intervals during both wet and dry seasons and analyzed using bulk powder X-ray diffraction (XRD), synchrotron-based micro X-ray diffraction (μ-XRD), and micro X-ray fluorescence (μ-SXRF) spectroscopy. There was a clear pattern of mineral distribution with depth that indicated the presence of an intense redox gradient. The oxidized reddish brown surface layer (0–10 cm) was dominated by goethite (α-FeOOH) and poorly crystalline akaganeite (β-FeOOH). Lead and arsenic were highly associated with these Fe oxides, possibly by forming inner–sphere surface complexes. Gypsum ($CaSO_4 \cdot 2H_2O$) was abundant in the layer as well, particularly for samples collected during dry periods. Fe (II)-containing minerals, such as magnetite (Fe_3O_4) and siderite ($FeCO_3$), were identified in the intermediate layers (10–30 cm) where the reductive dissolution of Fe(III) oxides occurred. A number of high-temperature minerals, such as mullite ($3Al_2O_3 \cdot 2Si_2O$), corundum (α-Al_2O_3), hematite (α-Fe_2O_3), and wustite (FeO) were identified in the subsurface and they probably formed as a result of a burning event. Several sulfide minerals were identified in the most reduced layers at depths >30 cm. They included realgar (AsS), alacranite (As_4S_4), galena (PbS), and sphalerite (Zn, Fe^{2+})S, and a series of Fe sulfides, including greigite ($Fe^{2+}Fe^{3+}{}_2 S_4$), pyrrhotite ($Fe_{1-x}S$), mackinawite (FeS), marcasite (FeS_2), and pyrite (FeS_2). Most of these minerals occurred as almost pure phases in sub-millimeter aggregates and appeared to be secondary phases that had precipitated from solution. Despite the elevated levels of Cd in the soil, no specific Cd phases were identified. The complex mineralogy has important implications for risk assessment and the design of in-situ remediation strategies for this and similar metal-contaminated sites.

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1. Introduction

Metal contamination of soils and groundwater at mine and smelter sites is a global environmental problem. Six of the 11 most common contaminants on the U.S. Environmental Protection Agency (USEPA) National Priority List are metals (USEPA, 1995). Among them, Pb, As, Cr, and Cd are of particular concern because of their toxicity and potentially harmful effects on the environment (Sparks, 2002).

Risk assessments currently use total metal contents to determine risk posed by metals in various environmental media (Basta et al., 2001). Metals in soils, however, exist in many geochemical forms with widely different solubilities and geochemical stabilities. Speciation thereby is the key to understanding metal mobility and bioavailability in the environment, and can provide important information for risk assessment and remediation strategies. Traditional chemical extraction techniques are often used for this purpose, but it is now widely recognized that the forms determined by sequential extractions are operationally defined and that transformation among forms may occur during extraction (Scheckel et al., 2003). Such bulk analyses may often under- or over-estimate metal bioavailability (Arai et al., 2006). Geochemical speciation models may assume the presence or absence of particular solid phases, but without direct identification, the validity of these models is often questioned (Johnston and Sposito, 1987).

X-ray diffraction (XRD) is the technique of choice for directly determining mineral phases in soil. Conventional laboratory-based bulk XRD usually requires 3–5% by weight of well-ordered crystalline material for phase identification. Even highly metal-contaminated soils rarely reach this concentration. In addition, several hundred milligrams of material is usually required to obtain a good diffraction pattern, so spatial differences can usually only be resolved over length scales of the order of centimeters. Although sub-millimeter variability can often be observed visually in a soil sample by variations in color or other physical features, sampling sufficient material of a particular

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type of feature still usually results in mineralogically complex diffraction patterns in which significant, but not abundant, phases are easily overlooked. Synchrotron X-ray beams, on the other hand, are now routinely focused to 10 × 10 μm spot sizes or smaller, allowing one to obtain diffraction patterns from sub-millimeter areas with ease.

Metals are often distributed heterogeneously in the soil matrix and concentrated in a few "hot spots" such as precipitates around roots, microbial colonies, or on the faces of cracks and pores (Thompson et al., 2005). Features down to ~1 mm in diameter are easily observed with the unaided eye when they contrast with the surrounding soil matrix. Even smaller features, down to ~50 μm in diameter, can be easily observed under a binocular microscope and sampled and manipulated with needles and fine tweezers. Synchrotron-based μ-XRD and μ-SXRF spectroscopy techniques make it possible to analyze these sub-millimeter areas directly, with the potential of providing new and significant insights into the mineralogy of contaminant metals in soils.

As part of a larger study aimed at identifying soil amendments to reduce the bioavailability of potentially toxic metals in contaminated soils (Szlezak, 2006), a highly metal-contaminated Histosol in an active wetland was sampled for use in greenhouse and laboratory studies. Initial studies indicated high toxicity to earthworms and lettuce, large amounts of extractable Pb, As, Cr, Cd, and other metals, and a complex mixture of mineral phases.

The objective of this study was to identify and characterize the mineral phases present in an organic soil that was highly contaminated with Pb, As, Cr, Cd, and other metals by using synchrotron-based μ-XRD and μ-SXRF techniques coupled with total chemical analysis. We discuss the results in the context of the geochemical processes of Pb, As, Cr, and Cd in this and similar wetland soils, and the implications for the use of a soil like this for greenhouse and laboratory studies of metal bioavailability.

2. Materials and methods

2.1. Field sampling

Samples were collected from a soil on a site in Indiana that had hosted a lead smelter from the 1920s to the 1980s (Fig. 1). The organic soil, mapped as a Houghton muck (euic, mesic, and Typic Haplosaprist), is in a wetland at the edge of the site and had apparently received runoff from the site over the years. The site has been remediated and is covered with common reed (*Phragmites australis*) and cattail (*Typha* sp.). The water table is at or slightly above the soil surface for much of the year, but the surface layer dries occasionally. The site was sampled 4 times, between March 2004 and August 2005.

Sample collection 1 (designated S1, March 11, 2004) — the first sampling was collected to a depth of ~50 cm to obtain a bulk sample for greenhouse and laboratory studies. Initial characterization indicated very complex mineralogy with the presence of both oxide and sulfide minerals that cannot be stable under the same redox conditions.

Sample collection 2 (S2, September 24, 2004) — the site was resampled with the objective of sampling more carefully controlled depth increments. Although there was no standing water on the soil surface, the surface was still moist and the water table was within a few centimeters of the soil surface. A small pit was excavated to a depth of ~40 cm and samples were collected over different depth intervals (Table 1) based on morphology, placed into plastic bags, transported to the laboratory at ambient temperature, and then air dried. The materials from 1–5 cm below the surface was distinctly greenish when sampled, but became brownish when exposed to the atmosphere for only a few minutes, perhaps indicating the presence of "green rust". Materials deeper in the profile were dark gray to black in color.

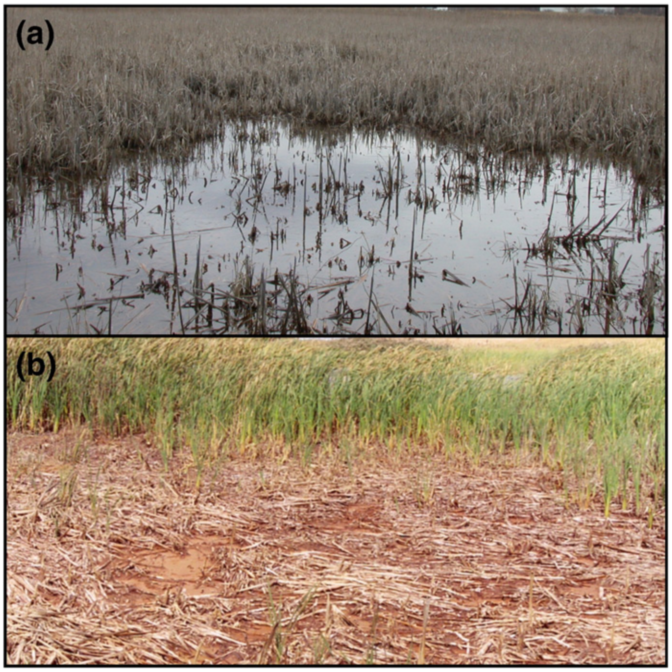

Fig. 1. (a) View of the sampling site on April 1, 2005 when the surface was covered by about 20 cm water. (b) View of the sampling site on August 5, 2005 when the water table was about 30 cm below the soil surface.

Table 1
Field sampling descriptions of the soil samples.

Sample date	Water table	Sample	Depth (cm)	Temp (°C)	pH	Munsell color	Descriptions
03/11/04	~10 cm above the soil surface	S1	0–50				Mixed soil
09/24/04	~5 cm below the soil surface, surface material was moist, but there was no free water	S2a	0–1				Reddish brown precipitates
		S2b	1–5				Greenish material
		S2c	10–18				Gray muck (sapric material)
		S2d	18–30				Gray muck (sapric material)
		S4e	30–40				Gray muck (sapric material)
04/1/05	~20 cm above the soil surface	S3a	0–10	9.3	5.30	5 YR 3/2	Dark reddish brown precipitate
		S3b	10–20	8.4	5.66	7.5 YR 3/2	Dark brown muck (sapric material)
		S3c	20–30	7.6	5.80	7.5 YR 5/1	Gray muck (sapric material)
		S3d	30–50	7.5	5.83	7.5 YR 5/1	Gray muck (sapric material)
		S3e	50–65	9.5	6.30	5 YR 3/1	Very dark gray muck (sapric material)
08/5/05	~30 cm below the soil surface	S4a	0–15				Reddish brown precipitates
		S4b	15–20				Faintly greenish material
		S4c	25–30				Gray muck (sapric material)

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