Speciation and mobility of Zn, Cu and Pb in a truck farming soil contaminated by sewage irrigation

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Abstract. The forms and mobility of Cu (290 mg/kg), Zn (1103 mg/kg), and Pb (535 mg/kg) in a soil used for intensive truck farming from the Region Ile-de-France, and which has been irrigated for more than a century with sewage water from the city of Paris, have been studied by chemical treatments and advanced x-ray techniques. Elemental associations and forms of metals were determined qualitatively and quantitatively by a combination of physical techniques, including μPIXE (Cu, Zn, Pb), μSXRF (Cu, Zn), μEXAFS (Zn) and powder EXAFS (Zn). The nature, number, and relative proportion of Zn species were obtained by principal component analysis and decomposition of Zn K-edge EXAFS spectra. These data collectively indicate that Cu is associated mainly with organic matter, and that Zn and Pb are bound essentially to mineral constituents. Four Zn-containing species were positively identified : Zn-phosphate and phyllosilicate as dominant species, and Zn-Fe oxyhydroxide and willemite (Zn_2SiO_4) as minor species. Studies are underway to determine the structural forms of Cu and Pb. Depending on the chemical treatment, up to 70% Cu, ~50% Zn, and ~85% Pb can be removed in a few days with citrate and EDTA. Citrate is generally at least as efficient as EDTA, and it has the advantage of being easily biodegradable and, hence, less harmful to ecosystems.

1. INTRODUCTION

Irrigation of agricultural lands by sewage waters is a common practice in many countries to improve the fertility and physical properties of soils. However, the presence of heavy metals (HMs) in these wastewaters represents a risk to ecosystems. The mobility and bioavailability of HMs largely depend on their chemical form (speciation) and on soil physico-chemical characteristics [1]. Recently, promising results in phytoextraction of HM contaminated soils have been obtained by enhancing metal uptake by plants with synthetic chelates and organic acids [2]. The aims of this study are two-fold, (i), to identify the nature of HMs (Zn, Cu and Pb) species in a representative irrigated agricultural soil and, (ii), to measure their mobility consecutively to the addition of ligands in order to elaborate efficient remediation strategies.

2. MATERIALS AND METHODS

2.1 Soil Samples and Characteristics

The soil comes from Pierrelaye, a large truck farming area located 30 Km to the West of Paris, which has been irrigated for more than a century with sewage water from the city of Paris. As a result of this practice, it contains 290 mg/kg Cu, 1103 mg/kg Zn and 535 mg/kg Pb.

The soil was collected, freeze-dried and fractionated by sieving and centrifuging at 2000, 600, 200, 50, 20 and 2 μm. Sandy fractions (2000-200 and 200-50 μm) are dominant and account for ~70 % of the soil weight, the fine sandy fraction (200-50 μm) representing ~43 wt%. The highest amounts of Zn, Cu and Pb are in the clay (<2 μm) and fine silt (2-20 μm) fractions : ~40 and ~30% of each HM, respectively. The clay fraction is also enriched fivefold in Fe and P compared to the bulk soil.

The soil was prepared for speciation studies as pressed pellets from the finely ground soil powder, and as micro-polished 30 μm-thick sections after embedding in epoxy resin.

2.2 Metal Extraction Experiments

The mobility of HMs in the soil was evaluated with EDTA and citrate. For EDTA extraction, 1 g of soil was mixed with 5 mL of 0.01 M Na_2EDTA at room temperature [3]. In the citrate treatment, 1 g of soil was mixed with 12 mL of 0.1 M citric acid, adjusted to pH 5.5 with 0.1 M NaOH [4]. In the first series of experiments (kinetics study), metal extractability was measured for different time of extraction (24 h, 72 h and 144 h). In the second series of experiments, metal extractability was measured following successive extraction cycles of 24 h with renewal of the extractant every cycle. All experiments were duplicated, and leachates and solid fractions were analyzed by ICP-AES.

2.3 Microprobe Analyses and EXAFS Spectroscopy

The lateral distribution of HMs was investigated on micrometer-scale using micro-particle-induced X-ray emission (µPIXE) and micro-synchrotron-based X-ray radiation fluorescence (µSXRF) performed on the soil thin sections. The µPIXE measurements were carried out at the nuclear microprobe facility of the Pierre Süe Laboratory (Saclay, France). Elemental maps were recorded by measuring with a Si(Li) detector the fluorescence radiation induced by a 2.5 MeV H^+ beam with a current of 300 pA and a cumulative charge of 2 µC. Samples were scanned with a 5 µm step and a beam dimension of 5×5 µm. The µSXRF maps were recorded on the 10.3.2 beamline at the Advanced Light Source (ALS, Berkeley, USA) operating at 1.9 GeV and 200-400 mA. The samples were scanned with a 5 µm step trough a 5×5 µm sized X-ray beam. The fluorescence-yield was measured using a 7-element Ge solid-state detector and normalized by I0.

The forms of HMs and their proportions were determined by extended X-ray absorption fine structure (EXAFS) spectroscopy. Zn- and Cu- K-edge µEXAFS spectra were recorded on the thin soil sections in fluorescence mode with a 10×5 µm sized beam delivered by the 10.3.2 beamline at the ALS. Bulk EXAFS measurements were performed on the pellet samples on the FAME beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The fluorescence signal on FAME was measured with a Canberra 30-element Ge solid-state detector. EXAFS data reduction was carried out following a standard procedure [5]. The nature, the number, and the proportion of Zn containing species were obtained by principal component analysis (PCA) and spectral decomposition using a linear combination of reference compounds [6, 7]. The uncertainty in the proportion of species is estimated to ±10%.

3. RESULTS AND DISCUSSION

3.1 Extractability of Heavy Metals

The mass percentages of HMs extracted with EDTA and citrate against time and number of washings are presented in Figure 1. The extractability of metals in 24 h ranks as follows Cu > Zn >> Pb for both extractants. Citrate extracted more Cu and Zn than EDTA, with values equal to 55 and 50% for Cu, and 43 and 40% for Zn, respectively. The contrasted behavior of Pb, and specifically its lower extractability compared to Zn and Cu (25% with EDTA and 10% with citrate), suggests that lead is more tightly bound to soil constituents. Single extraction for 144 h removed 65 to 70% Cu, 45 to 50% Zn, and 25 to 35% Pb. Kinetics studies showed that the extraction rate levelled off after 72 h with EDTA, whereas no equilibrium was reached with citrate after 144 h of treatment. In all cases, metal removal increased when the extraction procedure was repeated (Fig. 1b). The extraction curves have a logarithmic shape with citrate and a linear-shape with EDTA. Removal of Pb with citrate increased from 10% to 50% and to 85% with one, two and four extraction cycles.
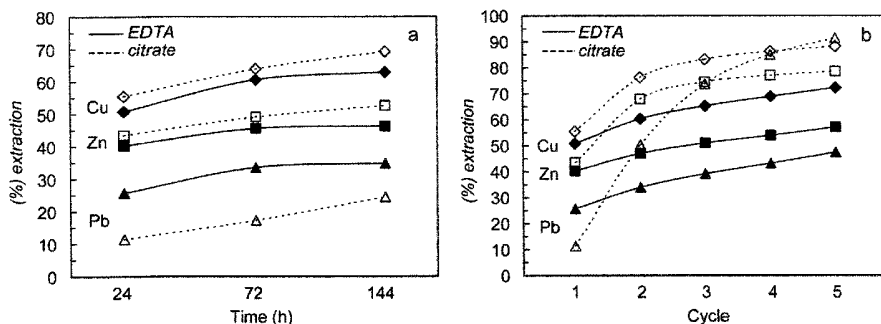
Figure 1. Metal extraction as a function of extraction time (a) and number of extraction cycles (b) with EDTA (solid line) and citrate (dotted line) expressed as mass percentages.

3.2 Speciation of Heavy Metals

μPIXE elemental maps (not shown) showed a heterogeneous distribution of Zn, P and Fe at the micrometer scale. High Zn amounts were observed in P-rich and Fe-depleted aggregates. Two different aggregates were examined and had the same Zn/P ratio of ~2. Pb, and also Zn, were detected in the fine clay matrix. The presence of multiple metal species (at least for Zn) was confirmed by μSXRF. Zn and Pb were highly correlated with Fe (cross-correlation value $\rho = 0.86$), suggesting an association with Fe oxides. Lower Cu-Fe correlation values were observed systematically, and Cu was found to be bound predominantly to organic debris. The contrasted behavior of Zn and Cu is illustrated in Figure 2 using the population-segmentation method [6].
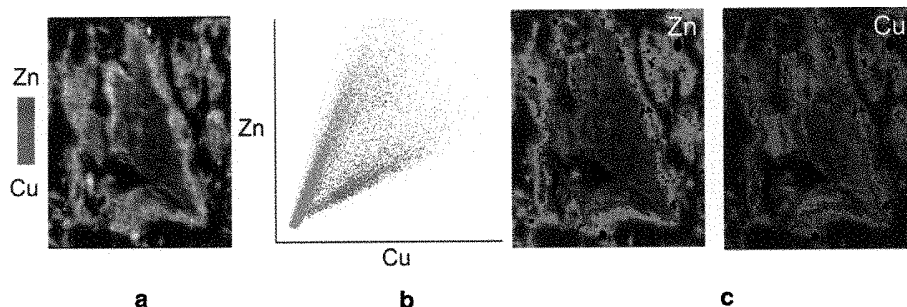

Figure 2. Population-segmentation method to isolate metal species. (a) Bicolor map of Zn (green) and Cu (red). The large reddish (Cu-rich) area in the center was identified by light microscopy as organic matter with a reticular structure. Wherever there is Cu, there is also Zn, but the Zn/Cu ratio varies throughout the area. (b) Zn vs. Cu scatterplot. There are two distinct branches of points with roughly constant Zn/Cu ratio in each population. The high-Zn/Cu population is colored in green, the low-Zn/Cu is in red. Intermediate area is in blue. (c) Greyscale maps for Zn and Cu colored according to membership in the populations defined as in part b. There are three regions, within the organic area, outside the organic area, and a border region. The brightness of each pixel is related to the Zn or Cu concentration. While the green region is relatively brighter in Zn that the red one, and vice versa for Cu, both metals are present in all regions, but probably in different forms.

Zn K-edge μEXAFS spectra were collected in three regions-of-interest: (Zn,P)-, (Zn,Fe,P)- and (Zn,clay)-rich areas. A selection of point spectra is presented in Figure 3a together with the bulk EXAFS spectrum. As expected, the bulk spectrum has an intermediate shape since it is a component spectrum corresponding to a weighted average of spectra from individual species. Four Zn species were positively identified so far : Zn-containing phosphate and phyllosilicate (herein modelled by kerolite) as dominant species, and Zn-sorbed amorphous Fe oxyhydroxide (modelled by ferrihydrite) and Zn-containing anhydrous silicate (willemite) as minor species. The bulk EXAFS spectrum was successfully reconstructed with a linear combination of the first three Zn species (Figure 3b), the fourth being quantitatively scarce. Studies are underway to determine the chemical forms of Cu and Pb.
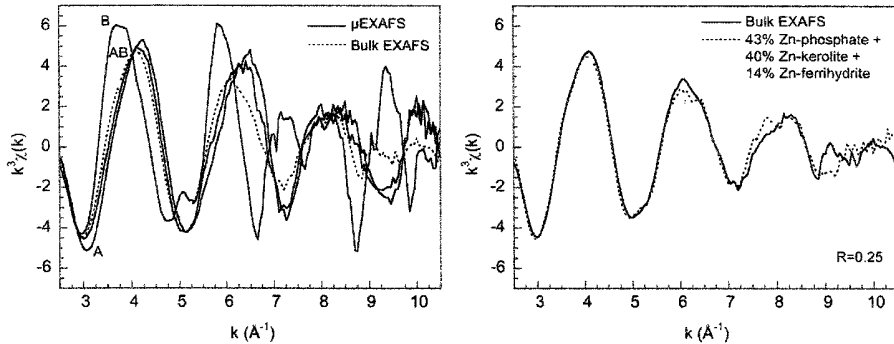
Figure 3. Zn K-edge EXAFS analysis. (a) μEXAFS spectra collected in (Zn,P)-, (Zn,clay)- and (Zn,P,Fe)-rich areas (A, B and AB, respectively) compared to the bulk EXAFS spectrum. (b) Three-component least-squares fitting of the bulk EXAFS spectrum by a linear combination of reference spectra. The best simulation was obtained for 43% Zn-phosphate ($Zn_3(PO_4)_2 \cdot 2H_2O$) + 40% Zn-kerolite ($Si_4(Mg_{1.78}Zn_{1.22})O_{10}(OH)_2 \cdot nH_2O$) + 14% Zn-ferrihydrite (estimated accuracy ±10% of the total Zn). Willemite (Zn_2SiO_4), firmly identified by μEXAFS, represents less than 10% of the total Zn because adding this component does not significantly improve the spectral simulation.

4. CONCLUDING REMARKS

In the studied truck farming soil, Zn is predominantly bound to phosphate (~40%) and phyllosilicate (~40%). The Zn-phosphate association probably results from soil fertilization. Zn-phyllosilicate either originates from Zn sorption on clay constituents from the soil, or from the co-precipitation (i.e., neoformation) of dissolved Zn and silica owing to the sandy nature of the soil and the presence of Zn in the wastewaters. The Zn-hydrous iron oxide association represents less than ~15%, and presumably corresponds to sorption of dissolved Zn on pre-existing Fe oxides. The origin of willemite is unknown. Organic matter is the main sink for Cu. Similarly to Zn, Pb appears to be mainly bound to inorganic constituents. Depending on the chemical treatment, up to 70% Cu, ~50% Zn, and ~85% Pb can be removed on a short period of time by organic ligands. Citrate is generally at least as efficient as EDTA, and it has the advantage of being easily biodegradable and, hence, less harmful to ecosystems.

Acknowledgements

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