Cd and Zn speciation and mobility in contaminated soil: physical micro-characterization techniques, chemical extraction methods and isotopic exchange kinetics.

Valérie Sappin-Didier [A] , Yann Sivry[B], Marguerite Munoz[C], Jean Riotte[D], Laurence Denaix[A], Bernard Dupré[C]

[A]INRA UMR 1220 TCEM, INRA Bordeaux-Aquitaine, av. E. Bourlaux, BP 81, 33883 Villenave d'Ornon (France)
[B]Laboratoire de Géochimie des Eaux, IPGP - UMR 7154, Université Diderot - Paris7, 75205 Paris Cedex 13, France
[C] Université de Toulouse-UPS (SVT-OMP), CNRS, LMTG, 14 av. E. Belin, 31400 Toulouse – France.
[D] Université de Toulouse-UPS (SVT-OMP), IRD, LMTG, 14 av. E. Belin, 31400 Toulouse – France.

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Abstract
Zinc and Cd distribution and mobility in a polluted soil were studied using a combination of micro-characterization, physical, chemical and isotopic techniques. The study was conducted in a fluvisol, polluted by non-ferrous metallurgical activities. Results showed large amounts of metals in mineral phases resulting from the industrial activity. The main mineral phases detected due to metallurgic activity were coal, coke, iron and multimetallic oxides, pure metal alloys, sulphides and glass. Zinc was mainly extracted in the reducible pool (64%). This pool comprised reducible FeIII oxides and oxy-hydroxide including hematite, goethite, magnetite and multimetallic oxide phases (franklinite). Only 10% of Zn was extracted in the exchangeable pool, whereas 40% of Cd was extracted in this pool and 46% in the reducible pool.
The isotopically exchangeable kinetic method showed that 60% of Cd and only 4% of Zn were exchanged after one week. Zn exchanges were quicker than Cd ones. Zn is preferentially located in anthropogenic mineral phases, involving a low exchangeability. In contrast, the high values of isotopically exchangeable Cd seem to be linked to its presence in the clay, coal and organic matter.

Introduction
Non-ferrous metallurgical activities have resulted in the release of trace elements in the biosphere such as Cd, Pb, As, Zn, which may lead to the accumulation of metals in soils and consequently in plants. The environmental risk is determined for a large part by the soil-solution equilibrium rather than by the total elemental concentration in soil. The assessment of this equilibrium is more complex in soils contaminated by non-ferrous metallurgical activities with inputs of different types of anthropogenic particles such as ore, slag and ash. Few studies have been conducted on the reactivity of these phases and on the transfer of metals (including Cd) from these phases to the soil solution.
The aim of the present study was to analyze the fate of Cd and Zn in a soil contaminated by non-ferrous metallurgical activities, and more specifically: (1) to identify mineral-bearing phases of Zn and Cd in the contaminated soil; (2) to establish the link between mineral-bearing phases and mobility of Cd and Zn. We used an original approach combining physical, chemical and isotopic methods. The location of Cd and Zn in the soil phases was identified using micro-characterization techniques (XRD, MEB-EDS, Electronic microprobe and LA-ICP-MS) and by a sequential extraction method. The mobility of the metals was analyzed using isotopic exchange kinetics.

Materials and Methods
The soil was sampled at a floodable site, affected by an industrial Zn-ore smelting plant. The soil is a sandy acid (pH 5.3) fluviosol formed on a clastic schist substratum. The soil characteristic and metal concentration in soil are presented in table 1.

Table 1. Soil characteristics and total metal concentration in V1 soil. (1) Baize 1997; (2) Kapata-Pendias et al. (2001).

	pH	Organic matter	CEC	Cd	Zn	Common French Soils Cd	Zn
		g/kg	cmol+/.kg	mg/kg		mg/kg	
V1 soil	5.3	43	6.7	47.5	2983	0.05-0.45 [(1)]	1-25 [(2)]

X-ray diffractometry (XRD) was performed on bulk powders and oriented preparations with an INEL CPS 120 diffractometer using Co Kα radiation. Mineral phases were identified using optical metallographic microscopy and then Scanning Electronic Microscopy (JEOL6360LV) coupled with Energy Dispersive Spectrometry (PGT Sahara). Chemical analyses were carried out with a CAMECA SX 50 (Samx automation) Electron Probe Micro Analyzer equipped with three spectrometers (LiF, PET and TAP crystals) at Toulouse University (France).

The metal distribution was quantitatively estimated by sequential extraction (Tessier and Campbell 1991). Isotopic exchange kinetic was carried out to measure the exchangeable Cd and Zn. The isotopic exchange kinetic was realised with stable isotopes ([106]Cd, [67]Zn).

Results. Discussion

Metal bearing phases.

The soil is mainly composed of common natural phases, among which XRD spectra indicate that quartz is the most abundant mineral, followed by micas, clay minerals (illite, chlorite, kaolinite) and albite. The presence of hematite was evidenced by XRD analysis in the fine fraction (< 20 μm).

Microscopic observation together with MEB-EDS, electron microprobe and LA-ICP-MS analyses, led to the characterization of numerous mineral phases in soil, related to metallurgic context. Numerous rounded shape grains, plain or vacuolar made up of metallic Fe, Fe oxides, glass (Si, Al, Ca, Fe) or mixed glass and oxides, typical of metallurgic contamination, occur in all granulometric fractions.

Other mineral fraction such as coal and coke grains, pure metal alloys and scarce sulfides were found.

The vitreous glass forming slag fragments and spheroids is plain or vesicular and contain metallic inclusions, most of them of spherical shape. Zn is a major constituent of spheroids (19 % in mass). LA-ICP-MS analyses carried out in large enough slag samples showed Cd contents ranging from 90 to 280 mg/kg.

The only metal bearing silicate found is willemite (Zn_2SiO_4) as a plurimicroning ring around a quartz grain. The FeII and FeIII oxide identified are wustite (FeO), magnetite (Fe_3O_4), hematite (Fe_2O_3), Fe-oxyhydroxides such as goethite (FeOOH) and the amorphous phase like ferrihydrite ($Fe(OH)_3$). Most contain significant levels of Zn with a maximum of 0.85% in goethite and iron metal, and 2.4% in hematite. Cd content is below the detection limit of the microprobe (0.05 %). In addition, franklinite ($ZnFe_2O_4$) is identified with a Zn content of 27 %. Up to 0.57% of Cd is detected in multimetallic Sn, Fe, Pb and Zn oxides.

Sulfide minerals identified are pyrite (FeS_2), sphalerite (ZnS) and chalcopyrite ($CuFeS_2$). In multimetallic sulfides, observed as spheroidal inclusions in slag particles, the Zn content is 21 % while Cd is not detected. Multimetallic alloy fragments as scarce grains of a few microns are found, with Cd contents up to 0.77%.

Numerous fragments of coal and coke were found in the riverine soil. Coal forms homogeneous, friable, matt fragments, while coke shows a typical hard glassy, shiny, vacuolar feature. The first type of coal had an origin from coal mine or thermic plant. In this coal, the Cd content was below the detection limit (300 mg/kg). On the other hand, the coke grains display metal enrichment zones at the edge of the grains. Zn appears significantly and Cd content amounts up to 2700 mg/kg. The coke displays characteristics of coal that had been submitted to high temperatures which, together with metal enrichment, suggest a metallurgical source.
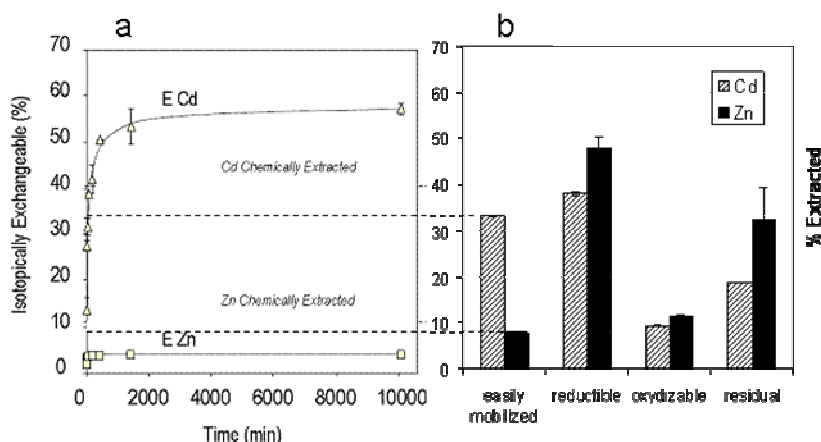

Figure 1. Mobility of Cd and Zn in the studied soil. a: Isotopic Exchange Kinetic results. The Cd and Zn exchangeable pools (ECd and EZn, respectively) are plotted as a function of the interaction time between the tracers and the soil solution. b: Chemical Sequential Extractions results. The proportions of Cd and Zn are reported for each geochemical pools.

Geochemical pool
The metal distribution has been quantitatively estimated by a sequential extraction procedure to discriminate between heavy metals *(1)* easily mobilizable (water-soluble, exchangeable and acido-soluble) *(2)* reducible pool, *(3)* oxidizable pool and *(4)* residual pool (Figure 1b). The chemical extraction provides additional information on metal scavenging or affinities when considering the cumulated amounts for each geochemical pool.

The (1) pool represents 41 % and 10.4% of total Cd and Zn, respectively. Contaminants may be adsorbed on iron oxide and oxy-hydroxide phases identified in this soil. The contribution of weak-bond sites on other particles such as coal, coke and vitreous spheroids should be taken into account. According to Arpa et al. (2000), it would be an efficient metal scavenging via ion exchange with carboxylic acid and phenolic hydroxyl functional groups on its surface. The large discrepancy between Cd and other metals (1% of As, Pb, Sn extracted) suggests that the way of Cd contamination may have been different from other metals: part of Cd was probably brought under dissolved form whereas other metals were included in particles. The (1) pool may correspond to metal adsorbed on clays (kaolinite, illite and chlorite), thanks to exchangeable interfoliaceous cations/high surface charges.

The (2) pool was constituted of 3 steps. The 1st step extracts theoretically the Mn oxides, the 2nd step extracts amorpheous iron oxy-hydroxides and the 3rd step the crystallised oxides. During the 1st step, 20% of Mn and 0.2 % of Fe were extracted. The 2nd and 3rd steps extract 19 and 21 % of Fe, respectivelly, and 22 and 12 % of Mn, respectivelly. Cd is released at 1st step (16%), but also in similar proportions as Mn in 2nd and 3rd steps (13% and 9 % respectively). This suggests that Cd is linked to the Mn oxides, either adsorbed or incorporated in their structure. Finally, the (2) pool contains the largest amounts of Cd and Zn, with 38 and 48 %, respectively. It concerns metal included on FeIII oxides and oxy-hydroxides detected in this soil (goethite, hematite, franklinite and magnetite) and also likely the multimetallic oxide phases, in which up to 5700 mg/kg of Cd was detected.

The (3) pool represents only 11.5 and 15.4 % of Cd and Zn, respectively. It corresponds to metallic elements complexed with organic matter, associated with sulphides and other reduced phases such as FeII oxides, pure metal phases and alloys. These latter might significantly contribute to this pool since they contain up to 7700 mg/kg of Cd.

Very small amounts of Cd and Zn are present in the (4) pool.

The exchange kinetic is very different between Cd and Zn (Figure 1a). The amount of Cd isotopically exchanged increased exponentially during the first day, to reach ~60% of the total Cd after one week. Equilibrium was not fully reached, which implies that maybe all the exchangeable Cd was not quantified. In other words, isotopically exchangeable Cd represents probably slightly more than 60% of total Cd. The amount of isotopically exchangeable Zn was strongly lower than that of Cd (4% of the total Zn) and the equilibrium value was reached before the end of the first day. Cd and Zn isotopic exchange kinetics are also very differents. During the first 30 minutes, the ECd value reaches 55% of the total exchangeable pool (i.e. 32 % of total Cd), whereas EZn reaches up to 78% of this pool during this same time. Then, Zn exchanges are smaller but faster than Cd exchanges in this soil.

In comparison to the sequential extractions results, it appears that the proportion of exchangeable Zn is slightly lower than the easily mobilized Zn (pool 1). On the contrary, the amount of isotopically exchangeable Cd is higher than the Cd easily mobilized (pool 1). Thus, the isotopically exchangeable Cd not only takes into account the Cd mobilized (pool 1), but also part of reducible pool. This result is consistent to that of Ahnstrom and Parker (2001), who show the absence of any direct correspondence between the Cd fractions determined by the sequential extraction and the IE Cd. These authors argue that the soluble/exchangeable, sorbed/carbonate and oxidizable fractions measured by the sequential extractions contribute to the measure of IE Cd. The assumption is that the isotopically exchangeable Cd takes into account the Cd in pool 1 and part of Cd extracted in the pools 2 and 3.

Conclusion
The combination of physical characterization techniques and chemical analyses in a polluted soil has helped to connect the low proportion of chemically exchangeable Zn to the anthropogenic origin of Zn bearing mineral phases. Zinc is localized in reducible phases (franklinite, multimetallic oxide, Fe oxide). It is much mobilized and exchangeable (4%). In contrast, Cd is highly exchangeable in this soil, s shown by chemical extractions and isotopic exchanges. The cadmium was detected in 4 mineral phases: coke, alloys multimetallic, multimetallic oxides and slag glass. But its distribution on clay and organic matter may explain the fastness of exchanges.

References

Ahnstrom ZAS, Parker D (2001) Cadmium reactivity in metal-contaminated soils using a coupled stable isotope dilution-sequential extraction. *Environment Science and Technologie* **35**, 121-126.

Baize D (1997) Teneurs totales en éléments traces métalliques dans les sols (France). (Ed. INRA: Paris) 410p.

Kabata-Pendias A, Pendias H (2001) Trace Elements in Soils and Plants (Boca Raton,Florida, USA)

Tessier A, P Campbell (1991) Comment on pitfalls of sequential extraction. *Water Research* **25**, 115-117.