Degryse F., Buekers J. & Smolders E. (2004). Radiolabile cadmium and zinc in soil as affected by pH and source of contamination. *European Journal of Soil Science*: 113-121.

Author manuscript

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Running title: Radio-labile Cd and Zn in soil

Radio-labile cadmium and zinc in soils as affected by pH and source of contamination

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Summary

The determination of radio-labile metals in soil has gained renewed interest for predicting metal availability. There is little information to what extent the fraction of labile metal is affected by the soil properties and the source of metal contamination. The radio-labile content (E value) of Cd and Zn was measured in field collected soils with Cd and Zn originating from different sources. The E values were erratic and sometimes even exceeded total metal content when the concentration in the soil extract was less than $8 \mu\text{g Zn l}^{-1}$ or less than $3 \mu\text{g Cd l}^{-1}$. Addition of EDTA (0.1 mM) to the radio-labelled soil suspension resulted in larger concentrations of Cd and Zn in solution and smaller E values for these soils. The E values were, however, unaffected by the presence of EDTA (0.1 mM) in soils with larger concentrations Cd and Zn in solution.

The % E values (E value relative to aqua regia soluble metal content) ranged from 9% to 92% (mean 61%) for Cd and from 3% to 72% (mean 33%) for Zn. No correlation between soil properties and % E was observed for Cd, and the % E of Zn was negatively correlated with soil pH ($r = -0.65$). There was a strong negative correlation between pH and % E in soils enriched with metals in soluble form (e.g. metal salts, corrosion of galvanized structures). In soils where Cd or Zn were added in a less soluble form, no such correlation was found, and % E values were generally less than in soils spiked with metal salts, suggesting that the source of the contamination controls mainly the labile fractions of Cd and Zn.

Introduction

There is a general consensus that total metal concentrations in soil bear little relationship to metal exposure or effect (Allen, 2001). Numerous studies have been undertaken to define metal availability more correctly than based on total concentrations only. The bioavailability of metals might correspond better to free ion activity in the soil solution (*intensity*) than to total metal concentration (Parker & Pedler, 1997). The concentration in solution is buffered by the amount of metals on the solid phase (*quantity*) that contributes to the distribution between solid and solution within a realistic time. The amount of metal fixed is defined as the difference between the total metal content and the amount in the labile pool. Fixed fractions of metals may be conceived as metals entrapped within minerals and not contributing to the immediate solid–solution distribution.

Metal fixation may be related to slow reactions in soil that remove metals from the sorption surface into interior sorption sites. Indeed, long-term metal sorption studies on soil and oxides (Barrow, 1986; Bruemmer *et al.*, 1988) and biological responses (Brennan, 1990) have identified slow immobilization reactions of heavy metals. In addition, metals can be fixed in soil because they entered the soil in an insoluble form, e.g. mine spoils, massive metallic forms (lead shot), etc. Spectroscopic methods, such as XAFS (X-ray absorption fine structure), XANES (X-ray absorption near edge) and EDS (Energy-dispersive X-ray) have been used to identify the solid-phase speciation of metals in sewage sludge (Essington & Mattigod, 1991) and soils (e.g. Roberts *et al.*, 2002). These studies have shown that metals from anthropogenic sources often occur in discrete mineral phases.

It is remarkably that still many chemical models predicting metal solubility in soil use the total (or aqua regia soluble metal) as the basis for this prediction. As fixed fractions of metals in soil may constitute between less than 10% and 100% of the total metal content (e.g. Young *et al.*, 2000), the level of uncertainty in the prediction of metal solubility may

be more than one order of magnitude. The labile metal pool, instead of the total metal amount, has been considered in some models. Including the (radio-)labile fraction of Cd and Zn in multivariate analysis improved the prediction of the solid–solution distribution of Cd and Zn (Degryse *et al.*, 2003). Streck & Richter (1997) used EDTA (0.025 M)-extractable Cd and Zn to model the transport of Cd and Zn in a sandy soil.

Various extracts have been used to approximate the labile metal pool. Organic complexing agents, such as 25 mM EDTA and 5 mM DTPA (Lindsay & Norvell, 1978), are commonly used. Young *et al.* (2000) proposed extraction of the labile Cd pool with 1 M CaCl_2 , as labile Cd is solubilized through complexation by Cl^- and competition for surface sites by Ca^{2+} , while it is unlikely that fixed Cd (occluded in minerals etc.) will be dissolved by CaCl_2 . Repeated desorption (e.g. Singh *et al.*, 1997) or continuous desorption (e.g. Roberts *et al.*, 2002) with neutral salt solutions may be used to estimate the labile pool, but this laborious technique is little used. Also sequential extraction schemes have been proposed to assess the availability of heavy metals in soils. However, though sequential extractions may give useful information about the associations of the metals in the soil, the results are difficult to interpret in terms of availability (Ahnstrom & Parker, 2001). The isotopically exchangeable pool of metals, also called the '*E*' value, may conceptually best represent the fraction of metals that is in dynamic equilibrium with metals in the solution phase. A small quantity of a suitable radio-isotope is added to a water or dilute salt extract, and the specific activity of the metal is measured after a set equilibration time, which allows to calculate the radio-labile metal content. The ratio of the *E* value to the total metal content (*%E* value) denotes the fraction of metals that is labile. Radiolabile fractions of Cd or Zn have been measured in soils polluted by sewage sludge, mine spoil and smelting, in soils amended with metal salts and in soils with background values of Cd and Zn (Tiller *et al.*, 1972a; Nakhone and Young, 1993; Smolders *et al.*, 1999; Sinaj *et al.*,

1999; Young *et al.*, 2000; Gerard *et al.*, 2000; Ahnstrom & Parker, 2001; Tye *et al.*, 2003). A negative correlation between pH and %*E* values of Cd and Zn was found by Tye *et al.* (2003) in metal salt spiked soils after 3 years of laboratory incubation. However, no or only weak relationships between soil properties and %*E* values of Cd or Zn were found in soils collected from the field (e.g. Young *et al.*, 2000), suggesting that the origin of the contaminant may influence the degree of fixation .

We have surveyed the labile fractions of Cd and Zn in soils with various sources of metals with, in some cases, known history of metal sources and input. We wanted to explain metal fixation in terms of soil properties, time since contamination, and source of pollution. In addition, the analytical problems encountered when measuring *E* values in soils with high pH and little metal are discussed.

Materials and methods

Soil samples

Topsoils (A horizon) were collected throughout Europe. These included both soils with background metal concentrations and Cd and Zn polluted soils (Table 1). Soils amended with sewage sludge were collected in London (UK), Paris and Bordeaux (France). The soils of London were amended with sludge in the 1960s. The soils in Bordeaux were amended with a sludge containing much Cd and Ni from 1976 until 1980 or with a sludge containing much Zn and Mn from 1974 until the beginning of the 1990s. The soils of Paris received sludge from 1977 till 1997. Soil samples near galvanized structures were collected under galvanized crash barriers at the roadside of two highways, one in UK (Woburn) and the other in Belgium (Machelen), and at different distances (from 0 m to a maximum of 80 m) of four galvanized pylons (three in Belgium and the other in UK). Total Zn increased with decreasing distance from the pylons from background value to 670 mg Zn kg⁻¹, and there was no contamination of other metals but Zn. Soils spiked with metal salts were collected from field trials in France (Bordeaux) and Hungary (Nagyhörcsök). For the French soils, Cd(NO₃)₂ was added at a rate of up to 40 mg Cd kg⁻¹, 9 to 12 years before sampling (M. Mench, personal communication). Soil samples were taken from plots with pH 5.3-5.6 and pH 6.8. In the Hungarian soils, Cd (as CdSO₄) or Zn (as ZnSO₄) were added at various rates up to 210 mg kg⁻¹, 10 years before sampling (Kádár, 1995).

Soil characterization

The soils were sieved (to pass 2 mm) and air-dried. The organic C content was measured on a combustion analyser (Skalar CA 100). The pH was determined in 0.01 M CaCl₂, in a soil:solution ratio of 1:10 kg l⁻¹ after 3 days of equilibration. The total metal content was

determined by aqua regia digestion or, for most of the Belgian soils, by microwave digestion with a mixture of HNO₃, HBF₄, H₃PO₄, HCl and HF. The comparison for five soils showed that total metal contents measured by the two methods are in good agreement (within 10 % difference). Concentrations of Cd and Zn in the digests were measured by ICP-OES (Perkin Elmer, Optima 3300 Dual View). An internal laboratory standard, verified against a soil sample with certified contents of Cd and Zn (sewage sludge amended soil, CRM 143 from the Central Bureau of Reference of the European Union) was used as quality control. Recovery of Cd and Zn for this standard was always between 90% and 110%. All analyses were done at least in duplicate.

Measurement of radio-labile Cd and Zn

Duplicate samples of 2.5 g soil were weighed in polypropylene centrifuge tubes, 25 ml of a 0.01 M CaCl₂ solution was added, and the suspensions were spiked with 0.25-0.5 ml carrier-free ¹⁰⁹Cd (~ 4000 Bq ml⁻¹, specific activity between 40 and 80 GBq g⁻¹) and ⁶⁵Zn (~ 10000 Bq ml⁻¹, specific activity between 20 and 87 GBq g⁻¹). The amount of Cd and Zn added through the radio-active spike was negligibly small. The suspensions were shaken end-over-end (27 rpm) for 16 hours or 3 days. After phase separation by centrifuging at 3000 g for 20 minutes, two 5-ml samples were taken from each tube. The γ activity of ¹⁰⁹Cd (energy window: 15-40 keV) and ⁶⁵Zn (1000-1200 keV) was measured (Minaxi, 5530 auto Gamma) on one sample. The other 5-ml sample was acidified to pH=1 with HNO₃, prior to analysis of stable Cd and Zn with ICP-OES (detection limit for Cd and Zn: 1 μ g l⁻¹). The radiolabile content (*E* value, in mg kg⁻¹) of Cd and Zn was calculated as:

$$E = [M] \cdot (K_d^* + V/W), \quad (1)$$

where [M] is the concentration (mg l⁻¹) of the metal in the supernatant, K_d^* (l kg⁻¹) is the distribution coefficient of the radio-isotope, *V* is the volume of solution (l) and *W* is the

mass of soil (kg). The %*E* value is the proportion of radiolabile metal to aqua regia soluble metal (M_{tot}).

$$\%E = \frac{E}{M_{\text{tot}}} 100. \quad (2)$$

For some samples of Hungary and France with high pH and moderate Cd and Zn content, the *E* value was determined in a solution of 0.01 M CaCl₂ and 0.1 mM Na₂EDTA. The concentrations of Cd and Zn in the CaCl₂ extract were small for these soils ($\leq 10 \mu\text{g l}^{-1}$), making the *E* values difficult to determine (see below). The addition of EDTA (0.1 mM) led to larger Cd and Zn concentrations in the extract.

The effect of filtration (0.45 μm), soil:solution ratio (1:500-1:5 kg l⁻¹), and electrolyte composition (0.5 to 10 mM Ca(NO₃)₂, 0.5 to 10 mM CaCl₂, 1.5 to 30 mM NaNO₃) was tested on three soils, but no significant effects were found, which accords with the results of Young *et al.* (2000). The effect of equilibration time (up to 18 days) on the measurement of the *E* values was investigated in ten soils.

Effect of EDTA addition on the E values

The *E* values of Cd and Zn were measured in 0.01 M CaCl₂ with addition of Na₂EDTA in different concentrations (0, 0.01, 0.1, 1 and 10 mM) for six soils. Three of these soils had a pH below 7 (pH 4.3, 6.3 and 6.5). The three other soils were calcareous soils (pH 7.2), from the Hungarian field trial. One of these soils had background concentrations of Cd (0.3 mg kg⁻¹) and Zn (53 mg kg⁻¹), the other soils were either amended with Cd salt (Cd_{tot}=45 mg kg⁻¹) or with Zn salt (Zn_{tot}=210 mg kg⁻¹), 10 years before sampling. The *E* values were determined in the same way as described above.

In another experiment, the *E* values of 55 of the soils included in this study were measured in 0.01 M CaCl₂ with and without addition of 0.1 mM Na₂EDTA.

Results and discussion

Effect of equilibration time on E values of Cd and Zn

The E values changed little ($< 10\%$) between 1 and 18 days of equilibration for eight of the ten soils tested ($\text{pH} \leq 6.2$). The E values of Cd and Zn increased about 30% for a soil with pH 7.1, and that of Zn increased up to 50% for a soil with pH 7.2. Concentrations of Cd in the extract were less than the detection limit in the latter soil. Smolders *et al.* (1999) and Young *et al.* (2000) found little change in E values of Cd beyond 1 day of equilibration. Sinaj *et al.* (1999) found E values of Zn to increase considerably between 1 and 15 days of equilibration, also in a fairly acid soil (pH 5.9). This might have been because they used water extracts for their measurements. We found isotopic exchange to be slower in water than in a CaCl_2 extract for two soils we studied (details not shown).

Changes in E with time were more pronounced in soils with higher pH, as is illustrated in Figure 1. Such increases might be due to an increase in the concentration of the stable element or a decrease in the activity of the radio-isotope, Equation (1). The increase in E observed in the high pH soils was the result of increasing adsorption of the radio-isotope; stable Cd and Zn concentrations were almost constant during the equilibration period.

Effect of EDTA addition on the E values

Adding EDTA increased the concentrations of Cd and Zn in solution as a result of complexation of EDTA with metal ions. For the three soils with $\text{pH} < 7$, there was no significant effect on the E value up to concentrations of 0.1 mM EDTA. A significant increase in E was found in two of the three soils for Cd and in all three soils for Zn, when EDTA was added in a concentration of 10 mM (e.g. Table 2, soil A).

For the calcareous soil with background Cd and Zn concentration, the measured E values decreased with addition of EDTA up to concentrations of 0.1 mM (Table 2, soil B). The E value of Cd measured without addition of EDTA ($1.1 \text{ mg Cd kg}^{-1}$), was higher than the total Cd content (0.3 mg kg^{-1}). Apparently, in soils with high pH and background concentrations of Cd and Zn, unrealistically large E values are obtained with the normal procedure. Addition of EDTA in a concentration of 0.1 mM reduced the E value to $0.2 \text{ mg Cd kg}^{-1}$. No increase in E was observed at the large EDTA concentrations in the calcareous soils.

The increase in E upon addition of EDTA at the larger concentrations (1 and 10 mM) in some soils suggests that non-labile Cd and Zn are solubilized. Mobilization of non-labile Cd with EDTA at large concentration (50 mM) was also observed by Nakhone & Young (1993) and Stanhope *et al.* (2000). Addition of EDTA enhances the dissolution of oxidized metal species (carbonates, hydroxides, oxides), but not of metal sulphides (Rumball & Richmond, 1996). Heavy metals may be occluded in hydrous metal oxides, e.g. by intraparticle diffusion (Trivedi & Axe, 2000). Therefore, dissolution of iron (hydr)oxides caused by addition of EDTA might cause non-labile Cd and Zn to be released. We used the GEOCHEM program (Parker *et al.* 1995) to simulate interactions of EDTA with heavy metals and iron hydroxide (Table 3). At high pH, EDTA is expected to have a large effect on the concentrations of Zn and Cd in solution. At low pH, however, only small effects are to be expected, because EDTA is preferentially complexed with Fe(III). Large fractions of iron hydroxides may be dissolved at low pH, especially at large concentration of EDTA in soil containing little iron hydroxide.

The decrease in E values upon addition of EDTA in the calcareous soil with background content of Cd and Zn (Table 2, soil B) suggests that more reliable measurements of E can be made in such soils by addition of EDTA in a concentration of 0.1 mM. We tested the

effect of adding EDTA (0.1 mM) on the E value by comparing E measured in 0.01 M CaCl_2 with and without addition of EDTA for 55 soils. Concentrations of Cd and Zn in solution were up to 100-fold larger upon addition of EDTA, with the strongest increases in the soils with low labile Zn content and $\text{pH} > 6$. Dissolution of iron (hydr)oxides, indicated by an increase in Fe concentration of the supernatant, was most pronounced at low pH, which accords with speciation calculations (cf Table 3). Although concentrations of Cd and Zn in solution strongly increased by addition of EDTA, the E values were scarcely affected in most soils. For the 49 soils with Cd concentrations in the CaCl_2 extract $> 3 \mu\text{g l}^{-1}$, the E values in the presence of EDTA were between 0.82 and 1.18 (mean: 1.01) of those measured without EDTA. For Zn, the E values in the presence of EDTA were between 0.85 and 1.17 (mean: 1.03) of those measured without EDTA, when the Zn concentration in the CaCl_2 extract exceeded $8 \mu\text{g l}^{-1}$. However, in soils with small concentrations of Cd ($< 3 \mu\text{g l}^{-1}$) and Zn ($< 8 \mu\text{g l}^{-1}$) in the CaCl_2 extract, which are the soils with moderate or high pH and small total Cd or Zn content, E values measured in the presence of EDTA were less than those measured without addition of EDTA (Figure 1).

Tiller *et al.* (1972a) measured both E values (in CaCl_2 0.05 M) and L values of Zn (plant radio-labile pool, determined by measuring the specific activity of plants grown on soils spiked with ^{65}Zn) on 25 soils. They found erratic and unrealistically large E values in alkaline soils, *i.e.* soils with $\text{pH}(\text{H}_2\text{O}) > 7.5$, while no such problems were encountered in the measurement of the L values. The ratio of E and L value (assumed to be a more reliable estimate of the labile Zn pool for these soils) is plotted as a function of the Zn equilibrium concentration in 0.05 M CaCl_2 , showing a same threshold value of $8 \mu\text{g Zn l}^{-1}$ less than which E exceeded L in most cases (Figure 2).

The presence of colloidal Cd and Zn that is not isotopically exchangeable might have caused the overestimation of E in these soils. A basic assumption in determination of E

values is that the stable element and the radio-isotope have the same fate in the sampled phase. Therefore, stable metal concentrations, and E values, will be overestimated if non-isotopically exchangeable metals are present in solution, Equation (1). Hens & Merckx (2001) have demonstrated the presence of non-isotopically exchangeable forms in solution for phosphorus. Lombi *et al.* (in press) measured E of Cd, Cu and Zn in soils treated with lime, beringite and red mud, by measuring the specific activity of the supernatant (filtered at $0.2\ \mu\text{m}$) before or after a resin purification step. They found smaller E values in soils of high pH when using the resin purification step, and they attributed these results to the presence of non-exchangeable colloidal metals in solution (that are not adsorbed by the resin).

The overestimation of E in the soils with small concentrations of Cd and Zn in solution might also be related to difficulties associated with the determination of these metals in such concentrations. The detection limit for Cd and Zn of the ICP-OES ($1\ \mu\text{g l}^{-1}$) is less than the threshold value of about $5\ \mu\text{g l}^{-1}$. However, contamination is the limiting factor for analysing Zn in small concentration (Ivahnenco *et al.*, 2001). Even though we washed all glassware with acid and took every care to avoid contamination, we cannot be sure that contamination did not interfere with Zn measurements at small concentration ($<5\ \mu\text{g l}^{-1}$).

We may conclude that large concentrations of EDTA can solubilize fixed Cd and Zn, but that E values seem to be unaffected by addition of EDTA in small concentration (e.g. $0.1\ \text{mM}$). Therefore, addition of EDTA in small concentration may be used to avoid analytical problems in determining E values in soils of high pH with small concentrations of Cd and Zn in solution.

Radio-labile Cd and Zn in topsoils

The %*E* values ranged from 9% to 92% (mean 61%) for Cd and from 3% to 72% (mean 33%) for Zn. The %*E* values were always larger for Cd than for Zn, except in three soils amended with sludge, for which %*E* of Cd was nearly equal to %*E* of Zn. The %*E* of Cd was unrelated to pH, but that of Zn was negatively correlated with pH ($r = -0.65$). No correlation was found between %*E* values and organic C content.

Metals may have been added to soil in insoluble forms in the field, which may explain the lack of correlation between soil properties and %*E* values. Nakhone & Young (1993) and Young *et al.* (2000) found indications that the origin of the contaminant strongly influences %*E* values of Cd and Zn, and so we examined radio-labile fractions according to the source of the contamination.

Metal spiked soils. The measurement of the radiolabile fraction in soils spiked with metal salts can be used to discover whether ageing reactions have taken place, resulting in metal fixation. We calculated the fraction of added metal that remained labile by correcting for background:

$$\%E(M_{\text{added}}) = \frac{E - E^{\text{control}}}{M_{\text{tot}} - M_{\text{tot}}^{\text{control}}} 100, \quad (3)$$

in which E^{control} and $M_{\text{tot}}^{\text{control}}$ are the *E* value (mg kg^{-1}) and total metal content (mg kg^{-1}) of the control soil (no metal salt added). The labile fraction of added Cd showed a negative correlation with the pH ($r = -0.91$) and with organic C content ($r = -0.73$). The labile fraction of added Cd was ~ 90% for the acid soils (pH~5.5) and ~ 75% for the near neutral ones (pH~6.8). If all added metal was initially 100% labile, this indicates that Cd fixation is limited and more pronounced at higher pH. The correlation with organic C content may be coincidence as organic C content and pH were positively correlated for these soils. In the

Hungarian field trial, the labile fraction of added Cd was between 70% and 75%, and the labile fraction of added Zn was between 28% and 32%, illustrating the higher fixation for Zn than for Cd. The large fraction of fixed Zn in these calcareous soils may be due to precipitation of ZnCO_3 . We found that acidification led to an increase of labile Zn in these soils (data not shown), which may indicate that Zn is present in a readily soluble mineral phase (Hamon *et al.*, 2002; Lombi *et al.*, in press). We found no changes in labile Cd upon acidification, indicating that other mechanisms (e.g. solid phase diffusion) were responsible for the (limited) fixation of Cd.

Tye *et al.* (2003) measured the proportion of radiolabile Cd and Zn in 23 topsoils that had been amended with $\text{Cd}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ (3 mg Cd kg^{-1} and 300 mg Zn kg^{-1}) after 3 years of laboratory incubation. The %E values decreased with increasing soil pH, and the trends in labile Cd and Zn over time suggested little further fixation of soluble Cd and Zn beyond 3 years. Figure 3 shows the relation between pH and %E values of Cd and Zn for these soils. The %E values of added Cd and Zn that we obtained for the soils spiked with metal in the field trials reasonably accord with this relation (Figure 3).

Soils with background metal concentration. The %E values were between 53 and 90% (mean 68%) for Cd and between 3 and 60 % for Zn (mean 27%). This shows that Cd is also more labile than Zn in soils with background values of Cd and Zn. In the case of Cd, no correlation was found between %E values and soil pH, but a significant negative correlation ($r = -0.85$) was found between %E values of Zn and pH, indicating larger labile fractions at lower pH for indigenous Zn.

Soils near galvanized structures. The labile fraction of Zn in the soil near the pylons or crash barriers was calculated according to Equation (3). Control soils were sampled at a distance of 40 to 80 m from the pylon, or 8 to 10 m from the road border, where the soil Zn

content was at background values. Zinc contamination in roadside soils may have sources (e.g. vehicle tyres) other than the corrosion of crash barriers. However, as the total Zn content of the soil sampled under the crash barrier was much larger than in soils sampled at the same distance from the road border in absence of a crash barrier, most Zn is probably derived from the corrosion of the galvanized crash barrier. Values of %E(Zn_{added}) were between 14 and 72% (mean 49%), with a strong negative relationship between %E(Zn_{added}) and pH ($r=-0.91$). This relation was similar to the one between pH and %E values of Zn derived for 23 soils spiked with 300 mg Zn kg⁻¹ after 3 years of incubation (Tye *et al.*, 2003) (Figure 3). Zinc from the galvanized structures is likely to be released as Zn²⁺ ion after oxidation of Zn in the coating (Lexmond, 1987). However, the Zn in the soil remained not totally labile, as ageing reactions have reduced the proportion labile Zn.

Soils affected by smelting. The %E values of soils contaminated by smelters were between 19 and 92% (mean 61%) for Cd and between 5 and 66 % for Zn (mean 37%). The %E values of Cd and Zn were well correlated ($r=0.84$). No significant correlation was observed between %E values and soil pH or organic matter content, and the %E values were often less than that in metal salt spiked soil at a similar pH (Figure 3).

The contamination in soils surrounding smelters may be due to atmospheric deposition or to contamination with smelter wastes. Cadmium and Zn in these soils may be present in various chemical forms. Zinc in dust emitted by a lead smelter in Northern France was present mainly as ZnS and ZnO, whereas Cd was found as CdS and CdSO₄ (Sobanska *et al.*, 1999). Roberts *et al.* (2002) found that Zn in a topsoil contaminated by a Zn smelter was mainly in the form of franklinite (ZnFe₂O₄) and sphalerite (ZnS). Only 11% of the total Zn amount in this soil was leached in a stirred-flow experiment. Manceau *et al.* (2000) identified franklinite (ZnFe₂O₄), willemite (Zn₂SiO₄), Zn-containing magnetite

($[\text{Fe,Zn}]\text{Fe}_2\text{O}_4$), and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$) in soils contaminated by smelters. Such soils are thus probably often enriched with Cd or Zn in a less soluble form than Cd or Zn salts, which may explain the smaller %E values than in soils spiked with metal salts (Figure 3).

Sludge-amended soils. The %E values of Zn in soils treated with sludge were, on average, 27%, and varied within a small range (16-41%). Those of Cd were larger (on average 49%) and ranged from 31% to 71%. No significant correlation was found between the %E values of Cd and those of Zn. The %E values of Cd were negatively correlated with pH ($r=-0.48$). The observed correlation between %E values and organic C content ($r=-0.79$) might be a coincidence. In the sludge amended soils of London, a larger organic C content corresponded with greater sludge (and metal) loadings. The smaller %E values at larger loadings may therefore be due to smaller contribution of background Cd (50% labile), that was more labile than Cd added in the sludge (30% labile). The %E values of Zn were negatively correlated with pH ($r=-0.72$); there was no correlation with organic matter content. The %E values of Cd and Zn were often less than in soils spiked with metal salt at similar pH.

The lability of Cd and Zn in sludge-amended soils is probably more related to the characteristics of the sludge than to properties of the soil, as also suggested by Stacey *et al.* (2001). The speciation of metals in the solid phase of sludge depends on the process by which the sludge has been treated. Carbonate and sulphide precipitation may control the solubility of metals in sludge (Lake *et al.*, 1984). Essington & Mattigod (1991) identified sphalerite in anaerobically digested sludge and a soil amended with this sludge.

Other sources of metals. Some soils were contaminated by mining and other industrial activities. The %E values were between 9 and 78 % for Cd (mean 54%) and between 3 and 34% for Zn (mean 20%). No correlation between %E values and pH was observed. The %E values of Zn in the five soils contaminated by mining activities were small (%E 3-33), which may be due to the presence of Zn in sulphide minerals, such as sphalerite.

Conclusions

Our results suggest that when Cd and Zn have entered the soil in soluble form (e.g. metal salts, corrosion of galvanized structures), the proportions labile Cd and Zn are related to the soil's pH. In soils where Cd or Zn were added in a less soluble form the %E values did not show this correlation, suggesting that the source of the contamination controls mainly the fraction that is labile. The labile fraction of Zn was generally less than that of Cd (Figure 4), indicating that Zn is generally added in a less soluble source and that ageing reactions are more pronounced for Zn than for Cd. In 75% of the soils studied, more than half of Cd in the soil was radio-labile (i.e. %E > 50). The smallest %E values of Cd were in soils that had been treated with sludge or mine spoil. Less than half of Zn was radio-labile in 75% of the soils (Figure 4). The %E values of Zn were smallest in calcareous soils with background Zn content, in soils contaminated by mining, and in some soils contaminated by smelters. Acid soils contaminated by corrosion of galvanized structures showed the largest %E values of Zn.

The presence of fixed fractions has implications for assessing the risk of contamination by heavy metals. Leaching of metals may be overestimated if one assumes that the total metal content on the solid phase is in equilibrium with the solution, when the metal is partly in a fixed form. It is possible that 'fixed' Cd and Zn will be gradually released when the labile pool is depleted (e.g. by dissolution of precipitates, diffusion out of oxides, etc.).

However, this remobilization is likely to cause a slow release of metals at small concentration over a long time.

Acknowledgements

We thank the Fund for Scientific Research-Flanders (Belgium) (F.W.O.-Vlaanderen) for a position as research assistant awarded to F. Degryse, and K. Broos, Professor S. McGrath (Rothamsted, UK), Dr M. Mench (INRA-Bordeaux, France) and Professor I. Kádár (Hungarian Academy of Sciences, Budapest) for providing soil samples.

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Table 1. Selected soil characteristics.

Source	Origin	pH (CaCl ₂)	OC ^a / %		<i>n</i>	<i>M</i> _{tot} ^b / mg kg ⁻¹	% <i>E</i> ^c
Sludge	France, UK	5.6-7.4	0.9-6.0	Cd	18	0.6-55	31-71 (49)
				Zn	14	81-1760	16-41 (27)
Metal salts	Hungary, France	5.3-7.2	1.2-2.8	Cd	10	7-212	70-92 (78) ^e
				Zn	3	76-211	28-32 (30) ^e
Metal smelters	Belgium	3.3-6.9	1.0-23.1	Cd	34	0.7-104	19-92 (61)
				Zn	32	50-34100	5-66 (37)
Background	Belgium, France,	3.3-7.5	0.9-16.3	Cd	9	0.2-2.8	53-90 (68)
	UK, Hungary			Zn	17	8-215	3-60 (27)
Pylons and roadside	Belgium, UK	4.6-7.2	2.3-6.7	Zn	22	44-935	14-72 (49) ^e
Other ^d	Belgium, UK	4.6-7.4	1.5-38	Cd	9	2.3-414	9-78 (54)
				Zn	21	248-35800	3-34 (20)

^a OC, Organic carbon^b *M*_{tot}, aqua regia soluble metal content^c range of %*E* (fraction radiolabile Cd or Zn), average between brackets^d alluvium, mine spoil, industrial wastes^e %*E* of added Cd or Zn, see Equation (3)

Table 2. The influence of addition of EDTA to a 0.01 M CaCl₂ extract on the amount of Cd, Zn and Fe extracted and on the *E* values of Cd and Zn. Soil A: pH 4.3, %C 1.8, Cd_{tot} 11 mg kg⁻¹, Zn_{tot} 770 mg kg⁻¹; Soil B: pH 7.2, %C 2.8, Cd_{tot} 0.3 mg kg⁻¹, Zn_{tot} 53 mg kg⁻¹ (standard errors of two replicates given in parentheses)

Soil	[EDTA]	Fe extracted / mM	Cd		Zn	
			extracted / mg kg ⁻¹	<i>E</i> / mg kg ⁻¹	extracted / mg kg ⁻¹	<i>E</i> / mg kg ⁻¹
A	0	0	2.1 (0.04)	3.3 (0.12)	130 (2.1)	191 (0.7)
	0.01	0.01	2.1 (0.04)	3.4 (0.06)	129 (0.9)	204 (0.8)
	0.1	0.06	2.2 (0.01)	3.6 (0.04)	126 (2.2)	203 (2.9)
	1	0.15	3.6 (0.16)	3.8 (0.20)	193 (4.9)	198 (2.8)
	10	0.37	4.0 (0.17)	4.3 (0.08)	240 (8.8)	256 (3.7)
B	0	0	0.01 (0.0001)	1.11 (0.018)	0.05 (0.006)	33.8 (0.78)
	0.01	0	0.07 (0.0003)	0.20 (0.0003)	0.21 (0.003)	1.60 (0.01)
	0.1	0	0.13 (0.0012)	0.17 (0.0008)	0.82 (0.009)	1.41 (0.01)
	1	0	0.15 (0.0005)	0.16 (0.0006)	1.36 (0.029)	1.51 (0.02)
	10	0.02	0.16 (0.0011)	0.16 (0.0003)	1.55 (0.012)	1.55 (0.01)

Table 3. Effect of EDTA addition on the amount of Zn complexed with EDTA or the amount of $\text{Fe}(\text{OH})_3$ dissolved (in % of total), as calculated with GEOCHEM (amorphous $\text{Fe}(\text{OH})_3$, $\log K_{\text{sp}} = -38.5$). Total $\text{Fe}(\text{III})$ concentration = 10 mM, concentration of CaCl_2 = 10 mM, Zn concentration = 0.1 mM.

pH	0.1 mM EDTA		10 mM EDTA	
	%Zn complexed	%Fe dissolved	%Zn complexed	%Fe dissolved
4	0.0	1.0	0.3	100
5	0.8	1.0	43.2	99.5
6	69.5	0.3	99.9	98.9
7	97.6	0.0	100.0	61.3

Figure Captions

Figure 1 The E value of (a) Cd and (b) Zn relative to the E value at 7 days of equilibration, as a function of equilibration time for three soils. The error bars denote standard error of three replicates. ($\square$ pH 4.6, %C 1.4, Cd_{tot} 13 mg kg⁻¹, Zn_{tot} 67 mg kg⁻¹; $\blacklozenge$ pH 6.1, %C 2.9, Cd_{tot} 32 mg kg⁻¹, Zn_{tot} 3630 mg kg⁻¹; $\triangle$ pH 7.1, %C 1.5, Cd_{tot} 2.6 mg kg⁻¹, Zn_{tot} 976 mg kg⁻¹)

Figure 2 The ratio of the E value measured in 0.01 M CaCl₂ to that measured in 0.01 M CaCl₂ + 0.1mM EDTA (open symbols), or the ratio of the E value (in 0.05 M CaCl₂) to the L value (closed symbols). Solution Zn refers to the solution free of EDTA, *i.e.* the solution in which E values are traditionally measured. ($\square$ calcareous soils (pH 7.2) amended with Cd or Zn salts (Hungary); $\circ$ soils (pH 5.8-7) amended with Cd salts (France); $\blacklozenge$ data from Tiller *et al.* (1972a and 1972b))

Figure 3 Lability of the added Cd or Zn, $\%E(M_{added})$, Equation (3), for soils amended with metal salts and soils sampled near pylons and crash barriers, and the proportion labile Cd ($\%E_{Cd}$) and Zn ($\%E_{Zn}$) for soils near Zn smelters. The lines describe the relations between pH and $\%E$ in 23 metal salt spiked soils after 3 years of laboratory incubation (Tye *et al.*, 2003). Labile fractions below this line may be related to insoluble sources of metals in these soils.

Figure 4 Box plots showing (a) the percentage radiolabile Cd or (b) the percentage radiolabile Zn for all soils or for soils grouped according to the source of contamination. The data shown as points are below the 10th percentile or above the 90th percentile. Numbers of samples are given in Table 1.

Figure 1

Figure 2

Figure 3

(a)

(b)

Figure 4