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Mobility of Cd and Zn in polluted and unpolluted Spodosols

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Short title: Mobility of Cd and Zn in Spodosols

Summary

Leaching of Cd and Zn in polluted acid, well drained soils is a critical pathway for groundwater pollution. Models predicting future ground water contamination with these metals have rarely been validated at the field scale. Spodosol profiles (pH 3.2–4.5) were sampled in an unpolluted (reference) field and in a field contaminated with Cd and Zn through atmospheric deposition near a Zn smelter. Average metal concentrations in the upper horizons were 0.2 mg Cd kg⁻¹ and 9 mg Zn kg⁻¹ in the unpolluted field, and 0.8 mg Cd kg⁻¹ and 71 mg Zn kg⁻¹ in the contaminated field. Isotopic dilution was used to measure the labile concentration of Cd and Zn, and the metal transport was modelled using measured sorption parameters that describe the distribution between the labile metal pool (instead of the total metal pool) and the solution phase obtained by centrifugation. Solutions were also collected by wick samplers in two polluted and one unpolluted profile at a depth of 70 cm. Concentrations in these solutions were in the order of 15 µg Cd litre⁻¹ and 0.8 mg Zn litre⁻¹ for the polluted profiles, and in the order of 1 µg Cd litre⁻¹ and 0.04 mg Zn litre⁻¹ for the unpolluted profile. The concentrations in these solutions agreed well with those in soil solutions obtained by centrifugation, which supported the use of the local equilibrium assumption (LEA). Present-day Cd profiles in the polluted field were calculated with the LEA, based on the emission history of the nearby smelter and taking spatial variability into account. Observed and predicted depth profiles agreed reasonably well, but total Cd concentrations in the topsoil were generally underestimated by the model. This may be attributed to the presence of non-labile Cd in the atmospheric deposition, which was not accounted for in the retrospective modelling. The large concentrations of non-labile Zn in the topsoil of the polluted field were also indicative that metals in the atmospheric deposition were (partly) in a sparingly soluble form, and that

release of these non-labile metals is a slow process. The presence of non-labile metals should be taken into account when evaluating metal mobility or predicting their transport.

Introduction

Large areas of land are contaminated with heavy metals from historical emissions of the non-ferrous metal industry. An example of extensive pollution by atmospheric deposition can be found in the Kempen, at the Dutch-Belgian border. Zinc smelters have been active in this region since the end of the 19th century. The soils in this area are mainly acid and sandy, and therefore vulnerable to heavy metal leaching. Groundwater pollution caused by leaching of these metals is a growing concern. Predictive modelling is necessary to evaluate the risk of ground water contamination, but models predicting the transport of Cd and Zn have rarely been validated at the field scale.

The transport of Cd and Zn can be assessed with solute transport models that typically rely on sorption parameters derived from batch equilibrium (adsorption or desorption) data. This approach can be successful in describing the transport of freshly added Cd and Zn salts (e.g. Christensen, 1985). However, metals in polluted soils can originate from sparingly soluble components (e.g. Roberts *et al.*, 2002), that are less mobile than metal salts. In addition, slow immobilization reactions can result in increased fixation of metals with time (Bruemmer *et al.*, 1988). Isotope dilution is a conceptually attractive method to discriminate between labile and non-labile metals in soil. It is usually assumed that non-labile metals do not participate in the solid–liquid distribution within a realistic time-frame. Based on this assumption, metal transport should be calculated using sorption parameters that describe the distribution between the labile metal pool (not the total metal pool) and the solution phase. Streck & Richter (1997) used EDTA (0.025 M)-extractable

Cd and Zn to model the transport of Cd and Zn in a sandy soil, assuming that this extractable fraction represents the labile pool.

Transport of reactive solutes is generally modelled with the equilibrium convection-dispersion equation (CDE) (e.g. Streck & Richter, 1997; Seuntjens, 2002). The use of the equilibrium CDE has been questioned in several column studies, where evidence was found that (chemical or physical) non-equilibrium conditions existed during the metal transport (e.g. Boekhold & van der Zee, 1992; Kookana *et al.*, 1994). However, these column studies were mostly done at high pore-water velocities, in the order of 50 cm day⁻¹ and more, and therefore, it cannot be concluded that non-equilibrium conditions will also prevail in the field, where the water velocity is much less.

Non-ideal transport can also result from preferential flow, whereby water and solutes are moving along certain pathways, while bypassing a fraction of the porous matrix. Column experiments have indicated that preferential flow can accelerate metal leaching through soil (e.g. Camobreco *et al.*, 1996), but these studies often used artificial boundary conditions (e.g. high flow rates). It is not clear to what extent preferential flow will contribute to metal leaching at the field scale. Bergkvist & Jarvis (2004) attributed the difference between modelled and observed Cd profiles in a well-structured clay loam soil, amended with sewage sludge, to the effects of macropore transport.

If non-equilibrium conditions prevail during transport or if preferential flow occurs, metal concentrations in solutions equilibrated with the soil might be smaller (during the adsorption phase) or larger (during the desorption phase) than the concentrations in the percolating water. Concentrations in the latter can be measured using *in situ* samplers, such as passive capillary samplers (PCAPS). A suction is generated by the hanging water columns, which allows the collection of soil solution from both saturated and unsaturated pores to a tension equal to that produced by the hanging column (Holder *et al.*, 1991).

Therefore, the PCAPS represent field conditions in contrast with suction cups or pan samplers. Suction cups apply a vacuum to the soil, and can sample non-mobile water. Pan samplers can only collect solution from saturated pores, which can lead to a disturbance of the flow regime and a change in the soil chemical conditions above the sampler (e.g. reduction reactions and concomitant pH increase).

The objectives of this study were (i) to assess the solid phase speciation of Cd and Zn in smelter contaminated Spodosols, and (ii) to validate the use of the equilibrium CDE to model the Cd transport in these soils. Soil profiles were sampled in a field contaminated by atmospheric deposition of heavy metals and in an unpolluted (reference) field. The polluted and unpolluted field were compared in terms of total, labile and solution concentrations of Cd and Zn. Concentrations measured in soil solutions obtained by centrifugation were used to derive the sorption parameters. This approach was validated by a comparison between concentrations in soil solution and in solutions obtained by wick samplers. We modelled Cd transport in the polluted field retrospectively, based on the emission history of the nearby Zn smelter. In addition, the future leaching of Cd to the groundwater was modelled, assuming that soil properties (pH, ionic strength) remain constant.

Materials and methods

Soils

Soils were sampled from two fields in a polluted and an unpolluted area in northern Belgium. The uncontaminated field is located in Houthalen (51°00'N, 5°27'E), and is part of a nature reserve. The contaminated field is situated in Balen (51°12'N, 5°16'E), in the 'Kempen' at the Dutch-Belgian border. This area is contaminated with Cd and Zn because

of atmospheric deposition by Zn factories over more than 100 years. The soils of both experimental fields are classified as dry podzols, Typic Placohumod according to the USDA (United States Department of Agriculture) classification. Soils were sampled in 2000, to the depth of the groundwater table or to a depth of 4 m. Six profiles were sampled in the unpolluted field, over an area of about 4 ha, and ten profiles were sampled in Balen over an area of about 100 ha. The samples were taken with an Edelman screw auger, at five or six depths corresponding to pedological horizons.

Wick samplers (see below) were installed in the unpolluted field of Houthalen, and in two polluted Spodosols in Lommel, close to the contaminated field in Balen. The two polluted profiles were separated by a distance of about 150 m. One profile was a wet Spodosol (Aquod), the other profile a dry Spodosol (Placohumod). A detailed description of the profiles is given by Seuntjens *et al.* (2001).

Soil characterization

Subsamples of the soils were sieved (< 2 mm) and air-dried at room temperature. The cation-exchange capacity (CEC) was measured at the soil pH with silverthiourea as the index cation (Chhabra *et al.*, 1975). The organic C content was measured by dry combustion (Skalar CA 100). The pH was determined in 0.01 M CaCl₂ at a soil:solution ratio of 1:10 kg litre⁻¹ after 3 days of equilibration. The ‘total’ metal concentration was determined by *aqua regia* digestion. Amorphous Fe and Al oxides were measured by extraction with ammonium oxalate-oxalic acid (Schwertmann, 1964).

Soil solution was collected from the field moist soils, within 2 days after the soil sampling. For each soil sample, two to four 30-ml syringes without plunger were filled with quartz wool and soil. The syringe was transferred to a centrifuge tube and centrifuged for 1 hour at 3000 g (within 2 days after the soil sampling). The soil solution was filtered

through a 0.45- μm pore-size membrane filter and acidified to pH 1 with 5 M HNO_3 . Concentrations of Cd, Zn, and macrocations (Ca, Mg, Na and K) in the soil solutions were measured with Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES, Perkin Elmer, Optima 3300 DV, dual view). Concentrations of Cd were measured with graphite furnace atomic absorption spectrophotometry (GFAAS, Varian Spectra AA20 Plus) if the Cd concentration was $< 5 \mu\text{g litre}^{-1}$.

The labile Cd and Zn in the soils was measured by isotopic exchange, as described elsewhere (Degryse *et al.*, 2004). Briefly, 25 ml of a 0.01 M CaCl_2 solution spiked with ^{109}Cd (as CdCl_2) and ^{65}Zn (as ZnCl_2) was added to 2.5 g of soil. The suspensions were shaken end-over-end for 3 days. After phase separation by centrifugation (20 minutes, 3000 g), two 5-ml samples were removed from each tube. The γ -activity of ^{109}Cd and ^{65}Zn was measured on one sample. The other sample was acidified to pH 1 with HNO_3 , prior to analysis of stable Cd and Zn with ICP-OES, or with GFAAS for Cd concentrations $< 5 \mu\text{g litre}^{-1}$. The radio-labile concentration (E , mg kg^{-1}) of Cd and Zn was calculated as

$$E = [M] \left(K_d^* + \frac{V}{W} \right), \quad (1)$$

where $[M]$ is the Cd or Zn concentration (mg litre^{-1}) in the supernatant, K_d^* is the distribution coefficient of the radioisotope (litre kg^{-1}), V is the volume of solution (litre), and W is the mass of soil (kg). For three representative soils, the E values were also measured after filtration ($< 0.45 \mu\text{m}$) of the supernatant. No effect of filtration was found for these soils and, therefore, the filtration step was omitted in the standard procedure.

Desorption isotherms

Desorption isotherms were obtained for a topsoil from the polluted field, by measuring Cd and Zn concentrations in solution at different soil:solution ratios in 10^{-3} M CaCl_2 . Filius *et*

147 *al.* (1998) have shown that desorption isotherms of metals determined by this technique
148 are in good agreement with isotherms determined by repeated extraction. The soil:solution
149 ratios ranged from 1:460 to 1:5 kg litre⁻¹. The soil (0.5–5 g) was weighed into a dialysis
150 bag (Visking 12-14000 Daltons, Medicell, London), and 5 ml of a 10⁻³ M CaCl₂ solution
151 was added. The dialysis bag was placed in the remaining CaCl₂ solution. Concentrations
152 of Cd and Zn in the equilibrium solution were measured with ICP-OES after 2 days of
153 end-over-end shaking. The same experiment was also carried out with 7 days equilibration
154 time.

156 *Collection of soil solution with Passive Capillary Samplers*

157 The wick samplers or Passive Capillary Samplers (PCAPS) were constructed as follows.
158 The wicks (Amatex 3/8-inch HI) were heated to 400°C, for 4 hours, to remove impurities
159 (Knutson *et al.*, 1993). A preliminary experiment showed that Cd and Zn did not adsorb
160 on the treated wicks. The upper end of the wicks was rolled up on a PVC-plate of 17 cm
161 by 34 cm (2 wicks per plate), and the plate was covered with a nylon cloth. One end of the
162 wick protruded through a hole in the plate, and was encased in a PVC pipe connected to a
163 collection flask (Figure 1). The optimal wick length was calculated according to the
164 procedure of Rimmer *et al.* (1995).

165 The PCAPS were installed in June 2000 at three locations. Two wick samplers were
166 installed in two polluted Spodosols close to the contaminated field of Balen, and one in the
167 uncontaminated field of Houthalen. The PCAPS were installed at a depth of 70 cm. A pit
168 with a depth of about 150 cm was dug, and an excavation (60 cm depth, 10 cm height) was
169 made in the wall at a depth of 70 cm. The top of the excavation was carefully leveled, and
170 the PVC-plate with the two PCAPS units was pushed against the top of the excavation.
171 Wooden blocks were hammered between the bottom of the excavation and the PVC-plate,

to ensure good contact between soil and PCAPS, and the excavation was refilled with soil. The collection flasks were placed at the bottom of the pit. The pit wall was covered with a plastic sheet and the pit was refilled.

Solution flasks were emptied approximately every two months through a sampling tube running from the bottom of the collection chamber to the soil surface. The amount of solution collected was determined by weighing, and the pH of the solution was measured. The solution was acidified to pH 1 with 5 M HNO₃, and concentrations of Cd, Zn, Cu, Pb, Fe, Al, Ca, Mg, Na and K in the solution were measured with ICP-OES, or with GFAAS for Cd concentrations < 5 µg litre⁻¹. Filtration (<0.45 µm) was found to have no effect on the concentrations and, therefore, no filtration step was included in the standard analysis. The solutions of the first sampling occasions were discarded, because of the large pH values and the large Ca concentrations, which probably resulted from weathering of the fibreglass wicking material, as was also observed by Brahy & Delvaux (2001). However, the pH and Ca concentrations declined rapidly to stable values after ~3 months.

On the last sampling occasion, the soil above the wick samplers was excavated. Soil solution was isolated by centrifuging the field moist soils for 1 hour at 3000 g. The soil solution was filtered through a 0.45-µm membrane filter, acidified to pH 1 with 5 M HNO₃, and analysed with ICP-OES. The pH was determined in a water extract in a soil:solution ratio of 1:5 kg litre⁻¹ after 1 day of equilibration.

Modelling

We modelled Cd transport in the polluted field by a simultaneous solution of the Richard's equation and the convection-dispersion equation, assuming local equilibrium between the labile metal pool and the solution phase. Transport was calculated for each soil profile separately, using the measured sorption properties of each soil sample, and results are

presented as a field averaged profile, *i.e.*, the arithmetic mean of all profiles. The transport was simulated from the start of the production (in 1889) till the year 2200. Transport calculations were made with the one-dimensional finite-element computer code HYDRUS-1D (Šimůnek *et al.*, 1998).

The hydraulic parameters (K_s and van Genuchten parameters) were taken from Seuntjens *et al.* (2001), who derived these parameters for similar soils from a nearby site. No effort was made to determine these parameters exactly, since a sensitivity analysis has shown that these parameters do not significantly affect the model outcome (Seuntjens *et al.*, 2002). The longitudinal dispersivity, λ , was obtained from Seuntjens *et al.* (2002), and was about 2 cm for all horizons. The boundary conditions for the water flow were constant water flux at the soil surface and zero-potential at the bottom boundary (water table). The stationary flux at the upper boundary was assumed to be 0.24 m year^{-1} , which is the long-term average precipitation surplus for the region. The water flux was assumed to be constant throughout the profile, *i.e.* root water uptake was neglected. For the solute transport, a third-type flux boundary condition (Cauchy type) was used at the top and a second-type (zero concentration gradient or Neumann type) boundary condition at the bottom.

The solid–liquid distribution was expressed with a Freundlich type equation:

$$s = k c^n, \quad (2)$$

where s is the (labile) adsorbed concentration (mg kg^{-1}), c is the concentration in solution (mg litre^{-1}), and k and n are empirical parameters. A value for n of 0.8 was derived from batch experiments on two soil samples. The value of k was calculated from the experimentally determined metal concentrations:

$$k = \frac{E}{[M]_{\text{pw}}^n}, \quad (3)$$

where E is the radio-labile concentration (mg kg^{-1}) and $[M]_{\text{pw}}$ the measured metal concentration in the soil solution (mg litre^{-1}). Thus, a value of k for each of the 60 soil samples (ten profiles at six depths) was obtained. It was assumed that there was no change in the sorption parameters with time. The pore-water concentration of Cd in the year 1889, when the Zn smelter began to operate, was assumed to be $1 \mu\text{g Cd litre}^{-1}$, which is of the same order as the pore-water concentration in an unpolluted field.

The Cd deposition rate from 1889 till 2000 was estimated from the Cd emission of the neighbouring non-ferrous industry, that was reconstructed by Seuntjens (2002). The cumulative deposition was estimated by integration of the experimentally derived depth profiles of the Cd concentration (Černík *et al.*, 1994). The amount of Cd recovered per unit area, in the upper 2 m of the profile, was around 6 kg Cd ha^{-1} for four of the ten profiles (see Results section). Since model calculations indicated that leaching from these profiles was negligible, it was assumed that the overall Cd deposition was 6 kg Cd ha^{-1} . It was assumed that Cd in the deposition was fully labile.

The deposition rate from the year 2000 onwards was estimated to be $2.3 \text{ g Cd ha}^{-1} \text{ year}^{-1}$ (corresponding to a Cd concentration in the infiltrating water of $1 \mu\text{g litre}^{-1}$). Measurements of wet deposition in The Netherlands (1998–2000) show that current deposition rates are indeed in the order of $1 \text{ to } 2 \text{ g Cd ha}^{-1} \text{ year}^{-1}$ (RIVM, 2001a,b).

Results

Selected soil characteristics are summarized in Table 1. Total Cd and Zn concentrations in the soil from Houthalen are within the background range for sandy soils in Flanders. The soil from Balen is enriched with heavy metals due to atmospheric deposition of heavy metals from the nearby smelter.

Metal speciation

Comparison between radio-labile and desorbable Cd and Zn. Desorption isotherms obtained by widening the soil:solution ratio showed that a fraction of Cd and Zn could not be extracted. This fraction corresponds well with non-labile fraction determined by isotopic dilution (Figure 2). Differences between the isotherms obtained after 2 days and after 7 days of equilibration were small, indicating fast desorption reactions in these low pH soils. Filius *et al.* (1998) also found little change in desorption isotherms of Cd between 2 and 50 days of equilibration in a low pH soil (pH 4.7), while slow reactions were detectable in soils with higher pH.

Desorption of metals from polluted soils is the first step in leaching of these metals. The presence of a metal fraction that cannot be extracted, and which is in agreement with the non-labile metal pool, suggests that labile metal concentrations rather than total metal concentration should be used to predict metal leaching in soil.

Depth profiles of total and labile Cd and Zn in the unpolluted soil. Total Cd

concentrations decrease with depth in the unpolluted soil. Most Cd is labile throughout the profile. Total Zn concentrations increase with depth except for the A horizon, where Zn concentration is greater than in the underlying horizons (Table 1). The increase in Zn concentration with depth indicates a loss of Zn by leaching (e.g. Jersak *et al.*, 1997). The greater concentrations in the upper horizon are likely related to cycling of metals in the soil-plant environment (Nowack *et al.*, 2001). Zinc in this upper horizon is more labile than in the deeper horizons (Table 1). Only between 6 and 20 % of the total Zn in the C horizon is in a labile form. Zinc in the parent material is probably enclosed in mineral lattices or within stable microaggregates, explaining the small labile fractions of Zn in the lower horizons.

Depth profiles of total and labile Cd and Zn in the polluted soil. Total Cd and Zn concentrations both decrease with depth in the polluted soil (Table 1). Despite the low pH, and consequently great mobility of Zn, a large fraction of the added Zn is present in the upper horizon, but Zn in this horizon is mainly in a non-labile form. The presence of Zn in an insoluble form in the upper horizon, preventing Zn leaching (cf. Figure 2), might therefore explain the large Zn concentration in the topsoil. The age of contamination (± 65 –110 years, since the gross of the deposition occurred between 1889 and 1935) is apparently not large enough to mobilize all non-labile Zn.

Differences in solid phase speciation of Zn between top- and subsoil of a smelter contaminated soil were also observed by Roberts *et al.* (2002). They found that Zn in the topsoil was mainly in the form of franklinite (ZnFe_2O_4) and sphalerite (ZnS). In contrast, aqueous or outer-sphere Zn^{2+} prevailed in the subsoil ($\sim 60\%$). The difference in speciation between subsoil and topsoil was also reflected in the desorption behaviour of Zn. Only 10 % of the total Zn amount in the topsoil could be desorbed in a stirred-flow experiment, while 70 % of the total Zn in the subsoil was desorbed.

Solid–liquid distribution of Cd and Zn. The *in situ* K_d was calculated as the ratio of total metal concentration in soil to that in the soil solution. The K_d values range between 2 and 446 litre kg^{-1} for Cd and between 2 and 237 litre kg^{-1} for Zn, showing a similar range in the polluted and the unpolluted fields. The largest K_d values are observed in the A horizon and the B_h horizon, and the smallest in the C horizon.

The K_d values were correlated to soil properties by stepwise regression analysis, using SAS (Release 6.12). All variables were transformed to their logarithms (base 10), except for pH which is already a logarithm. The logarithmic transformation was used to normalize the data and to linearize relationships. The organic matter content explained

most of the variation in $\log K_d$ ($R^2=0.85$ for Cd and 0.24 for Zn, cf. Figure 3). Introducing pH into the regression model had no significant effect. Soil pH is usually the most important factor explaining the K_d of Cd and Zn (e.g. Anderson & Christensen, 1988). In the present study, however, the variation in organic C content was large (from 0.05 to 5.6%), and the variation in pH was small (Table 1).

The solid–liquid metal distribution was also expressed with respect to the E value instead of the total metal concentration. The regression analysis was also performed for this K_d^{lab} ($=E/[M]_{\text{pw}}$). No improvement in R^2 was found for Cd by using the radio-labile instead of total metal concentration. Non-labile fractions of Cd were generally small (Table 1), which explains this lack of improvement. Only in three (top)soils of the polluted field was more than half of Cd in the soil non-labile. In contrast, the R^2 improved strongly – from 0.24 to 0.72 – when the K_d of Zn was expressed with respect to radio-labile instead of total Zn concentration (Figure 3b). The much stronger correlation between K_d and soil properties when using E values instead of total metal concentrations suggests that the radio-labile metal pool represents the metals that are participating in the sorption-desorption reactions. Tye *et al.* (2003) found no or only small improvements when using radio-labile instead of total metal concentration to predict pore-water concentrations of Cd and Zn with an extended Freundlich model. However, the major portion of the dataset of their study consisted of metal salt-spiked soils. The fraction radio-labile metal was greatly pH dependent in these soils. Therefore, the variation in the fraction labile metal was already partly accounted for by pH.

The K_d^{lab} is smaller for Zn than for Cd at similar OC content, which indicates that (labile) Zn is more mobile than Cd in these low pH soils.

Solution sampled by wicks versus soil solutions

The Cd and Zn concentrations in the solutions sampled by the wicks are much larger for the soils of Lommel than for the unpolluted soil (Table 2). The Cd concentrations are well above the Flemish groundwater threshold of $5 \mu\text{g Cd litre}^{-1}$, although the concentration in the topsoil is only about 1 mg Cd kg^{-1} , *i.e.*, lower than the Flemish soil clean-up value for natural and agricultural areas (2 mg Cd kg^{-1} for a standard soil with 2 % organic matter and 10 % clay). This discrepancy is due to the great mobility of heavy metals in these acid soils, which is also illustrated by the relatively large Cd concentration in the solution of the uncontaminated podzol.

The concentrations in the solutions sampled by the wick showed a temporal variation (Figure 4). The Ca concentrations were largest in September (Autumn), while Al concentrations showed a peak in April (Spring). This seasonal variation was related to the variation in pH; the pH of the solution was between 0.5 and 1 pH-unit greater in September than in April. These seasonal acidification and alkalization phases are probably caused by nitrogen transformations. In Spring, the rate of nitrification might exceed the rate of nitrate uptake, which results in a decrease of the pH in soils with low base saturation (Matzner, 1989). The lower pH in spring explains the larger metal concentrations between February and June (Figure 4).

Concentrations of Cd and Zn measured in the soil solution, obtained by centrifugation of the soil at the end of the experiment, agreed well with the concentrations of the solution sampled by the wick (Table 2, Figure 4). Only in the unpolluted soil did the Zn concentration in the soil solution fall outside the range of concentrations in the solutions sampled by the wick. This could possibly be due to laboratory-handling contamination during the soil solution isolation. Good correspondence between concentrations in the soil solution obtained by centrifugation and those in the wick sampled solutions at the last

sampling occasion was also found for most other elements. For K, however, concentrations in the soil centrifugates were considerable larger than in the solutions sampled by the wick.

The concentrations in the solution sampled by the PCAPS could be interpreted as the flux concentrations, while the concentrations in the centrifugates are more representative of the resident concentration. Prediction of solute transport based on resident concentrations might lead to biased results if non-equilibrium conditions occur. The good agreement between both sampling methods is indicative that non-equilibrium processes, e.g. by-pass flow and chemical non-equilibrium, do not prevail in these soils. Therefore, it seems justified to model the transport of Cd and Zn based on the local equilibrium assumption (LEA).

The mean drainage flux was 0.25 m year⁻¹ for the soil in Houthalen, 0.16 m year⁻¹ for the Aquod at Lommel, and 0.11 m year⁻¹ for the Humod at Lommel. The latter profile was surrounded by trees, which may explain the lower flux.

Leaching of Cd and Zn

The total amount of Cd and Zn present in the profile (M_{profile} , kg ha⁻¹) was calculated, for each profile sampled, by summing the metal amount in all horizons:

$$M_{\text{profile}} = \sum_i 0.1 d_i \rho_i M_{\text{tot},i}, \quad (4)$$

where d is the horizon thickness (cm), ρ is the bulk density (g cm⁻³) (determined by Seuntjens *et al.* (2001) for similar soils adjacent to the site of this study), and M_{tot} is the total metal concentration (mg kg⁻¹) of the soil horizon. Results are given in Table 3.

Unpolluted soil. The leaching rate (L , g ha⁻¹ year⁻¹) can be calculated from the pore-water concentration ($[M]_{\text{pw}}$, µg litre⁻¹) and the annual precipitation surplus (F , m year⁻¹), which is in the order of 0.2 m year⁻¹:

$$L = [M]_{pw} 10 F. \quad (5)$$

The Cd concentration in the pore-water of the unpolluted field is in the order of 1 µg litre⁻¹ (Table 2), and the estimated loss by leaching is, therefore, 2 g Cd ha⁻¹ year⁻¹.

The input of Cd and Zn is mainly from atmospheric deposition, since no fertilizers or other soil amendments are added to these soils. Tjell & Christensen (1985) estimated that atmospheric deposition of Cd in Denmark was around 7 g Cd ha⁻¹ year⁻¹ between 1923 and 1980. The deposition in rural areas has likely been > 2 g Cd ha⁻¹ year⁻¹ during the last decades and, therefore, there has probably been a net accumulation during this period. Current atmospheric deposition of Cd in Western Europe, which is in the order of 1–2 g ha⁻¹ year⁻¹ (RIVM, 2001a,b), is less than historical input, due to increased emission control. This suggests that the Cd balance is close to steady state in these soils.

The Zn concentration in the pore-water of soil in the unpolluted field is in the order of 40 µg litre⁻¹ (Table 2), and the estimated loss by leaching is therefore ~80 g Zn ha⁻¹ year⁻¹. The atmospheric deposition of Zn is estimated to be of the same order (RIVM, 2001a,b). Therefore, no conclusion can be made whether accumulation or loss of Zn has occurred in this soil. However, as mentioned above, the increase in Zn concentration with depth indicates that a net loss of Zn has occurred (Table 1).

Polluted soil. The amount of metal in the polluted soil, averaged for the 10 profiles sampled, is 7.2 kg Cd ha⁻¹ and 461 kg Zn ha⁻¹ (Table 3). The (relative) difference in amount of metal between the polluted and unpolluted soil is much larger for Cd than for Zn, which is indicative of the greater mobility of Zn in low pH soils. The variation in amount of metal between the profiles is large. The amount of Cd is between 4 and 6 kg ha⁻¹ in most profiles. Considerably smaller amounts were observed in two profiles that had little organic matter (<0.7 %OC) below the A-horizon, and showed no podzolisation

(profiles 2 and 6, Table 3). The lack of Cd accumulation in these profiles might therefore be due to greater leaching of Cd. The largest amounts of Cd are found in profiles 8 and 10 (Table 3), that were located close to a smelter waste dump. These profiles were therefore not included in the model calculations.

Present-day Cd profiles were calculated based on the emission history from the nearby smelter. The predicted field-averaged Cd concentration profile (in the year 2000) is shown in Figure 5. The predicted Cd profile corresponds reasonably well with the observed profile. This indicates that long-term field scale transport of Cd in these sandy soils can be modelled with the equilibrium assumption. However, predicted Cd concentrations in the upper horizons are smaller than the measured (total) concentrations, and correspond more with the measured labile concentrations. Deposition of metals in soils surrounding smelters can be due to atmospheric deposition (primary deposition) or to secondary pollution (e.g. resuspension of contaminated soils, or roasted ores used for road construction). Cadmium is probably deposited in a partly insoluble form, which is also suggested by the small $%E$ values of Cd in the upper horizons of the polluted field (mean value 50%, minimum 17%), which indicates that Cd in the deposition load was partly in an insoluble form. The model assumed that all Cd deposition occurred as labile Cd. Therefore, the presence of Cd in a partly insoluble form, preventing Cd leaching, could explain the deviation between observed and predicted Cd concentration in the upper horizons.

Concentrations in the seepage water were calculated by averaging the solution concentrations at the bottom of all soil profiles. According to the model calculations, 1.7 kg Cd ha⁻¹ was, on average, transported to the groundwater in the past ~100 years. Between 2.5 and 4.1 kg ha⁻¹ is predicted to have leached from the profiles with smaller retention capacities (profiles 1, 2, 3 and 6). The amount of Cd in these profiles (Table 3) is indeed < 6 kg Cd ha⁻¹, which was assumed to be the overall Cd deposition load. The

model predictions indicate that Cd leaching from the other profiles (4, 5, 7 and 9) has been negligible ($\sim 0.3 \text{ kg Cd ha}^{-1}$), and that considerable amounts of Cd will start to leach from these profiles from the year 2050 on. The model predicts that, on average, $2.8 \text{ kg Cd ha}^{-1}$ will leach to the groundwater during the next 100 years at concentrations around 10 to $15 \mu\text{g Cd litre}^{-1}$, and that almost all excess Cd will be transported to the groundwater by the year 2200. The field-averaged breakthrough curve shows a double peak. The first peak is due to transport of Cd from the profiles with smaller retention capacities, while the second peak is caused by leaching from profiles with greater retention capacities. It is possible that if profiles would have been sampled at a greater density, a smooth breakthrough curve would have been obtained. However, the conclusion would presumably have been the same, *i.e.* the gross load of Cd deposited on these soils is transported to the groundwater between 100 and 250 years after the start of the deposition.

We made no prediction for the Zn transport. Model calculations indicate that most of the Zn deposited on the soil should be leached out if all added Zn is labile, because of the great mobility of labile Zn at low pH. Labile Zn concentrations are indeed small, but the total Zn concentrations in the upper horizon are still elevated (Figure 5). We speculate that most labile Zn has been leached, while Zn that was added to the soil in a sparingly soluble form (e.g. franklinite) is only slowly released.

Discussion

The reasonable agreement between predicted and observed present-day Cd profiles in the polluted field indicates that the equilibrium CDE can be used to predict Cd leaching in these sandy soils. The assumption of local equilibrium (LEA) was also supported by the good agreement between ‘flux’ concentrations of Cd and Zn (in solutions obtained by wick samplers) and ‘resident’ concentrations (in solutions obtained by soil centrifugation). It

was found that sorption parameters can vary strongly between profiles in the same field. This spatial variability should be taken into account when modelling metal transport at the field scale. Streck & Richter (1997) also found that transport of Cd and Zn in a sandy soil (pH~5.3) could be successfully modelled based on the LEA basis, if spatial variability of sorption was taken into account. However, it cannot be concluded that the LEA is always valid for modelling metal transport. Preferential flow is likely to occur in more structured soil, and could affect metal leaching (e.g. Maeda & Bergstrom, 2000; Bundt *et al.*, 2001).

Root water uptake was not taken into account in the model. The water flux used in the calculations was representative for the long-term average flux below the root zone. If root water uptake had been considered, the modelled water flux in the topsoil would have been larger, and hence, faster metal transport would have been predicted. However, since rooting was shallow in these soils (most roots in top 5 cm), neglecting root water uptake is expected to have only a minor effect on the model outcome.

Observed cadmium concentrations in the topsoil of the polluted field exceeded the predicted concentrations. The presence of non-labile Cd in the deposition load, which was not accounted for in the retrospective modelling, might explain this deviation between observed and predicted values. This non-labile metal in the deposition is not, or only very slowly, mobilized. Ideally, the labile fraction of metal in the deposition and the weathering rate, *i.e.* the rate with which the metal is transformed from the non-labile to the labile form (e.g. through solid state diffusion, dissolution of a metal-bearing phase ...), should be known to predict the long-term fate of this metal. However, it seems acceptable to model the transport of Cd assuming that Cd in the deposition load was fully labile, in view of the large labile fractions of Cd in soil, observed for the soils in this study and also for a large collection of soils covering a wide range of soil properties and contamination source (Degryse *et al.*, 2004). On the other hand, the presence of a non-labile metal pool cannot

be neglected when evaluating the mobility of Zn in soils. Leaching of Zn would be greatly overestimated if it is assumed that all Zn is in equilibrium with the solution phase. Zinc in the topsoil of the polluted field was present in considerably larger concentrations than in the unpolluted field, despite the great mobility of (labile) Zn in these acid soils. Zinc in the deposition load was, presumably, mainly present in a non-soluble form, from which it is only slowly released (on a time scale of decades to centuries or longer), which explains the relatively large concentrations of non-labile Zn in the upper horizons of the polluted field.

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Table 1 Soil properties, total and labile concentrations (*E*) of Cd and Zn for the unpolluted (Houthalen) and the polluted (Balen) field.

Values are means for 6 (Houthalen) or 10 (Balen) profiles (standard deviations in brackets).

Horizon ^a	Depth ^b / cm	pH	OC / %	Fe _{ox} ^c / mmol kg ⁻¹	Cd _{tot}	Zn _{tot}	<i>E</i> _{Cd}	<i>E</i> _{Zn}	% <i>E</i> _{Cd}	% <i>E</i> _{Zn}
Unpolluted										
A	0–10	3.3 (0.1)	3.35 (1.31)	18.5 (7.8)	0.18 (0.07)	9.4 (4.7)	0.11 (0.05)	4.5 (3.1)	62 (8)	46 (12)
E	10–25	3.3 (0.1)	2.24 (0.70)	15.8 (5.5)	0.17 (0.07)	4.5 (2.1)	0.12 (0.06)	2.1 (1.0)	72 (11)	49 (14)
B _h	25–40	3.7 (0.2)	1.38 (0.80)	30.8 (10.4)	0.15 (0.07)	6.3 (2.9)	0.13 (0.07)	1.9 (1.0)	85 (15)	32 (14)
BC	40–60	4.0 (0.1)	0.38 (0.20)	11.4 (4.9)	0.03 (0.03)	9.5 (2.5)	0.03 (0.02)	1.1 (0.4)	104 ^d (27)	12 (5)
C ₁	60–100	4.0 (0.02)	0.15 (0.06)	8.9 (6.3)	0.02 (0.01)	10.6 (4.4)	0.02 (0.01)	1.2 (0.6)	106 ^d (25)	11 (3)
C ₂	> 100	4.0 (0.1)	0.10 (0.04)	6.4 (1.0)	0.01 (0.01)	13.3 (4.7)	0.01 (0.01)	1.8 (0.4)	108 ^d (14)	16 (7)
Polluted										
A	0–10	3.7 (0.2)	2.57 (0.59)	26.9 (14.8)	0.82 (0.40)	70.7 (43.0)	0.42 (0.33)	10.9 (6.8)	50 (21)	19 (11)
E	10–20	3.8 (0.2)	1.57 (0.90)	24.0 (21.9)	0.73 (0.84)	27.1 (25.0)	0.52 (0.60)	7.2 (9.6)	80 (24)	31 (21)
B _h	20–35	4.0 (0.3)	1.58 (1.10)	29.8 (19.0)	0.94 (0.86)	19.9 (17.9)	0.81 (0.78)	10.1 (17.2)	90 (16)	39 (25)
BC	35–60	4.2 (0.2)	0.85 (1.22)	10.9 (7.0)	0.24 (0.24)	11.4 (4.8)	0.21 (0.21)	3.2 (4.3)	91 (15)	25 (22)
C ₁	60–100	4.3 (0.2)	0.28 (0.41)	6.3 (6.0)	0.22 (0.48)	14.4 (9.9)	0.20 (0.44)	4.5 (9.3)	91 (19)	20 (21)
C ₂	> 100	4.3 (0.1)	0.13 (0.10)	3.7 (1.7)	0.07 (0.09)	10.8 (5.7)	0.07 (0.08)	2.5 (1.3)	89 (11)	24 (11)

^a Approximately (not all profiles showed clear podzolisation).

^b Approximate depths, since thickness of horizons differed between profiles.

^c Ammonium oxalate extractable Fe.

^d %*E* values > 100, probably because of inaccuracy in total Cd determination at these small concentrations.

Table 2 Comparison between pore-water concentrations (mean value, standard deviation of 2 replicates in parentheses) and concentrations in solutions sampled by passive capillary samplers (PCAPS), about every 2 months, over a period of 18 months (mean value, range in parentheses).

	Lommel (Aquod)		Lommel (Humod)		Houthalen	
	pore-water	PCAPS	pore-water	PCAPS	pore-water	PCAPS
pH	4.18 ^a (0.03)	4.6 (4.1–5.5)	4.65 ^a (0.02)	4.6 (4.0–5.5)	4.77 ^a (0.05)	4.8 (4.3–5.6)
Cd /µg litre ⁻¹	17 (1.3)	12 (6–18)	17 (0.6)	19 (14–25)	1.0 (0.1)	0.6 (0.2–2)
Zn /mg litre ⁻¹	0.81 (0.05)	0.58 (0.36–0.84)	0.83 (0.02)	0.67 (0.45–0.91)	0.06 (0.01)	0.04 (0.02–0.05)
Ca /mg litre ⁻¹	2.1 (0.5)	3.8 (1.1–7.8)	0.9 (0.07)	1.6 (0.7–3.8)	0.38 (0.01)	0.9 (0.2–2.9)
Mg /mg litre ⁻¹	0.5 (0.1)	0.3 (0.2–0.5)	0.4 (0.07)	0.1 (0.1–0.2)	0.31 (0.01)	0.1 (0.1–0.2)
Na /mg litre ⁻¹	3.7 (0.1)	1.4 (0.6–2.2)	2.5 (0.2)	1.9 (1.4–2.3)	1.7 (0.002)	1.2 (0.6–1.9)
K /mg litre ⁻¹	3.7 (0.6)	0.5 (0.1–0.9)	0.8 (0.001)	0.1 (0.1–0.2)	1.6 (0.01)	0.2 (0.0–0.4)
Al /mg litre ⁻¹	2.0 (0.2)	2.3 (1.0–3.8)	0.8 (0.2)	1.6 (0.3–3.0)	0.29 (0.01)	0.9 (0.3–1.3)

^a pH measured in a soil water extract (soil:solution ratio = 1:5 kg litre⁻¹)

Table 3 Amount of Cd and Zn (in kg ha⁻¹) present in the profiles of the unpolluted and the polluted field. Calculations were made for the upper 2 metres.

Unpolluted											
	Profile										Mean
	1	2	3	4	5	6					
Cd /kg ha ⁻¹	1.27	1.2	1.04		1.84	0.75		2.01			1.35
Zn /kg ha ⁻¹	340	287	271		388	331		290			318

Polluted											
	Profile										Mean
	1	2	3	4	5	6	7	8	9	10	
Cd /kg ha ⁻¹	3.7	1.2	3.7	5.1	5	1.3	5.8	13.8	6.2	25.6	7.2
Zn /kg ha ⁻¹	213	291	361	463	406	365	513	633	480	889	461

FIGURE CAPTIONS

Figure 1 Schematic diagram of a Passive Capillary Sampler (PCAPS).

Figure 2 Desorption isotherms (in 10^{-3} M CaCl_2) of a polluted sandy soil with pH 3.9 obtained by widening the soil:solution ratio for (a) Cd and (b) Zn, after 2 days ($\circ$) or 7 days of equilibration ($\bullet$). Labile and non-labile metal concentrations, as determined by isotopic dilution, are indicated by the horizontal dashed lines.

Figure 3 The K_d (closed symbols) and K_d^{lab} (open symbols) of (a) Cd and (b) Zn, as a function of organic C content for the polluted field ($\bullet, \circ$) and the unpolluted field ($\blacktriangle, \triangle$).

Figure 4 The water flux, and the concentrations of Cd and Zn measured by passive capillary samplers at 70 cm of depth in (a) a polluted podzol (Humod, Lommel), and (b) in an unpolluted podzol (Houthalen) (open and closed symbols refer to the two wicks of one sampler). The concentration in soil solution obtained by centrifugation of the soil is indicated by the dash.

Figure 5 Measured (bars) and modelled (line) field-averaged concentrations of (a) Cd, and (b) Zn as a function of depth, for the polluted field. For the measured field-averaged profile, the mean concentrations were calculated in 5 cm increments. The light-shaded area of the bars represents the field-averaged values of the radio-labile concentration. The predictions were made with a convection-dispersion model. (Profiles 8 and 10 not included).

Figure 6 Predicted field-averaged concentration in the seepage water of the polluted field, calculated by averaging the solution concentrations at the bottom of all soil profiles. The vertical line represents the year 2000.

Figure 1

(a)

(b)

Figure 4

Figure 5

Figure 5