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Short title: Mobilization of Cd upon soil acidification

Mobilization of Cd upon acidification of agricultural soils: column study and field modelling

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Summary

The potential effect of acidification of contaminated sandy soils on Cd transport in the unsaturated zone was assessed. Forty-eight soil profiles were sampled at five depths in a polluted field that was set aside in 1992. The Cd concentration in the top 30 cm of this field was, on average, 10 mg kg^{-1} . A column experiment was carried out with one of the topsoil samples. Homogeneously packed columns were leached with 0.001 M CaCl_2 , adjusted to pH 3 or pH 5.7, at a pore water velocity of 6 cm day^{-1} . The Cd and proton transport was predicted with coupled transport equations. The Cd transport was modelled by assuming local equilibrium and by using sorption parameters derived from batch experiments, while acidification was modelled with a kinetic approach, on the assumption that proton buffering was due to cation exchange and mineral weathering. Organic matter was the main contributor to the cation exchange capacity of these soils. Observed and predicted pH and Cd profiles in the columns agreed well. With the same model, the proton and Cd transport at field-scale was calculated for each of the 48 profiles sampled ('grid model'). It was predicted that the field-averaged Cd concentration in the seepage water will increase from $6 \mu\text{g l}^{-1}$ at present to $200 \mu\text{g l}^{-1}$ over 260 years, which greatly exceeds the maximum permissible concentration (MPC) in groundwater of $5 \mu\text{g l}^{-1}$. Predictions of Cd transport using field-averaged soil properties yielded a later breakthrough time and a larger peak Cd concentration than predicted with the grid model, which illustrates the impact of spatial variability on solute transport. Continuation of liming practices is a possible solution to prevent breakthrough of Cd at concentrations far in excess of the MPC.

Introduction

As a result of set-aside policy, agricultural land is converted to forest or wetland to reduce arable crop production and to restore natural ecosystems. Afforestation of agricultural land results in a decrease of the soil pH, because of the termination of regular lime applications. Acidification can be accelerated by anthropogenic deposition of SO₂, NH₃, and NO_x. In sandy soils, with little buffering capacity, this decrease in pH may be fast. Römken & de Vries (1995) found that the pH in the topsoil of Dutch soils converted to forest decreased from 6 to 4 within 20 to 30 years.

It has been suggested that acidification might lead to a strong and sudden increase in plant uptake and leaching of Cd, because Cd sorption is strongly pH dependent (Stigliani *et al.*, 1993). Column experiments have indeed shown a fast breakthrough of Cd and Zn when soils are leached with an acid influent (Voegelin *et al.*, 2003). Increased metal leaching of heavy metals due to enhanced soil acidification has also been observed in field experiments (e.g. Berthelsen *et al.*, 1994), but no attempt was made to model the transport of heavy metals in these studies.

Column experiments can be used to estimate the transport of heavy metals at field scale. However, care should be taken when extrapolating results from column experiments to the field, because of the much larger water fluxes in the column experiments. Moreover, the solute transport at field scale is strongly influenced by soil variability. Heterogeneity in soil chemical parameters, such as pH, has a large impact on the transport of heavy metals (e.g., Streck & Richter, 1997). The moment of first breakthrough may be underestimated if field heterogeneity is not taken into account (van der Zee & van Riemsdijk, 1987). To take field heterogeneity into account, transport at the field scale can be modelled by representing the field as a collection of soil stream tubes that are not connected (i.e., no

transverse mixing). Numerical Monte Carlo simulations may be used to describe the transport in each stream tube by an equilibrium convection-dispersion equation (e.g., Seuntjens *et al.*, 2002). Another approach is the 1-D simulation of solute transport for all profiles sampled, based on measured parameters. In contrast to Monte Carlo simulations, this ‘grid model’ yields a three-dimensional distribution of concentrations as output. Streck & Richter (1997) used both the grid model and Monte Carlo simulations to model displacement of Cd and Zn at the field scale in a sandy soil after 29 years of wastewater irrigation. They used EDTA-extractable Cd and Zn to model the transport, and assumed that this extractable fraction represents the metal pool that is in dynamic equilibrium with metals in the solution phase. Both models yielded similar results, in good agreement with measured data, which indicates that Cd and Zn transport at the field scale may be predicted by assuming local equilibrium between the labile metal pool and the solution phase. A single extraction with a complexing agent, such as EDTA, is a convenient method to measure the labile pool. Another method to measure the labile pool is the isotopic dilution technique, which seems conceptually more attractive, since it measures the amount of metal in soil that has the same fate as a freshly-added metal salt (e.g., Smolders *et al.*, 1999).

The objective of this study was to assess the long-term effect of acidification on Cd transport in a sandy field, taking spatial variability into account. Forty-eight profiles were sampled in a field that was set aside in 1992, located in the northern part of Belgium. Heavy metal concentrations in this field are elevated due to Zn smelter activities. Acid deposition is relatively large in this region, because of industrial activities and intensive cattle breeding. Sorption of Cd and pH buffering of the soils was measured in batch experiments. The Cd transport and proton transport was modelled with coupled transport equations, assuming that only labile Cd will be leached. A column experiment was carried

out to validate the transport model. The Cd transport at field scale was calculated with this model, by simulating the transport for each of the 48 profiles sampled ('grid model').

Materials and methods

Approach

The transport model was validated with a column experiment, where homogeneously packed columns were leached with 0.001 M CaCl₂, adjusted to pH 3 or pH 5.7. The hydraulic parameters were obtained from ³⁶Cl⁻ breakthrough experiments. The radio-labile Cd concentration was used as the initial Cd content, on the assumption that non-labile metal is not available for leaching. The pH dependence of the solid–liquid distribution coefficient (K_d) of Cd and the pH buffer capacity of the soil are important input parameters in the transport model, since the transport of Cd is highly dependent on the sorption parameters. These soil chemical parameters were obtained independently in batch experiments. The pH profiles in the acidified columns could not be described using an equilibrium approach; kinetic parameters for the proton buffering had to be included that were based on a literature survey and adjusted to fit the experimental data.

The same approach was used to model the transport at the field scale for each of the 48 profiles sampled. Soil chemical parameters were measured in batch experiments for all soil samples. The precipitation surplus, the dispersion length, and the acid input were estimated from literature data.

Soil and soil characterisation

Soil samples were taken in a field that is part of a nature reserve (Hageven) in Neerpelt (51°15'N, 5°25'E), situated in the 'Kempen' (northern Belgium). The field is former arable land that was set aside in 1992. The soil is strongly contaminated with Cd and Zn due to emissions from a nearby Zn refinery that was in operation until 1995. The soil is classified as a Typic Haplaquod (USDA system), a wet sandy soil with a plough layer. The groundwater table fluctuates between about 60 and 120 cm depth.

Soil samples were taken in 1997, in a 20-m by 20-m grid. At each of the 48 points, samples were taken with an Edelman screw auger at 5 depths (0-15, 15-30, 30-45, 45-60, and 60-90 cm). The samples were air dried and passed through a 2-mm aperture sieve.

The pH was measured in 0.001 M CaCl₂ in a 1:10 soil:solution ratio, and was assumed to be a good estimate of the pH of the soil solution which had similar ionic strength to the CaCl₂ extract. Air-drying and differences in soil:solution ratios may affect the pH, but these effects are usually small (e.g. Davey & Conyers, 1988). Organic C content was measured by dry combustion (Skalar CA 100, Breda, The Netherlands). The radio-labile Cd concentration, also called the *E* value, was determined by isotopic dilution, in a 0.001 M CaCl₂ extract in a 1:10 soil:solution ratio. Soil samples of 2.5 g were weighed into a polypropylene centrifuge tube, 25 ml of 0.001 M CaCl₂ were added, and the suspensions were shaken end-over-end for 24 hours. The suspensions were spiked with 0.2 ml of a carrier-free ¹⁰⁹CdCl₂ solution (30 kBq ml⁻¹), and shaken for another six days. After phase separation by centrifugation (25 minutes, 3700 g), samples were taken from each tube and acidified to pH 1 with HNO₃ pending determination of ¹⁰⁹Cd (gamma counting) and stable Cd. Stable Cd concentrations were measured with flame (FAAS) or graphite furnace (GFAAS) atomic absorption spectrophotometry, depending on the concentrations. The *E* values were calculated as described elsewhere (Smolders *et al.*, 1999). Pore-water concentrations of Cd were not measured, but were approximated by the concentration in

the 0.001 M CaCl_2 extracts. The soil solution composition was determined in two soil profiles, and it was found that the ionic strength of the solution was between 2.0 and 4.7 mM, comparable to the ionic strength of the CaCl_2 extract. Partitioning of Cd in this extract is therefore considered to be a good approximation of the field situation (Streck & Richter, 1997).

Four topsoils (0–10 cm) of a nearby field, with similar soil characteristics but with a more acid pH (between 4 and 4.6), were used in a liming experiment, from which the results were used to derive a Gapon exchange constant of protons against base cations (see below). Lime (analytical grade CaCO_3) was added to the field moist soils at rates of 0.43, 0.86 and 1.28 g CaO per kg dry soil. The soils were thoroughly mixed, and incubated for two weeks at 25°C. After incubation, the soils were air dried. The pH was measured in 0.001 M CaCl_2 (solid:liquid ratio 1:10), and the CEC and concentrations of exchangeable bases were measured at the soil pH with silver-thiourea as the index cation (Chhabra *et al.*, 1975).

Batch experiments

Proton buffer curves and pH dependence of the K_d of Cd were determined by equilibrating soil samples with 0.001 M CaCl_2 in a 1:10 soil:solution ratio, at four or five concentrations of HNO_3 (0–120 mmol $\text{HNO}_3 \text{ kg}^{-1}$). The suspensions were shaken end-over-end for 24 hours, and spiked with 0.2 ml of a carrier-free $^{109}\text{CdCl}_2$ solution (30 kBq ml^{-1}). The samples were shaken for a further seven days, centrifuged, and the pH of the supernatant was measured. The ^{109}Cd activity of the supernatant was determined, which allowed calculation of the (isotopic) solid–liquid distribution coefficient.

Column experiment

The soil used for the column experiment was sampled from the surface layer (0–10 cm) of the same field where the 48 profiles were sampled. The soil had a pH (measured in 0.001 M CaCl₂) of 6.3, an organic C content of 2.75 % and a total metal concentration (determined by *aqua regia* digestion) of 10.1 mg Cd kg⁻¹ and 682 mg Zn kg⁻¹.

Sixteen polypropylene columns (3 cm i.d.) with a porous glass plate at the base were filled with 1 cm calcined sea sand, 5 cm air-dried soil and 1 cm calcined sand. A glass fibre filter was placed on top of the column to ensure homogeneous distribution of the feeding solution over the column. Sorting of the particles during packing was avoided by placing a piston of slightly smaller diameter than the column on the surface of the soil after each increment and by tapping the column. The soil was packed to a bulk density of 1.34 g cm⁻³. The packed columns were slowly saturated from top to bottom with 0.001 M CaCl₂ to remove entrapped air. After one week, a 0.001 M CaCl₂ solution was applied by a peristaltic pump at a flow rate of 14 ml day⁻¹, which corresponds to a pore water velocity of ~6 cm day⁻¹. A suction of 25 kPa was applied at the bottom of the columns to establish unsaturated flow in the columns. Saturation of the soil was avoided because soil reduction and concomitant changes in pH are likely to affect the partitioning of Cd. The different treatments were started after one week of equilibration. A 0.001 M CaCl₂ solution acidified to pH 3 with H₂SO₄ was applied to eight columns; the other (control) columns received 0.001 M CaCl₂ (pH 5.7). The columns were kept at a constant temperature of 14 °C. The effluents were collected through a Teflon funnel into polypropylene bottles. Effluent samples were collected weekly and the volume was recorded by weight. The samples were acidified to pH 1 with HNO₃ and analyzed for Cd with GFAAS.

Prior to dismantling, physical transport parameters were estimated from ³⁶Cl⁻ breakthrough curves. A 2-hour ³⁶Cl⁻ pulse was applied to each column. Every 3 to 4 hours

samples were collected, until complete breakthrough. Activity of $^{36}\text{Cl}^-$ in the samples was determined with a liquid scintillation counter (Packard Tricarb 1600 CA, Perkin Elmer, Zaventem, Belgium).

For each treatment, two columns were dismantled after two and four months and the remaining columns were dismantled after six months. The soil core was removed and sliced into 1-cm layers. Every layer was weighed before and after being air dried. All samples were analyzed for 'total' Cd concentration by extraction with 0.43 M HNO_3 (1:10 soil:solution ratio, 2 hours of equilibration). The pH, the E value and the solution concentration of Cd were measured in 0.001 M CaCl_2 as described above.

Modelling

The solute transport in case of local equilibrium can be described with the convection-dispersion equation (CDE):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - \frac{\rho}{\theta} \frac{\partial s}{\partial t}, \quad (1)$$

where c is the solution concentration, s is the concentration on the solid phase, ρ is the soil bulk density (g cm^{-3}), θ is the volumetric water content ($\text{cm}^3 \text{ cm}^{-3}$), D is the dispersion coefficient ($\text{cm}^2 \text{ day}^{-1}$), v is the pore water velocity (cm day^{-1}), t is the time (days), and z the distance (cm).

The dispersion coefficient D ($\text{cm}^2 \text{ day}^{-1}$) combines the effects of molecular diffusion and of hydrodynamic dispersion caused by velocity variations in the advective transport:

$$D = \lambda v + \tau D_0, \quad (2)$$

where λ is the dispersivity (cm), τ is the tortuosity factor (-), and D_0 is the diffusion coefficient in water ($\text{cm}^2 \text{ day}^{-1}$). The tortuosity factor was calculated from the water

content, θ , and the porosity, ϕ ($\text{cm}^3 \text{ cm}^{-3}$), using the relationship of Millington & Quirk (1961):

$$\tau = \frac{\theta^{7/3}}{\phi^2}. \quad (3)$$

Proton transport. This was modelled with a kinetic approach, on the assumption that proton buffering was due to cation exchange and mineral weathering (see Results section). Therefore, proton transport was described as

$$\frac{\delta c_H}{\delta t} = D_H \frac{\delta^2 c_H}{\delta z^2} - v \frac{\delta c_H}{\delta z} - \frac{\rho}{\theta} R_w - \frac{\rho}{\theta} R_x, \quad (4)$$

where c_H (mol l^{-1}) is the proton concentration in solution, R_w ($\text{mol}_c \text{ kg}^{-1} \text{ day}^{-1}$) is the rate of proton consumption through weathering reactions, and R_x ($\text{mol}_c \text{ kg}^{-1} \text{ day}^{-1}$) is the rate of proton consumption through exchange with cations on the exchange surface. The weathering rate, R_w , was calculated from:

$$R_w = -\frac{dM_w}{dt} = k_w M_w c_H^\gamma v^\beta, \quad (5)$$

where M_w represents the weatherable mineral amount (in $\text{mol}_c \text{ kg}^{-1}$), k_w is a rate constant ($\text{day}^{-1} \text{ M}^{-\gamma} (\text{cm day}^{-1})^{-\beta}$), and γ and β are dimensionless exponents (van der Salm *et al.*, 1996). The inclusion of c_H in Equation 5 expresses the pH dependence of the dissolution rate. The water velocity, v , is included in the model to incorporate its effect on the weathering rate (van der Salm *et al.*, 1996).

The proton consumption through cation exchange, R_x , was calculated on the assumption that the cation exchange rate is determined by the diffusional transport of base cations between the bulk of the solution and the active sites on the exchange surface (Warfvinge & Sverdrup, 1989):

$$R_x = -\text{CEC} \frac{dX_{\text{BC}}}{dt} = -\text{CEC} k_x (c_{\text{Ca}} - c_{\text{Ca,s}}), \quad (6)$$

where CEC ($\text{mol}_c \text{ kg}^{-1}$) is the *potential* cation exchange capacity (*i.e.* at neutral pH conditions), X_{BC} is the base saturation of the exchange complex, k_x ($\text{l mol}^{-1} \text{ day}^{-1}$) is the mass transfer coefficient, and c_{Ca} and $c_{\text{Ca,s}}$ are the Ca concentrations (mol l^{-1}) in the bulk solution and at the surface of the exchanger phase, respectively. The concentration of Ca at the exchange surface was calculated from the Gapon exchange equation:

$$c_{\text{Ca,s}} = (K_G c_{\text{H,s}} \frac{X_{\text{BC}}}{1 - X_{\text{BC}}})^2, \quad (7)$$

where K_G is the Gapon exchange constant. The proton concentration at the exchange surface ($c_{\text{H,s}}$) was solved from a charge balance equation, which assumed that Ca is transported from the exchange surface to the bulk solution with counter-diffusion of protons ($c_{\text{Ca}} + 2c_{\text{H}} = c_{\text{Ca,s}} + 2c_{\text{H,s}}$), a method simplified from Warfvinge & Sverdrup (1989).

Cadmium transport. The solid–liquid distribution of Cd was described with the Freundlich isotherm:

$$s_{\text{Cd}} = k c_{\text{Cd}}^n, \quad (8)$$

where s_{Cd} is the labile concentration of Cd on the solid phase (E value, mg kg^{-1}), c_{Cd} is the solution concentration (mg l^{-1}), and k and n are empirically derived sorption parameters. It was assumed that only labile metals can be leached and, therefore, the E value and the sorption parameters which describe the equilibrium between the radio-labile metal pool and solution phase were used in the model calculations. Substitution of Equation (8) in Equation (1) yields:

$$\frac{\delta c_{\text{Cd}}}{\delta t} (1 + \frac{\rho}{\theta} n k c_{\text{Cd}}^{n-1}) = D_{\text{Cd}} \frac{\delta^2 c_{\text{Cd}}}{\delta x^2} - v \frac{\delta c_{\text{Cd}}}{\delta x}. \quad (9)$$

Equation (9) was used to model the Cd transport in the control columns (no pH change).

Sorption of Cd is strongly pH dependent and, therefore, the changes in solid–liquid distribution of Cd with decreasing pH must be taken into account when modelling the Cd transport under acidifying conditions. The pH dependency of the sorption isotherm was quantified using an extended Freundlich equation of the form:

$$s_{\text{Cd}} = k' (c_{\text{H},s})^a c_{\text{Cd}}, \quad (10)$$

where $c_{\text{H},s}$ is the proton concentration (mol l^{-1}) at the exchange surface, and k' and a are sorption parameters derived from the batch experiments. The Freundlich parameter for Cd, n , was assumed to be 1, since the batch experiments did not reveal any dependence on Cd load (see below). For the prediction of the field-scale transport, the dependence of the sorption parameter, k' , on the organic C content was described with:

$$\log(k') = \log(k^*) + b \log(\% \text{OC}), \quad (11)$$

where k^* and b are constants obtained by regression analysis (see Results section).

Substitution of Equation (10) in the CDE, Equation (1), yields the transport equation:

$$\frac{\partial c_{\text{Cd}}}{\partial t} + \frac{\rho}{\theta} k' (c_{\text{H},s})^a \frac{\partial c_{\text{Cd}}}{\partial t} + \frac{\rho}{\theta} c_{\text{Cd}} k' a (c_{\text{H},s})^{a-1} \frac{\partial c_{\text{H},s}}{\partial t} = D_{\text{Cd}} \frac{\partial^2 c_{\text{Cd}}}{\partial z^2} - v \frac{\partial c_{\text{Cd}}}{\partial z}. \quad (12)$$

The transport equations for the Cd transport, Equation (12), and proton transport, Equations (4)–(7), were solved numerically together with Matlab (Release 12), by using finite differences with an explicit scheme.

Estimation of acid input. Atmospheric deposition of the acidifying compounds SO_2 , NO_x , and NH_3 is an important cause of acidification. Ammonia only acidifies the soil if it is nitrified and the resultant nitrate is leached:

One mole SO_2 corresponds to 2 acid equivalents, while 1 mole NO_x or NH_3 corresponds to 1 acid equivalent. Reaction equation (13) seems to imply that one mole ammonia may result in the production of 2 mole H^+ . However, half of the acidity in NH_4^+ originates from an acid substance (e.g., SO_2) that has transferred a proton to NH_3 .

Values of acid deposition for the region studied were obtained from the Flemish Environment and Nature Report (VMM, 2002). These values are based on emission data that are converted to deposition data with an atmospheric transport model. Average values in 2001 for Flanders were $1.2 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$ for SO_2 deposits, $1.3 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$ for NO_x deposits, and $2.1 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$ for NH_3 deposits, or a total acid deposition of $4.6 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$. The large contribution of NH_3 to the acid deposition is due to the intensive cattle breeding. Maps showing the regional distribution of the acid deposition indicated that the deposition in the region studied is around the mean value for Flanders. Values for H^+ deposition in rain are small in comparison and are in the order of $0.1 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$.

Internal proton sources may also contribute to the acidification of the soil. Ecosystems that increase in biomass acidify the soil, if net assimilation of cations exceeds that of anions. In steady-state ecosystems, however, mineralization equals assimilation and the soil does not acidify because of nutrient assimilation. Deprotonation of CO_2 or organic acids may lead to acidification. This proton source is usually of minor importance in soils with moderate or acid pH. Deprotonation of CO_2 may be a significant proton source in soils where the pH exceeds the pK_a for proton dissociation of CO_2 ($\text{pK}_a=6.3$).

Proton balances have shown the importance of acid deposition to acidification near centres of anthropogenic activities. In central and north-western Europe, acid deposition is a major fraction of the total proton loading in ecosystems with small to intermediate rates

of internal proton production (van Breemen *et al.*, 1984). Therefore, the acid deposition, estimated to be $4.7 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$, was used as value for the total acid input.

Results

Soil characteristics

Selected soil characteristics are summarized in Table 1. The soils were sampled five years after the field was set aside, which explains the slightly more acid pH in the upper layers. The plough layer (A_p) extends to a depth of 30 cm. The humic B horizon is located between 30 and 45 cm depth. The C horizon, characterised by the yellow colour because of the small organic C content, starts at 45-cm depth in most profiles. However, the organic C content is still larger than 1% in the 45–60 cm layer for 11 of the 48 profiles.

The largest Cd concentrations are found in the plough layer (0–30 cm) (Table 1). The radio-labile Cd concentration (E value) in this layer reaches 22 mg Cd kg^{-1} . Total Cd concentrations were determined by *aqua regia* digestion for five samples from one profile. It was found that the E value ranged from 75 to 100% of the total Cd concentration. These large labile fractions indicate that Cd has entered the soil in soluble form or that Cd in insoluble form has been transformed to labile Cd.

Proton buffering

The pH buffering of a soil arises from cation exchange reactions and from dissolution and precipitation reactions, e.g. of CaCO_3 at high pH and Al compounds at low pH. The pH buffer capacity of the soil (pH BC, $\text{cmol}_c \text{ kg}^{-1} \text{ pH}^{-1}$) is expressed as the amount acid or

base that must be added to change the pH by one unit. Figure 1(a) shows titration curves for three soil samples, obtained by HNO₃ addition to soil suspended in 0.001 M CaCl₂.

The relationship between pH and H⁺ added to the soil was approximately linear for pH values above 4. Linear regression curves were fitted through this part of the buffer curve, and the pH BC was calculated as the reciprocal of the slope of this regression line (see Figure 1a). The pH BC (above pH 4) ranged from 0.6 to 6.9 cmol_c kg⁻¹ pH⁻¹, and correlated well with the organic C content (Figure 1b). This good correlation suggests that organic matter is a main contributor to pH buffering in these soils, but the non-zero intercept indicates that it is not the only source of pH buffering. The slope of the regression line indicates that 79 cmol H⁺ per kg of organic C is needed to lower the pH by one unit. Magdoff *et al.* (1987) found a value of 70 cmol_c pH⁻¹ per kg C for North American forest soils. Aitken *et al.* (1990) reported values of about 90 cmol_c pH⁻¹ per kg C for soils from Queensland (Australia).

In the pH range 4 to 6, cation exchange is an important buffering mechanism (Reuss & Walthall, 1990). If soil buffer capacity is only due to cation exchange, the pH BC corresponds to the loss in exchangeable bases when the pH is lowered by one unit. The pH is related to the base saturation of the exchange complex, which can be expressed with a Gapon exchange constant:

$$K_G = \frac{1 - X_{BC}}{X_{BC}} \frac{\sqrt{c_{Ca}}}{c_H}, \quad (14)$$

where X_{BC} is the base saturation of the exchange complex, here defined as the ratio of base cation content to the CEC at pH~6. A value for K_G was estimated from the results of the liming experiment. The base saturation, X_{BC} , was calculated as the ratio of exchangeable base (Ca, Mg, K, and Na) content to the CEC at the largest lime dose (pH between 6 and 6.4). The relationship between pH (measured in 0.001 M CaCl₂) and X_{BC} was well

described using a value for K_G of $3000 \text{ M}^{-0.5}$ (Figure 2a), which is in good agreement with values reported in the literature (e.g. de Vries & Posch, 2003). If buffering between pH~6 and 4 is indeed mainly due to cation exchange, the CEC (at pH~6) is expected to correspond approximately with $(1.63\%OC+1.84)$, *i.e.* the predicted pH BC (Figure 1b) multiplied by 2, which was indeed the case for the soils in the liming experiment. The amount of H^+ that must be added to lower the pH to a certain value can then be calculated as:

$$\text{H}^+_{\text{added}}^{\text{pH}_{\text{ini}} \rightarrow \text{pH}} = \text{CEC} (X_{\text{BC}}^{\text{ini}} - X_{\text{BC}}) \approx (1.63 \%OC + 1.84) (X_{\text{BC}}^{\text{ini}} - X_{\text{BC}}), \quad (15)$$

where CEC refers to the CEC observed at pH~6 and where X_{BC} at the respective pH values can be calculated from Equation (14). It was found that buffering above pH 4 for the soil samples in this study was well-described with Equation (15) (Figure 2b), which supports the hypothesis that buffering in this pH range is mainly related to cation exchange.

Buffering between pH 3 and 4 was mostly stronger than above pH 4, except for soils with large organic C contents, and varied less between soils (Figure 1a). It is likely that pH buffering below pH 4 is mainly due to dissolution of Al-hydroxy compounds. The ammonium oxalate extractable Al content was around 3 cmol kg^{-1} in these soils.

These results justify the use of a proton transport model, Equation (4), that assumes proton buffering to be related to cation exchange (mainly above pH 4) and mineral weathering (mainly below pH 4).

Effect of pH on solid–liquid distribution of Cd

For all soils, the (isotopic) distribution coefficient of Cd, K_d , was measured in 0.001 M CaCl_2 extracts at various pH values obtained through HNO_3 addition. Linear regression

analysis of $\log K_d$ with respect to the pH (measured in the extract) and the organic matter content of the soil gave:

$$\log K_d = -1.43 + 0.84 \log \%OC + 0.62 \text{ pH}, R^2 = 0.90, n = 1095. \quad (16)$$

Since most Cd is radio-labile in these soils (see above), the isotopic distribution coefficient, which expresses the equilibrium between labile metal pool and solution phase, is similar to the total K_d .

For the soil of the column experiment (2.7 %OC), the distribution coefficient was determined at 1-cm depth intervals after 2, 4, and 6 months of acid leaching in 0.001 M CaCl_2 . The pH dependence of the K_d could be described with following equation:

$$\log K_d = -0.23 + 0.46 \text{ pH}, R^2 = 0.98, n = 35. \quad (17)$$

The K_d predicted with Equation (17) corresponds reasonably well (within a factor of 2) with the prediction using Equation (16) for a soil with 2.7 %OC. In the control columns, the K_d increased with decreasing Cd load. The solid–liquid distribution of Cd could be well-described with a Freundlich isotherm ($s = k c^n$):

$$s = 47 c^{0.41}, R^2 = 0.81, n = 40. \quad (18)$$

The parameter n of the Freundlich isotherm is unusually small in this case, which may be caused by leaching of those cations which compete with Cd for sorption (e.g., Zn).

Christensen (1987) found that the K_d of Cd at a Zn concentration of 0.5 mg l^{-1} was only half of the K_d at Zn concentrations below 0.05 mg l^{-1} . A decrease in Zn concentrations in the upper part of the column due to leaching has probably resulted in larger K_d values of Cd and, hence, a large dependence of the K_d on the metal load (*i.e.* small n). No effect of Cd load was found for the acidified samples. This effect may have been masked by the pH effect, since pH and Cd concentrations were correlated.

Column experiment

Parameter estimation. The input parameters used in the transport model are summarized in Table 2. The parameters v and D of the convection-dispersion equation were obtained from the breakthrough of $^{36}\text{Cl}^-$, by fitting an analytical solution of the one-dimensional convection-dispersion equation (Toride *et al.*, 1995). The breakthrough curves of $^{36}\text{Cl}^-$ were well described with the CDE model, indicating that there was (physical) local equilibrium. The pore water velocity, v , was between 5.2 and 6.8 cm day^{-1} . The tortuosity factor, τ , was calculated with the Millington-Quirk relation, Equation (3), and ranged from 0.23 to 0.32. The dispersivity, λ , was derived from the dispersion coefficient D of $^{36}\text{Cl}^-$, the diffusion coefficient D_0 (1.3 $\text{cm}^2 \text{day}^{-1}$ for $^{36}\text{Cl}^-$) and the pore water velocity (Equation 2), and ranged from 0.12 to 0.30 cm. The dispersion coefficients of Cd^{2+} and H^+ were calculated from v , λ , τ and D_0 (0.8 $\text{cm}^2 \text{day}^{-1}$ for Cd^{2+} and 8.1 $\text{cm}^2 \text{day}^{-1}$ for H^+) (Equation 2). The estimated dispersion coefficient ranged from 0.9 to 2.0 $\text{cm}^2 \text{day}^{-1}$ for Cd^{2+} , and from 2.8 to 4.0 $\text{cm}^2 \text{day}^{-1}$ for H^+ . The larger dispersion coefficient of protons results from the larger diffusion coefficient. The dispersion coefficient is usually dominated by the hydrodynamic dispersion term, but the diffusion term may become important in repacked columns at low pore water velocity (Jury *et al.*, 1991).

The sorption parameters used in the transport model were obtained from the batch experiments. The values derived for the parameters k and n in Equation (8), used to describe the Cd distribution in the control columns, were 47 and 0.41, respectively (cf. Equation 18). The values derived for the parameters k' and a in Equation (10), used to describe Cd distribution in the acidified columns, were 0.59 and -0.46, respectively (cf. Equation 17).

The parameter γ , that expresses the pH dependence of the mineral weathering rate, was assumed to be 0.7, based on a literature survey (e.g. Bloom & Erich, 1987; van

Grinsven *et al.*, 1992). The percolation rate dependence, β , was assumed to be 1.2 (van der Salm *et al.*, 1996). A value of $0.12 \text{ (d}^{-1} \text{ M}^{-\gamma} \text{ (cm d}^{-1})^{-\beta})$ was selected for k_w , to make the weathering rates predicted by Equation (5) agree with measured weathering rates reported in the literature (e.g. van der Salm *et al.*, 1996; van Grinsven & van Riemsdijk, 1992). The initial content of weatherable minerals was assumed to correspond with the acid neutralizing capacity between pH 4 and pH~2.7, which was around $7 \text{ cmol}_c \text{ kg}^{-1}$ for most soil samples (Figure 1b).

The mass transfer coefficient for cation exchange, k_x , was assumed to be $20 \text{ M}^{-1} \text{ day}^{-1}$, or $2.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Warfvinge & Sverdrup (1989) reported values for k_x between 0.7×10^{-4} en $25 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$.

Proton transport. Depth profiles of pH (in 0.001 M CaCl_2) were measured 2, 4 and 6 months after the start of the experiment. The control columns showed no change in pH, although the pH of the feeding solution (5.8) was slightly more acid than the pH of the soil (6.3). The pH decreased clearly in the columns that were fed with the acid solution (Figure 3). The pH profiles were well-predicted, though the pH was slightly underestimated in the upper part of the column.

Cadmium transport. Only a small decrease in total and solution concentration of Cd was observed in the upper layer of the control columns, since Cd retention was great ($K_d \sim 500 \text{ l kg}^{-1}$). The concentration profiles in the control columns were well predicted with the convection-dispersion equation, based on the local equilibrium assumption (Figure 4). Most Cd was removed from the upper 2 cm of the acid columns after 6 months of leaching (Figure 3), since the strong decrease in pH resulted in weak retention of Cd in these layers.

Accumulation of Cd was observed in the deeper layers, where the pH was not or only slightly affected. The solution concentrations showed a peak in the solution concentration of Cd at the depth of the pH front. Predicted Cd profiles were in good agreement with observed profiles (Figure 3).

Table 3 gives the amounts of Cd lost by leaching, calculated from the product of leachate volume and metal concentration in the leachate, or from the decrease in the total Cd concentration. Both methods gave similar results. The Cd concentration in the effluent of the control columns did not change within the period of observation (6 months), which was equivalent to about 210 pore volumes (PV). The amount leached from the control columns agrees well with the amount predicted to be leached from the columns according to the CDE model (Table 3). The model calculations showed that a decrease in the Cd concentration in the effluent of the control columns is not to be expected before 600 pore volumes. The metal losses were larger in the acidified columns than in the control columns. The concentrations of Cd in the effluent of the acidified columns clearly increased after ~130 PV. The effluent concentration at the end of the experiment (~210 PV) was around 0.05 mg Cd l⁻¹ (Figure 5). The modelled increase in effluent concentrations is smaller, and as a result, the predicted amount of Cd leached from the acidified columns is smaller than measured (Table 3). The model calculations predict a peak in the effluent concentration of Cd after about 400 pore volumes, when the Cd front reaches the bottom of the column (Figure 5). It is expected that this peak in the breakthrough would indeed have occurred if the experiment had been carried out for longer time, in view of the good agreement between observed and predicted depth profiles of Cd (Figure 3).

Transport at the field scale

Parameter estimation The parameters used to model the transport at the field scale are summarized in Table 4. The transport was simulated for each of the 48 profiles sampled. The pH and the radio-labile Cd concentrations measured in 1997 were used as the initial values. The stationary flux at the upper boundary, q , was assumed to be $23.4 \text{ cm year}^{-1}$, which is the long-term average precipitation surplus for the region. The lower boundary was taken at 90-cm depth. The acid input was assumed to be $4.7 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$ (see Methods), which corresponds to a H^+ concentration of 0.002 M in the infiltrating water. Predictions of the Cd transport were also made in case the acidification is prevented by regular liming. In this case, an acid input was assumed that is equivalent to a pH of 6.3 in the infiltrating water. The deposition rate was assumed to be $2.3 \text{ g Cd ha}^{-1} \text{ year}^{-1}$, corresponding to a Cd concentration in the infiltrating water of 0.001 mg l^{-1} . Estimates for the current Cd deposition, based on Cd concentrations in rainwater in The Netherlands, are in the order of $1 \text{ to } 2 \text{ g Cd ha}^{-1} \text{ year}^{-1}$ (RIVM, 2001).

The dispersion length, λ , was assumed to be 10 cm , which is a normal value for solute transport at a comparable field scale (e.g., Butters & Jury, 1989). The volumetric water content, θ , was assumed to be $0.20 \text{ (cm}^3 \text{ cm}^{-3})$. The use of an approximate value for θ is justified since the water content has only a small influence on the transport of sorbing chemicals (e.g. Seuntjens *et al.*, 2002).

The sorption parameters were obtained from the batch experiments. The parameters a (Equation 10), k^* and b (Equation 11) were derived from regression Equation (16) relating the K_d of Cd to soil properties, which yields a value of $0.037 (=10^{-1.43})$ for k^* , -0.62 for a , and 0.84 for b .

For the weathering rate parameters (γ , β , k_w) and the content of weatherable minerals, the same values were used as for the column experiment. The mass transfer coefficient for

cation exchange, k_x , is inversionally proportional to the diffusion distance to the exchange surface. Since this diffusion distance is probably longer at smaller water velocities, a smaller value for k_x was used to predict the transport at the field scale, where the water velocity is about 30 times smaller than in the column experiment. The diffusion distance was assumed to be inversionally proportional to the square root of the water velocity, as it is for nonturbulent flow parallel to a flat plate, which results in an estimate for k_x that is 5.5 times smaller than for the column experiment, *i.e.* $3.6 \text{ M}^{-1} \text{ day}^{-1}$.

Solute transport. Figure 6 shows the calculated profiles of pH and Cd concentration, averaged over all 48 profiles. It is predicted that the acidification front and the peak in Cd concentration will have reached a depth of ~30 cm after 100 years, and a depth of ~70 cm after 200 years. In other words, the acidification front is predicted to travel with a velocity of about $0.35 \text{ cm year}^{-1}$. The field-averaged pH profile shows more spread than that calculated for a single profile. This field-scale dispersion is due to the variation in pH BC among profiles, which is related to the variation in organic C content.

The strong mobilization of Cd upon acidification results in elevated concentrations in the seepage water, calculated as the average pore-water concentration at the bottom of the profile (90-cm depth). It is predicted that the Cd concentration in the seepage water will increase after about 100 years, *i.e.* around the year 2100, and will be in the order of 0.2 mg Cd l^{-1} by the year 2260 (Figure 7b, solid line). The maximum permissible concentration (MPC) for groundwater in Flanders is $5 \text{ } \mu\text{g l}^{-1}$. When the pH is maintained at current values, the K_d values of Cd remain in the order of 500 l kg^{-1} in the topsoil and the Cd plume travels slowly because of this relatively strong retention. Approximately $250 \text{ kg CaCO}_3 \text{ ha}^{-1} \text{ y}^{-1}$ would be required to maintain the current soil pH, assuming that the acid deposition remains at the current level of about $5 \text{ kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$. The concentration in the

seepage water is predicted to remain below $13 \mu\text{g Cd l}^{-1}$ under that scenario (Figure 7a).
As a result, it would take about 2000 years before all excess Cd is removed from the soil.

The Cd transport under acidifying conditions was also simulated with a model where the field was treated as one single column with average soil properties (Figure 7b, dotted line). In this case, a later breakthrough and a larger peak concentration were predicted. Variability in soil properties should be taken into account when predicting the transport of sorbing solutes, as was also pointed out by van der Zee & van Riemsdijk (1987).

Discussion

The prediction of Cd transport in soil is strongly dependent on chemical sorption parameters (Seuntjens *et al.*, 2002). We compared the regression equation which relates the K_d of Cd to soil properties (pH and OC) derived from this study, Equation (16), with equations reported in literature (Table 5). Within the most relevant range of pH (3–6.5) and OC content (0.3–5 %OC), all equations predict K_d values that agree well with the values predicted with our equation, the difference amounting to at most a factor of 3. The outcome of the transport calculations is essentially the same when using one of these equations instead of the equation derived from our own data, *i.e.* the main breakthrough is predicted to occur between 2250 and 2300 with Cd concentrations in the seepage water in the order of 0.2 mg l^{-1} .

Peak concentrations of Cd are found at the depth of the acidification front (Figure 3), which agrees with the model predictions and as was also observed by Kjller *et al.* (2004) for trace metals in a sandy, non-calcareous aquifer. As a result, the predicted breakthrough time of Cd is strongly dependent on the predicted travel velocity of the acidification front

(v_{acid}), which depends on the proton buffering capacity of the soil. This velocity can easily be estimated with the following equation:

$$v_{\text{acid}} = \frac{AL}{ANC}, \quad (19)$$

where AL is the acid load and ANC is the acid neutralising capacity. For instance, in the study of Kjller *et al.* (2004), the acid load was in the order of 3 kmol_c ha⁻¹ year⁻¹ (Hansen & Postma, 1995). Proton buffering was mainly through cation exchange, and the CEC of the sediment was around 0.003 mol_c kg⁻¹. Assuming a bulk density (ρ) of 1.8 g cm⁻³, the ANC is predicted to be 0.54 kmol_c ha⁻¹ cm⁻¹, which results in an estimate for v_{acid} of 5.5 cm year⁻¹, and which agrees well with the observed velocity. In an agricultural soil at Rothamsted that was converted to woodland at the end of the 18th century, time-averaged acid loads were in the order of 5 kmol_c ha⁻¹ year⁻¹ (Sverdrup *et al.*, 1995). On the assumption that proton buffering is only through cation exchange, and using a value for ρ of 1.2 g cm⁻³ and an initial CEC (pH~6.2) of 0.17 mol_c kg⁻¹ for the upper layers (Sverdrup *et al.*, 1995), the ANC is estimated to be in the order of 20 kmol ha⁻¹ cm⁻¹. Hence, the predicted v_{acid} is 0.25 cm year⁻¹, and the predicted total distance travelled by the acidification front over the last 110 year is 27 cm, which agrees reasonably with the measured depth of the acidification front (Blake *et al.*, 1999). These studies, as well as ours, illustrate the importance of cation exchange for proton buffering in non-calcareous soils and sediments, and indicate the vulnerability of non-calcareous, low CEC soils (e.g. sandy soils with small OC contents) to acidification.

The transport model used in this study holds a lot of implicit simplifications. Possible effects of the fluctuating groundwater table on pH and on Cd transport were not taken into account. The build-up of organic matter in the top layer upon afforestation and the recycling of cations by vegetation were not considered, and may result in a slower

acidification in the top layer than predicted. However, this possible underestimation of the pH in the top layer is not expected to have large impact on the prediction of Cd transport, since this effect is restricted to the upper centimetres of the profile (Sverdrup *et al.*, 1995) and Cd will be transported to deeper layers in a relatively short time. Complexation of Cd with dissolved organic matter (DOM), of which the concentration may increase upon afforestation, was not taken into account, because the affinity of DOM for Cd is rather small. Nolan *et al.* (2003), who measured free ion fractions of metals in soil solutions of agricultural or contaminated soils, found that the free ion fraction of Cd was generally larger than 50%, except for soils with pH>7.7 and one soil with an extremely large sulphate concentration. Effects of Ca concentration on retention and transport of Cd were also not considered. The solid–liquid distribution of Cd was measured in 0.001 M CaCl₂, since the ionic strength of the pore water in the field studied is in the order of 0.003 M. The Ca concentration and ionic strength may change over time. However, even a tenfold difference in the Ca concentration, which is not likely to occur, would only affect the K_d by a factor of ~2 (Temminghoff *et al.*, 1996), which is a minor effect compared with that of the change in pH. Overall, the most important processes, with respect to the prediction of the Cd transport, are probably covered by our model, notwithstanding its numerous simplifications.

In conclusion, the set-aside of agricultural lands that are heavily contaminated with Cd, may have large environmental impacts, especially where the groundwaters are shallow and when the soil is vulnerable to acidification (low CEC, no free CaCO₃). In contaminated agricultural soils, only a small fraction of Cd has migrated downward out of the plough layer, because a high pH (pH>6) is maintained. Acidification due to set-aside will result in a strong mobilization of Cd accumulated in the plough layer ('chemical time

bomb’). Continuation of liming practices is a possible solution to prevent breakthrough of Cd at concentrations far above the maximum permissible concentration.

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Figure 1 (a) Titration curves for three soils with an organic C content of 1.0 %, 0.7 %, and 0.1 %. The lines show the buffer curves that assume a pH buffer capacity above pH 4 of 1.9, 1.45, and 1.0 $\text{cmol}_c \text{ kg}^{-1} \text{ pH}^{-1}$, respectively, and a pH buffer capacity below pH 4 of 5.0 $\text{cmol}_c \text{ kg}^{-1} \text{ pH}^{-1}$ for all soils. (b) The pH buffer capacity (above pH 4) as a function of the organic C content. Symbols are measured values ($n=239$), and the line is the linear regression line.

Figure 2 (a) The relation between base saturation (X_{BC}) and pH (measured in 0.001 M CaCl_2). The symbols are observed values for four soils amended with lime at three different rates. The line gives the theoretical curve, using a Gapon constant, K_g , of $3000 \text{ M}^{-0.5}$ (Equation 14). (b) Titration curve for a soil with 1.7 %OC. The line is calculated based on the assumption that pH buffering is only related to cation exchange (see text; Equation 15).

Figure 3 Measured and predicted depth profiles of pH, solution concentration and total concentrations of Cd for the column experiment, after 2, 4, and 6 months of acid leaching. The bars show the measured values; error bars denote the standard error of the mean. The line shows the predicted depth profile; symbols (squares) are means of the predicted values per layer.

Figure 4 Measured and predicted depth profiles of (a) solution concentration and (b) total concentrations of Cd after 6 months of leaching (~ 200 pore volumes) for the control columns. The bars show the measured values; error bars denote the standard error of the mean. The line shows the predicted depth profile; symbols are means of the predicted values per layer.

Figure 5 Observed (circles) and predicted (line) Cd concentration in the effluent of the acidified columns.

Figure 6 Field-averaged profiles of (a) pH and (b) solution concentrations of Cd. The solid line gives the values measured in the year 1997, and the dotted lines give the modelled values after 50, 100, and 200 years from 1997 onwards, assuming an acid input of $4.7 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$.

Figure 7 Modelled Cd concentrations in the seepage water (a) at constant pH, and (b) for an acid input of $4.7 \text{ kmol}_c \text{ ha}^{-1} \text{ year}^{-1}$. The solid line gives the simulation of the grid model, where the transport was calculated for all profiles using the measured soil properties. The dotted line (b) gives the simulation for a single-profile with field-averaged properties.

TABLES

Table 1 Summary of pH (measured in 0.001 M CaCl₂; 1:10 soil:solution ratio), organic C content, radio-labile Cd concentration (*E*), and Cd concentration in solution (0.001 M CaCl₂). Values are means per soil layer for all 48 profiles (standard deviation between parentheses)

Depth	pH	OC	<i>E</i>	Cd _{sol}
/cm		/%	/mg kg ⁻¹	/mg l ⁻¹
0–15	6.16	2.02	10.0	0.025
	(0.30)	(0.44)	(2.85)	(0.008)
15–30	6.31	1.88	9.96	0.023
	(0.25)	(0.42)	(3.66)	(0.007)
30–45	6.37	1.05	3.75	0.014
	(0.22)	(1.04)	(4.93)	(0.012)
45–60	6.37	0.98	1.40	0.010
	(0.21)	(1.61)	(2.25)	(0.012)
60–90	6.37	0.49	0.53	0.006
	(0.25)	(0.77)	(0.72)	(0.009)

Table 2 Input parameters used in the transport model for the column experiment

	Parameter	Symbol	Value	Unit
Hydraulic	Pore water velocity	v	5.2 -6.8	cm day^{-1}
	Dispersion coefficients; Cd^{2+}	D_{Cd}	0.9 -2.0	$\text{cm}^2 \text{ day}^{-1}$
	H^+	D_{H}	2.8 – 4.0	$\text{cm}^2 \text{ day}^{-1}$
Chemical	Sorption of Cd in control columns, Eq. (8)	k	47	$\text{mg}^{1-n} \text{ l}^n \text{ kg}^{-1}$
		n	0.41	–
	Sorption of Cd in acidified columns, Eq. (10)	k'	0.59	$\text{l kg}^{-1} \text{ M}^{-m}$
		a	-0.46	–
	Proton buffering through mineral weathering, Eq. (5)	k_w	0.12	$\text{day}^{0.2} \text{ M}^{0.7} \text{ cm}^{-1.2}$
		γ	0.7	–
		β	1.2	–
	Proton buffering through cation exchange, Eq. (6)	k_x	20	$\text{M}^{-1} \text{ day}^{-1}$
		CEC	0.066	$\text{mol}_c \text{ kg}^{-1}$
		K_G	3000	$\text{M}^{-0.5}$
Column	Length	L	5	cm
	Water content	θ	0.29 – 0.34	–
	Bulk density	ρ	1.34	g cm^{-3}
Initial/ Boundary conditions	Initial concentrations in solution	$c_{\text{Cd}, t=0}$	0.020	mg l^{-1}
		$c_{\text{H}, t=0}$	$10^{-6.3}$	mol l^{-1}
	Initial weatherable minerals	$M_{\text{w}, t=0}$	0.07	$\text{mol}_c \text{ kg}^{-1}$
	Acid input	$c_{\text{H}, \text{in}}$	0.001	mol l^{-1}
Numerical	Spatial discretization	Δz	0.05	cm
	Time discretization	Δt	0.0025	day

Table 3 Measured and predicted amounts of Cd lost by leaching in acidified and in control columns. The measured amounts were calculated from the metal amount recovered in the leachate or from the decrease in total Cd concentration in the soil ($\Delta\text{Cd}_{\text{tot}}$). The initial Cd content in the columns was 470 μg .

Cd leached from column / μg						
Time /months	Measured				Predicted	
	Acidified		Control		Acidified	Control
	Leachate	$\Delta\text{Cd}_{\text{tot}}$	Leachate	$\Delta\text{Cd}_{\text{tot}}$		
2	20	26	13	11	15	15
4	26	33	26	21	30	30
6	86	89	42	39	47	45

Table 4 Input parameters for the field modelling

	Parameter	Symbol	Value	Unit
Hydraulic	Water flux density	q	0.064	cm day ⁻¹
	Moisture content	θ	0.25	–
	Dispersion length	λ	10	cm
Chemical	Sorption of Cd,	k^*	0.037	–
	Eqs (10) and (11)	a	-0.62	–
		b	0.84	–
	Proton buffering through	k_w	0.12	day ^{0.2} M ^{-0.7} cm ^{1.2}
	mineral weathering, Eq. (5)	γ	0.7	–
		β	1.2	–
	Proton buffering through	k_x	3.6	M ⁻¹ day ⁻¹
	cation exchange, Eq. (6)	CEC	(1.63 %OC+1.84)	mol _c kg ⁻¹
		K_G	3000	M ^{-0.5}
Soil Profile	Length	L	90	cm
	Bulk density	ρ	1.35 (top) – 1.55 (bottom)	g cm ⁻³
Initial /	(Initial pH and labile Cd concentration as measured)			
Boundary	Initial weatherable minerals	$M_{w, t=0}$	0.07	mol _c kg ⁻¹
conditions	Acid input (4.7 kmol _c ha ⁻¹ y ⁻¹)	$c_{H,in}$	0.002	mol l ⁻¹
	Cd input (2.3 g ha ⁻¹ y ⁻¹)	$c_{Cd,in}$	0.001	mg l ⁻¹
Numerical	Spatial discretization	Δz	1	cm
	Time discretization	Δt	0.1	day

Table 5 Summary of linear regression equations, reported in literature, relating $\log K_d$ (l kg^{-1}) of Cd to pH and organic C content (OC, in %)

Reference	Regression coefficient			Comments
	intercept	pH	logOC	
This study	-1.32	0.62	0.84	240 soil samples of one field, pH adjusted to different values; (isotopic) K_d and pH measured in 0.001 M CaCl_2
Sauvé <i>et al.</i> (2000)	-0.65	0.48	0.82	Compilation of studies ($n=751$)
de Groot <i>et al.</i> (1998)	-0.39	0.40	0.77	37 soils with wide range of properties; pore-water based K_d ; pH measured in 0.01 M CaCl_2
Lee <i>et al.</i> (1996) ^a	-0.88	0.52	1.0 ^b	15 soils, pH adjusted to different values; (adsorption) K_d and pH measured in 0.01 M NaNO_3
Christensen (1989) ^a	-0.98	0.51	0.51	63 soils with wide range of properties; (adsorption) K_d and pH measured in 0.001 M CaCl_2
van der Zee & van Riemsdijk (1987) ^c	-0.97	0.50	1.0 ^b	Based on data from Chardon (1984)
Gerritse & van Driel (1984)	-1.57	0.59	1.0 ^b	33 soils with wide range of properties; (adsorption) K_d and pH measured in dilute salt extract ($\text{IS}=0.011$ M)

^a The regression equation was reported with respect to organic matter content (OM). The intercept was recalculated to obtain the equation with respect to organic C content, assuming that $\text{OM} = 1.7 \text{ OC}$.

^b The coefficient 1 was not derived from regression analysis; the K_d was normalized with respect to the organic matter content, prior to regression with pH.

^c The equation reported was of the form $s_{\text{Cd}} = k \text{ OC } c_{\text{H}}^{-0.5} c_{\text{Cd}}^{0.85}$. The (constant K_d) equation given in the Table predicts the same K_d as this Freundlich-type equation if $c_{\text{Cd}} = 0.005 \text{ mg l}^{-1}$, and gives reasonable approximations (within a factor of 2) for relevant concentrations (c_{Cd} between $0.1 \text{ } \mu\text{g l}^{-1}$ and 0.25 mg l^{-1}).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7