

Analysing the preferential transport of lead in a vegetated roadside soil using lysimeter experiments and a dual-porosity model

S. ROULIER, B. ROBINSON, E. KUSTER & R. SCHULIN

Institute of Terrestrial Ecosystems, ETH Zurich, Universitätstrasse 16, 8092 Zürich, Switzerland

Summary

Lead (Pb) from the traffic accumulates in roadside soils, which are usually vegetated to control erosion. Plants release soluble organic substances that bind Pb. Root macropores also create preferential pathways through which water can flow. Both these processes may enhance Pb mobility. We used large lysimeters to investigate the transport of Pb in a contaminated ($445 \text{ mg Pb kg}^{-1}$) soil under vegetation (*Phacelia tanacetifolia*). Despite the high soil pH (7.2), Pb leached into the drainage water during the 5-month experiment. The fast response of the system to intense rainfall events indicated the presence of preferential flow. By comparing Pb concentrations in filtered and unfiltered leachates, we found that Pb was leaching primarily on suspended material. An increase in Pb concentration in the leachate at the end of the experiment indicated the remobilization of Pb, possibly by decaying vegetation. We parameterized the dual-porosity MACRO model using the experimental results. The simple parameterization of MACRO used to simulate the Pb concentrations in the drainage water produced an overall model efficiency of 0.81: MACRO simulated the Pb concentrations well, but it failed to predict the observed increase of Pb in the leachate at the end of the experiment. The model gave the best prediction of Pb concentrations with a small partition coefficient ($k_d = 150 \text{ cm}^3 \text{ g}^{-1}$). Long-term simulations of Pb mobility showed that for our specific conditions preferential flow was the main process determining the fate of Pb.

Introduction

Soil adjacent to busy roads has exceptionally large concentrations of lead (Pb). Whereas it is commonly assumed that Pb is immobile in topsoil (McBride, 1994), several studies have shown downward migration of Pb. Cao *et al.* (2003) found Pb to be highly mobile in soil of shooting ranges that was rich in both lead and organic matter. Deiss *et al.* (2004) observed enhanced Pb mobility in an acidic, peat soil, and Lamy *et al.* (2006) reported Pb leaching in sandy soils irrigated with wastewater.

Roadside soils are usually vegetated to control erosion and improve aesthetic appearance. This vegetation may immobilize contaminants by reducing leaching and increasing sorption by the addition of organic matter to the soil (Robinson *et al.*, 2003). However, in some cases, vegetation enhances the mobility of contaminants. Roots often grow into macroporous interstices, creating continuous preferential pathways (Hatano *et al.*, 1988). Preferential flow is a physical process in which strongly adsorbing compounds move through the soil at a similar rate

to that of mobile compounds (Flury, 1996). The rapid transfer of a compound through a small portion of the pore system reduces its interactions with binding sites in that system. This contact time is of critical importance, because the mobility of a compound in soil is profoundly affected by its sorption on to the soil matrix (Bruemmer *et al.*, 1988). Root channels provide contaminants with rapid preferential paths towards the deeper layers of the soil that bypass the chemically and biologically reactive rhizosphere.

Roots also exude organic substances that complex metals. Lead forms strong complexes with organic matter, and the organic exudates in the soil solution can augment the preferential transport of lead through the root macropores (Camobreco *et al.*, 1996; Kim & Corapcioglu, 2002).

In Switzerland concentrations of Pb have been found to exceed guideline values up to 6 m from the road (VBBö, 1998). The world has *c.* 20 million km of paved roads, and so some 240 000 km² may be affected world-wide. A management strategy is required to minimize the environmental risk posed by Pb in these soils. Such a strategy could include soil amendments that limit the mobility of Pb, combined with a vegetation cover

Correspondence: S. Roulier. E-mail: stephanie.roulier@env.ethz.ch

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that not only controls surface erosion and provides an appealing vista, but again limits Pb mobility, either downward into groundwater, laterally to surface waters, or upward into the aerial portions of the plant. It is impractical to test experimentally all combinations of soil, amendment and vegetation tailored to the plethora of environmental, economic and cultural conditions that occur worldwide. Instead we must rely on models to elucidate combinations that are likely to fulfil the aforementioned conditions.

There is, at present, no comprehensive modelling framework for investigating the long-term fate of Pb in soils in relation to the vegetation cover. Solute transport models need to incorporate the complexation of Pb with organic matter and particles, combined with the effect of the root system on the soil structure. Such models are necessarily complex and so of limited use because of the many parameters required (Jacques *et al.*, 2002; Simunek *et al.*, 2005). To determine the fate of Pb in soils efficiently, we need methods that combine experimental data describing Pb mobility in field-like conditions, with transport models that are easy to parameterize.

With the above in mind, (i) we investigated the short-term mobility of Pb in a freshly settled roadside soil under vegetation cover in a lysimeter, (ii) we evaluated the performance of the one-dimensional dual-permeability solute transport model MACRO (Larsbo *et al.*, 2005), using easily-obtainable parameters, to simulate Pb transport, and (iii) we investigated the combined effects of vegetation and preferential flow on the long-term mobility of Pb.

Material and methods

Soil properties and experimental set-up

The soil used in this study was taken from the top 20 cm of the median strip of a Swiss motorway (A2) that links the cities of Luzern and Zürich. It is a sandy loam (USDA) with 17% clay and 3.51% organic matter, which made it prone to preferential flow (Jarvis *et al.*, 2007). The main mineral components of the soil fraction smaller than 2 mm were quartz, calcite, Na-plagioclase, microcline, muscovite and chlorite. The CaCO₃ content is 12.0% and pH was 7.2. The initial Pb concentration was 445 mg kg⁻¹.

The experiment was done at the lysimeter station (47°10'N; 8°18'E), of Horw, near Luzern. The average rainfall and temperature at the site are 1171 mm and 8.8°C, respectively. In August 2005, two rectangular lysimeter basins (5 × 3.5 m surface area, 1 m deep) were filled with a 50-cm layer of the soil, overlying a 20-cm layer of drainage sand (particle size between 1.5 and 2.2 mm). The herbaceous, shallow-rooted plant *Phacelia tanacetifolia* was sown 14 days after filling. Plants emerged 1 week later and reached a maximum height of 70 cm after 5 weeks. The vegetation died in the beginning of November, when the first frost occurred. The plant material was left on the soil surface until mid-April 2006. After the residues were

removed, new plants were sown on 12 May 2006. Roots and shoots were sampled 7, 26 and 34 days after emergence. The Pb concentrations of each plant part were measured by XRF with four replicates per sample. In late April 2006, 3 weeks before the new plants were sown, four soil cylinders, each of 1000 cm³, were collected to determine the water retention curve. The top 25 cm of the two lysimeters were sampled at eight locations with a Humax auger. Total Pb concentration was measured by XRF. Soluble Pb was extracted by 0.1 M NaNO₃ and by 0.1 M EDTA. Extracts in NaNO₃ are used in Switzerland as a legal standard to estimate the solubility and bioavailability of polluting metals in soils (VBBo, 1998). Lead sorbed to surfaces of mineral and organic constituents can be removed by EDTA, which will also dissolve some Pb precipitated as carbonate and represent the potentially long-term mobilizable Pb.

A 3% slope at the bottom of each lysimeter allowed the percolation water to flow in two separate 2-m³ closed tanks, through a drainage pipe. Every week we took two samples of the leached solution from each lysimeter. The accumulated weekly drainage from the lysimeters was measured, and the tanks were then emptied and flushed. One part of each drainage sample was filtered, removing particles > 0.45 μm in diameter, and acidified by addition of 1 ml of concentrated (69%) HNO₃. The other part was first acidified with the same HNO₃ solution and then filtrated with the same kind of filter as previously. The four replicate Pb concentrations at each sampling date in these filtrates were measured by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). The measured concentration in the first sample described the amount of free Pb in solution and the amount possibly bound to the soluble fraction of organic matter. In the second sample, we measured the total concentration in the leachates, including Pb bound to particulate organic matter. Weekly cumulated outflows were collected from 30 August 2005 to 19 July 2006. Concentrations of Pb on the leachate were measured from 18 August 2005 to 15 January 2006.

Hourly rainfall and daily meteorological data were recorded at the nearby (3 km) SwissMeteo meteorological station. Potential evaporation was calculated with the Penman equation, based on the recorded data.

Model description

We used the one-dimensional dual-permeability model MACRO to analyse Pb transport in our experimental conditions. Here, we report only aspects of MACRO that are relevant to this study. Larsbo *et al.* (2005) describe the model in full.

The model MACRO is based on the concept of two separate pore domains, each characterized by distinct flow rates and solute concentrations: the micropores, or matrix domain, and the macropores. The boundary between the two flow domains is characterized by a user-defined soil water pressure head h_b [L] with corresponding values for the saturated matrix water

content θ_b [$L^3 L^{-3}$] and hydraulic conductivity K_b [$L T^{-1}$]. Water flow in the micropores is governed by the Richards equation. Water retention and unsaturated hydraulic conductivity in this domain are described using a modified form of the van Genuchten–Mualem model (Vogel *et al.*, 2001; Larsbo *et al.*, 2005). Water flow in the macropores, q_{mac} [$L T^{-1}$], is assumed to be driven purely by gravity and is modelled with a modified numerical form of the kinematic wave equation (Germann, 1985):

$$\frac{\partial \theta_{mac}}{\partial t} = \frac{\partial q_{mac}}{\partial z} \pm S_w \quad (1)$$

$$q_{mac} = (K_{sat} - K_b) \left(\frac{\theta_{mac}}{\theta_{mac,sat}} \right)^{n^*}, \quad (2)$$

where θ_{mac} is the macropore water content [$L^3 L^{-3}$], K_{sat} is the saturated conductivity of the total pore system [$L T^{-1}$], $\theta_{mac,sat}$ is the saturated macropore water content [$L^3 L^{-3}$], and n^* is a ‘kinematic’ exponent reflecting macropore size distribution and tortuosity. Water exchange from macropores to micropores S_w [$L^3 L^{-3} T^{-1}$] is treated as a first-order approximation to the water diffusion equation that results from Richards equation when the influence of gravity is neglected:

$$S_w = \left(\frac{3D_w \gamma_w}{d^2} \right) (\theta_b - \theta_{mic}), \quad (3)$$

where d is the effective diffusion pathlength [L], characteristic of the degree of macropore flow in the system, D_w is an effective water diffusivity [$L^2 T^{-1}$], γ_w is a dimensionless scaling factor introduced to match the approximate and exact solutions to the diffusion problem (Gerke & van Genuchten, 1993), and θ_{mic} [$L^3 L^{-3}$] is the water content in the micropores. Water flow in the reverse direction occurs if the water potential in the matrix exceeds h_b . Uptake of water by the roots is calculated from evaporative demand, root distribution and soil water content, and it is distributed within the root depth according to the stress in each layer (Jarvis, 1989). The root distribution is assumed logarithmic with depth, and is defined by two parameters: the root depth and an empirical root distribution parameter that defines the percentage of the root length in the top 25% of the root depth.

Solute transport in the micropores is calculated from the convection–dispersion equation, with source and sink terms U_i to represent mass exchange between flow domains, kinetic sorption, and solute uptake by roots:

$$\frac{\partial (C\theta_{mic} + (1-f-f_{ne})\rho_d S)}{\partial t} = \frac{\partial}{\partial z} \left(D\theta_{mic} \frac{\partial C}{\partial z} - qC \right) \pm \sum U_i, \quad (4)$$

where S [$M M^{-1}$] is the sorbed concentration in the equilibrium pool, C [$M L^{-3}$] is the concentration in the liquid phase,

ρ_d [$M T^{-3}$] is the bulk density, f is the fraction of sorption sites in the macropores, f_{ne} is the fraction of soil providing kinetic sorption sites, q [$L T^{-1}$] is the water flow rate and D [$L^2 T^{-1}$] is the dispersion coefficient. Equilibrium sorption partitioning is calculated with the Freundlich isotherm:

$$S = k_d C^\beta, \quad (5)$$

where k_d [$L^3 M$] is the sorption coefficient, and β is the Freundlich exponent. An equivalent approach is used to calculate transport in the macropores, with dispersion set to zero because solute transport is assumed to be dominated by convection, and with only equilibrium sorption considered.

Mass transfer of solute between the two flow domains is given by a combination of a diffusion component and a mass flow component:

$$U_e = \left(\frac{3D_e \theta_{mic}}{d^2} \right) (C_{mac} - C_{mic}) + S_w C', \quad (6)$$

where D_e [$L^2 T^{-1}$] is an effective diffusion coefficient, C_{mac} and C_{mic} [$M L^{-3}$] are the solute concentrations in macropores and matrix, respectively, and C' [$M L^{-3}$] indicates either the solute concentration in macropores or matrix, depending on the direction of water exchange S_w . The source term accounting for kinetic sorption describes the variation with time of the mass of solute stored per unit soil volume at the kinetic sites A_{ne} [$M L^{-3}$]. It depends on a first-order mass transfer coefficient α_k [T^{-1}] and follows the approach described by Altfelder *et al.* (2000):

$$U_k = \frac{\partial A_{ne}}{\partial t} = \alpha_k \left(\rho_d S - \frac{A_{ne}}{f_{ne}} \right). \quad (7)$$

Solute uptake in the transpiration stream occurs at the maximum rate, unrestricted by the crop (i.e. passive crop uptake), and is described as a function of root water uptake and solute concentration. The transfer of solute in the soil solution towards the root is purely convective and does not take into account diffusive processes.

Modelling strategy

We used a blind simulation (direct modelling) to simulate drainage from the lysimeters. We obtained the necessary parameters for Pb transport by inverse modelling and calibrated them against the measured Pb concentrations in the lysimeter drainage. These parameters were integrated into the calibration procedure because they were essential and could not be estimated accurately by other means. Finally, using the parameterization for the water transfer and the solute transport based on the inverse modelling, we investigated the long-term mobility of Pb in relation to vegetation cover.

Model parameterization

When not calibrated, the model parameters were based on direct measurements, estimated by pedo-transfer functions, set as default values of the model, or based on expert judgements. The parameters of the Van Genuchten (1980) function were fitted to measured water retention data with the RETC code of Van Genuchten *et al.* (1991). The boundary between matrix flow and macropore flow h_b was set to an equivalent pressure head of -10 cm, based on consistent results of solute breakthrough experiments on undisturbed soil cores at various pressure potentials (Seyfried & Rao, 1987; Jardine *et al.*, 1993; Langner *et al.*, 1999). This value was used to estimate the corresponding saturated matrix water content θ_b . We estimated the saturated matrix hydraulic conductivity K_b , the total saturated hydraulic conductivity K_{sat} , and the diffusion pathlength d using the internal transfer function included in MACRO. Values are given in Table 1.

The fraction f of sorption sites in the macropores, Equation (4), was set to zero, to account for particulate-facilitated transport, because MACRO does not describe complexation of Pb with mobile colloids. We assumed here that particulate-facilitated transport occurred in the macropores only, and that all Pb that entered the macropores would instantaneously be fixed on mobile colloids. In batch sorption experiments by Serrano *et al.* (2005), Pb showed two stages time-dependent behaviour: an initial rapid sorption, followed by a much slower phase. This process can be assimilated to biphasic adsorption, differentiating rapid reactions on readily accessible sites from slow reactions on less accessible sites (Jardine, 1991). By transposing this behaviour at macroscopic time scales, that is, assuming that adsorption took place initially on the accessible sites and thereafter on the less accessible sites, we assumed that sorption sites were mainly of kinetic types. Therefore, the fraction of soil f_{ne} providing non-equilibrium sorption sites, Equations (4) and (7), was set to 0.95. From our observations we set the maximum root depth to 0.15 m and maximum plant height to 0.70 m. The leaf area index (LAI) and the percentage of the root length in the top 25% of the root depth ξ were set to the default values of 5 and 25%, respectively.

Table 1 Model parameters used in the direct modelling exercise

Parameter	Value
Saturated water content $\theta_{sat}/\text{cm}^3 \text{cm}^{-3}$	0.700
Residual water content $\theta_r/\text{cm}^3 \text{cm}^{-3}$	0.223
Shape parameter of the van Genuchten equation N	1.446
Shape parameter of the van Genuchten equation α	0.149
Saturated matrix water content $\theta_b/\text{cm}^3 \text{cm}^{-3}$	0.570
Saturated hydraulic conductivity $K_{sat}/\text{mm hour}^{-1}$	221
Saturated matrix hydraulic conductivity $K_b/\text{mm hour}^{-1}$	1.88
Kinematic exponent n^*	4
Diffusion pathlength d/mm	20

The initial Pb concentration C_{ini} in soil solution, the sorption coefficient k_d and the Freundlich coefficient β , Equation (5), and the sorption rate coefficient α_k , Equation (7), were calibrated with the global search algorithm SUFI (Abbaspour *et al.*, 1997). We chose to calibrate those parameters because too little information on their value was available for our study, and only those to avoid an ill-posed problem. The iterative procedure in SUFI starts with a user-defined prior uncertainty domain on the parameters to be estimated, which is subsequently reduced as the parameters become more conditioned by the measured data. Each domain is divided into equidistant strata, and parameter values are defined by the midpoint of each stratum. The model MACRO is then run for every combination of parameter values. For each run, the goal function is expressed as the difference between the target simulated and measured output. We used the root mean square error (RMSE) between the measured and the simulated concentrations of Pb in the outflow as that function. In this case, the optimized parameter set for a given iteration is the one for which the RMSE is minimal. The procedure ends when a user-defined stop-criterion is reached. The optimized values are then given with a reduced posterior uncertainty domain.

We estimated the sensitivity of the model to the calibrated parameters with a one-at-a-time sensitivity analysis. For each parameter the maximum ratio of variation of the model target output to the variation of the model input MAROV (Dubus & Brown, 2002) was calculated. The MAROV index for our study was

$$\text{MAROV} = \text{MAX} \left| \frac{\frac{1}{N} \sqrt{\sum_{i=1}^N (P_i - O_i)^2}}{I - I_C} \times \frac{I_C}{\bar{O}} \right|, \quad (8)$$

where N is the number of observations, O_i and P_i are the observed and simulated values, respectively, I is the input parameter to be calibrated, I_C is its calibrated value, and \bar{O} is the average value of the observations. The larger is MAROV, the larger is the influence of a given input parameter I on a given output of the model. If MAROV is less than 1 then a variation in the input parameter will be attenuated throughout the model.

Model evaluation

The model efficiency EF (Loague & Green, 1991) was used to evaluate the performance of the model. It is

$$\text{EF} = \frac{\sum_{i=1}^N (O_i - \bar{O})^2 - \sum_{i=1}^N (P_i - O_i)^2}{\sum_{i=1}^N (O_i - \bar{O})^2}. \quad (9)$$

If all observed and predicted values are identical then EF will be 1 (maximum and ideal value), whereas a negative value of EF indicates a poor fit, meaning that the average value of the observations is a better predictor than the model estimates.

Effect of the vegetation cover on the long-term mobility of Pb

Vegetation on contaminated sites may mobilize the pollutants in the soil by creating preferential flow pathways in root macropores. Retaining the parameterization of MACRO for the short-term mobility of Pb based on the lysimeter experiments, we ran a 20-year simulation to calculate the long-term transport of Pb under a perennial vegetation. We used a 100-cm soil profile with two horizons: a 50-cm top layer of contaminated soil with 500 mg of Pb kg⁻¹, overlying a 50-cm horizon of the same soil that was uncontaminated. Three scenarios were simulated, in order to investigate the long-term effects of root macropores on Pb mobility. These scenarios were:

- 1 Transport under a shallow-rooted grass.
- 2 Transport under deep-rooted trees, for which the root depth does not exceed the contaminated soil layer (50 cm).
- 3 Transport under deep-rooted trees, where the root system extended through the whole soil profile (100 cm).

In the first case, the shallow root depth limits transpiration, thereby allowing a greater volume of water to pass through the profile. Due to its shallow depth, this root system is unlikely to generate much macropore flow through the whole soil profile. The two other scenarios are based on deep-rooted plants that reduce, via evapotranspiration, the water flux through the soil profile, but are likely to create more deep root-macropores. We simulated preferential flow associated with the root system by adjusting the diffusion pathlength d and the saturated matrix hydraulic conductivity K_b . We assumed that the presence of roots in one or the other layer of soil increased the degree of preferential flow in this layer. Table 2 shows the parameters used in the simulations. We assessed the mobility of Pb by simulating the profiles of total Pb concentration in the soil at 5, 10, 15 and 20 years. We used synthetic climate data that were based on records taken at a nearby meteorological station for the previous 20 years.

To support the results found for the three scenarios, we ran a Monte Carlo sensitivity analysis to assess the most important parameters that affect the mobility of a strongly sorbed compound such as Pb. The parameters included in the analysis were the root depth z_r , the diffusion pathlength d , and the saturated matrix hydraulic conductivity K_b , for both the contaminated and the uncontaminated horizons. We selected initial ranges (Table 2) for each parameter, and we generated 600 parameter sets by sampling those domains using the Latin hypercube method. The target output variable was the total amount of Pb leached out of the layer at 60 and 100 cm. Partial rank correlation coefficients were calculated between the parameters and the target outputs.

Results and discussion

Soil and plant Pb concentration

Of the total measured concentration, 445 mg kg⁻¹, 74% was extractable with 0.1 M EDTA, yet only 0.03% was soluble in the 0.1 M NaNO₃ extract.

The Pb concentrations in the roots did not significantly differ between 7 and 26 days after sowing, but decreased by 67% thereafter (Figure 1). An unknown quantity of Pb might have arisen from attached soil particles attached to the roots, and could explain the large Pb concentrations.

The Pb concentration in the shoots decreased significantly (80%) as the plants grew, between the three sampling dates. The plant–soil transfer coefficient, defined as the quotient between the plant shoot concentration and the soil concentration, for *Phacelia tanacetifolia* was 0.024. The transfer coefficients for Pb depend on species. Kloke *et al.* (1994) reported values between 0.01 and 0.1. The transfer coefficient estimated for the lysimeter experiments was thus within this range. Given the small above-ground biomass of the *Phacelia tanacetifolia* (< 2 kg dry matter per lysimeter) and an average Pb concentration of less than 10% of the soil Pb concentration, the amount of Pb extracted by the plants was insignificant at ≈30 mg compared with that remaining in the lysimeter (5.7 kg). It is unlikely therefore that Pb would accumulate from plant material on the surface of the soil. Nevertheless, uptake of Pb,

Table 2 Plant and soil parameters used for the long-term simulation of lead mobility

	1. Grass	2. Tree – root system only in the contaminated layer of the soil	3. Tree – root system in the entire profile	Initial ranges for the Monte Carlo analysis
Root depth z_r /m	0.15	0.5	1	0.1–1
Diffusion pathlength d /mm				
$0 < z < z_r$	50	300	300	1–300
$z_r < z < L^a$	20	20	300	1–300
Saturated matrix hydraulic conductivity K_b /mm hour ⁻¹				
$0 < z < z_r$	0.1	0.1	0.1	0.1–2
$z_r < z < L$	2	2	0.1	0.1–2

^a L is the depth of the soil profile.

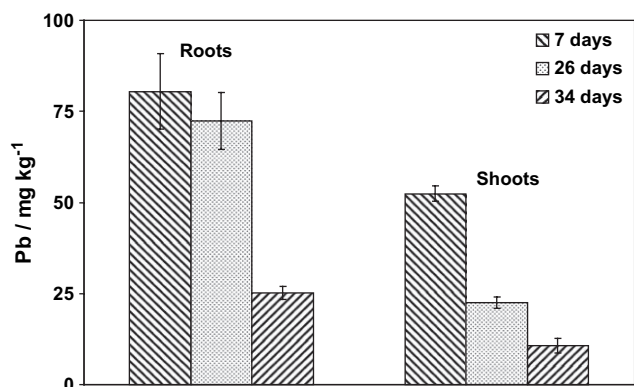


Figure 1 Measured Pb concentrations in *Phacelia tanacetifolia* (roots and shoots) 7, 26 and 34 days after sowing. Error bars are standard errors ($n = 4$).

even at small concentrations, might facilitate the entry of this toxic element into the food chain.

Drainage volumes and Pb concentrations

The dynamic and the amount of the weekly drainage discharge did not differ between the two lysimeters. Therefore, only the drainage from one lysimeter is shown in Figure 2. The first drainage peak, approximately 10 mm in 1 week, came at the end of October 2005, after 290 mm of cumulative rainfall. This amount corresponded approximately to 1 pore volume, indicating that the soil was close to residual water content at the beginning of the experiment. Thereafter, the drainage volumes

followed the rainfall volumes except at the end of the measurement period. This was due to an 18-day dry period in late May and beginning of June 2006, associated with hot sunny weather. Consequently, the measured drainage did not respond to the rainstorm of 17 June.

Figure 3 shows the average Pb concentrations in the drainage. The total Pb concentration in the drainage, that is both particle-bound and dissolved Pb, was much larger than the concentration of Pb in solution. This confirmed that the leached Pb was primarily bound to colloids or particulate matter. Several concentration peaks occurred after intense rainfall events, indicating preferential leaching of Pb. For example, the drainage response to a heavy rainstorm (29.1 mm in 3 hours) on 9 September came within 24 hours, with a Pb concentration peak of 7.83 mg m^{-3} on 11 September, in small amounts of drainage (Figure 2). The first concentration peaks that occurred at the beginning of the experiment might have been associated with both preferential flow and transport of suspended material. Totsche *et al.* (2006) also observed such a phenomenon in freshly settled soils. The total concentration of Pb in the drainage stayed close to the soluble concentration throughout the autumn, but increased again at the end of the monitoring period (starting at the beginning of December). This might have been caused by re-deposition of organic matter and subsequent remobilization of Pb by particulate leaching. Jiang *et al.* (2006), for instance, showed that a mulch treatment in a bamboo crop increased water-soluble organic carbon in the soil by 72%, and Camobreco *et al.* (1996) showed enhanced transport of Pb in the presence of dissolved organic matter, so that Pb became comparable to Zn in terms of mobility.

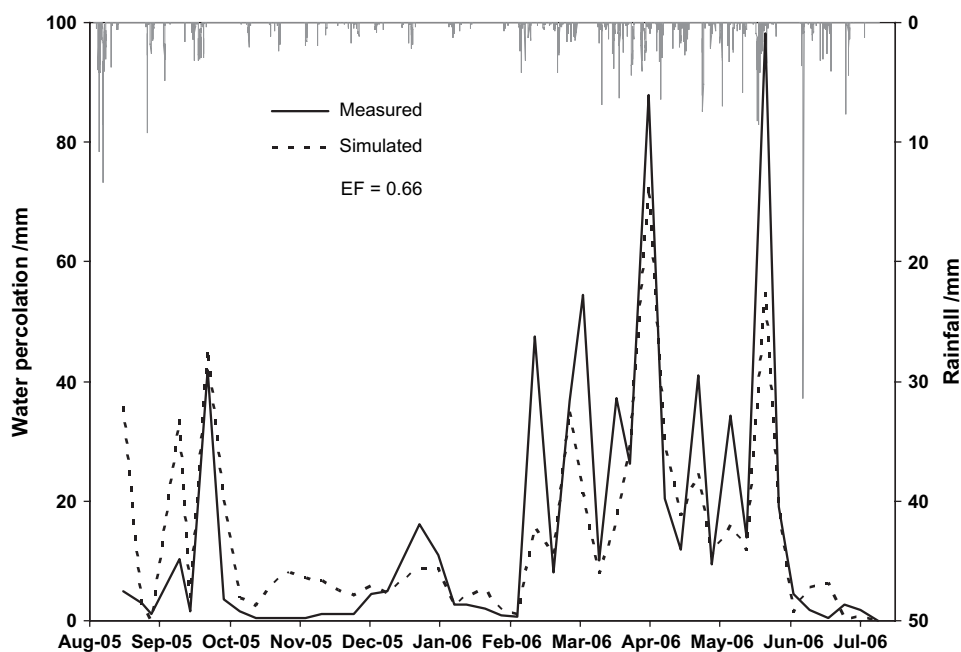


Figure 2 Measured and simulated drainage for the period 30 August 2005 to 20 July 2006. The downward bars represent the rainfall measured for the same period.

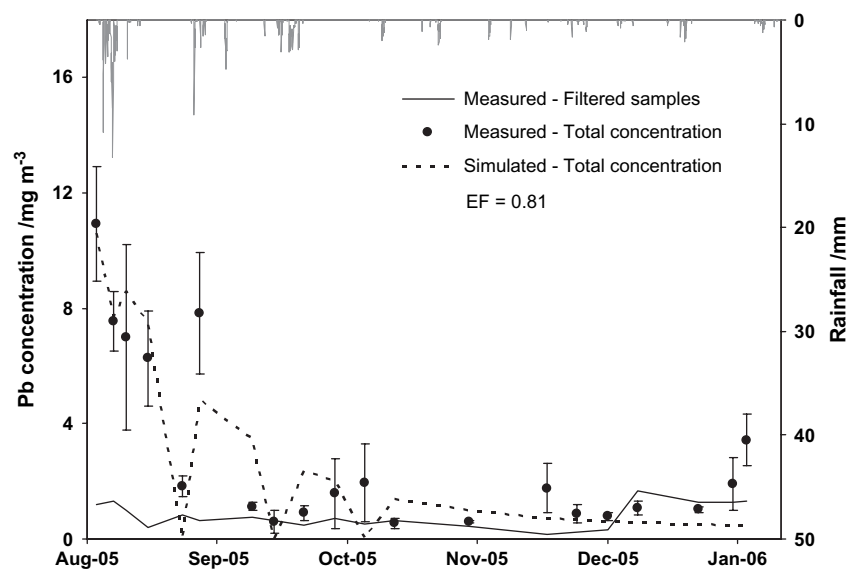


Figure 3 Lead concentration in drainage water for the period 18 August 2005 to 15 January 2006. Error bars are standard errors ($n = 4$). The downward bars represent the rainfall measured for the same period.

Modelling of the short-term mobility of Pb

The results of the direct simulation, that is without calibration, of the drainage volumes agreed well with our measurements (Figure 2). The total amount of drainage during the 11-month experiment was well simulated (678 mm measured vs. 637 mm simulated, not shown), and the dynamic of the drainage was well reproduced by the model, resulting in a model efficiency of 0.66. However, the model underestimated the main maximum of drainage that occurred in the second part of the experiments.

The simulated and measured total concentrations of Pb in the drainage were in good agreement ($EF = 0.81$, Figure 3). MACRO reproduced well the initial decrease and the following peak of Pb concentration. However, it failed to reproduce the increase of concentration in the last part of the monitoring period. If this were due to remobilization of Pb by particulate leaching then we should not expect the model to reproduce it, because MACRO does not allow for an external factor that changes the mobility of a metal. Table 3 shows the parameters we estimated using inverse modelling together with their posterior uncertainty range and the values of the MAROV index. The

Table 3 Parameters estimated by inverse modelling with posterior uncertainty ranges given in parentheses and MAROV sensitivity index

Parameter	Estimated value	MAROV
Initial lead concentration in soil solution $C_{ini}/\text{mg m}^{-3}$	13.5 (11–17)	1.569
Sorption rate coefficient $\alpha_k/\text{hour}^{-1}$	70×10^{-6} ($50 \times 10^{-6} - 100 \times 10^{-6}$)	1.819
Sorption coefficient $k_d/\text{cm}^3 \text{g}^{-1}$	150 (100–300)	0.975
Freundlich exponent β	0.85 (0.75–0.9)	1.233

result of the one-at-a-time sensitivity analysis showed that all MAROV indexes exceeded 1, except for the adsorption coefficient: MAROV in this case was 0.975. It indicates that a variation of k_d was slightly attenuated in the model, which explains the large posterior uncertainty range found for this parameter (Table 3). However, the values reported in the literature for the adsorption coefficient were one order of magnitude greater than both the calibrated value ($k_d = 150 \text{ cm}^3 \text{g}^{-1}$) and the upper value of the posterior uncertainty range of k_d ($300 \text{ cm}^3 \text{g}^{-1}$). The main parameter influencing k_d for Pb is soil pH (Morera *et al.*, 2001), which was 7.2 in our experiment. Based on regression models obtained from results of batch experiments by Sauvé *et al.* (1997) and Carlon *et al.* (2004), at this pH we should expect k_d to be at least $10^3 \text{ cm}^3 \text{g}^{-1}$. Persicani (1995) reported the same result when simulating profiles of Pb concentration in sludge amended soil with an early version of HYDRUS (Kool & Van Genuchten, 1991). He found k_d calculated for field conditions two orders of magnitude smaller than those based on conventional batch studies. The k_d calibrated in our study was small to compensate for Pb remobilization due to redeposition of organic matter, which was not accounted for in the model. This value could thus be assimilated to an effective sorption coefficient, and could be estimated only in dynamic conditions. We should therefore be cautious when using batch experiments to estimate k_d input values to simulate field transport of strongly sorbed compounds.

Simulation of the long-term transport of lead

Figure 4 shows the results of the long-term simulation of Pb transport under three vegetation covers, described in Table 2. After 5 years of transport under a shallow-rooted plant, the calculated Pb concentration in the plant's root zone peaked at a depth of between 8 and 12 cm (Figure 4a). This peak decreased

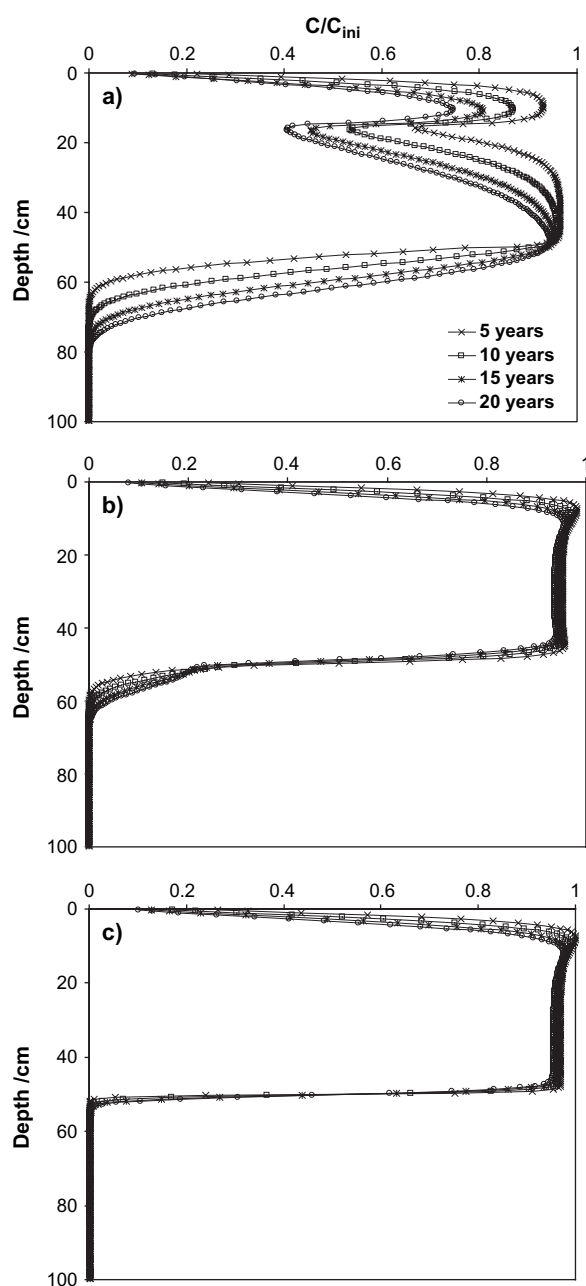


Figure 4 Predicted lead concentration profiles after 5, 10, 15 and 20 years following (a) scenario 1, shallow-rooted grass, with root system in the first 15 cm of soil, (b) scenario 2, deep-rooted tree, with root system in the contaminated soil layer only and (c) scenario 3, deep-rooted tree, with root system in the whole profile. The corresponding input parameters are reported in Table 2.

to 70% of the initial concentration after 20 years. However, it remained at the same depth and became narrower as a result of the combined effects of plant uptake and leaching. Below the root zone, in the contaminated layer, the Pb moved downwards, and leached into the uncontaminated layer to a 60 cm depth after only 5 years. After 20 years, the calculated penetration depth of

the Pb front was 80 cm. This showed that in this scenario, with moderate preferential flow throughout the soil profile, some of the Pb was retained in the root zone and some transported through the matrix into the deeper layers of the uncontaminated zone. However, there was no breakthrough of lead at the bottom of the profile (100 cm).

In the second scenario, where the root system occupied the entire contaminated layer, and subsequently where there was more preferential flow, Pb concentration decreased at the surface as a result of plant uptake. Deeper in the root zone (50 cm), the Pb concentrations remained close to initial values (Figure 4b). Consequently, there was less Pb penetration into the uncontaminated layer than in the first scenario, with the Pb front reaching 68 cm. For strongly sorbed compounds such as Pb, the bulk of contaminant that is stored in the matrix is by-passed by the water that flows into the macropores when preferential flow occurs (Larsson & Jarvis, 2000). This same pattern occurred in the contaminated layer for the third scenario (Figure 4c). However, after 10 years MACRO calculated that the Pb front broke through the base of the soil profile (100 cm), indicating that Pb migrated into the deeper layers of the soil through the root macropores, with less influence of Pb uptake by roots.

Table 4 shows the water and solute mass balances after 20 years for each scenario. The predicted evapotranspiration was smallest for the first scenario, because of the shallow root system, and resulted in the least solute uptake by the plants. The calculated evapotranspiration was larger in scenarios 2 and 3. As a result of the large preferential flow in the uncontaminated layer for scenario 3, however, MACRO calculated leaching from the bottom of the soil profile and less solute uptake by plants. These results indicated that preferential flow was a dominant factor affecting Pb mobility.

Table 5 shows results of the Monte Carlo analysis based on 600 random combinations of root depth and degree of preferential flow in the system. Initially, the analysis was run for two target outputs: the leaching at 60 cm and the leaching at the bottom of the profile (100 cm). However, no leaching was observed at 100 cm for the two first scenarios of the previous exercise. Therefore, only the results for the leaching at 60 cm are shown. The overall squared correlation coefficient between the parameters included in the analysis (Table 2) and the target output was $R^2 = 0.61$. These results accord with the hypothesis that Pb mobility is affected primarily by preferential flow

Table 4 Predicted mass balances after 20 years, in relation to cumulative rainfall and initial solute concentration

	Scenario 1	Scenario 2	Scenario 3
Water percolation /%	59	31	26
Evapotranspiration /%	40	68	73
Solute leached at the bottom of the soil profile /%	—	—	4
Solute uptake by the plant /%	13	30	23

Table 5 Partial rank correlation coefficients (PRCC) between predicted Pb concentration at 60 cm depth and selected input parameters ($R^2 = 0.61$)

Parameter	PRCC
Saturated matrix conductivity in the contaminated layer	-0.627***
Diffusion pathlength in the contaminated layer	0.454***
Diffusion pathlength in the uncontaminated layer	0.305***
Root depth	-0.181*

*** $P < 0.001$.

* $P < 0.05$.

because the most sensitive parameters were those controlling the degree of preferential flow in the contaminated layer, and the diffusion pathlength in the uncontaminated soil. Root depth was also important, but to a lesser extent. However, these calculations did not account for production of organic matter, or for the subsequent redeposition of lead during the simulated period. This process may further exacerbate Pb leaching.

Conclusions

Our monitoring of Pb transport in soil under vegetation showed that Pb leached from the upper 50 cm of contaminated soil, despite a soil pH of 7.2 at which Pb is supposedly immobile. Lead was transported on mobile particles and colloids in solution. Some of these moieties might have resulted from organic matter produced by roots and decaying shoots. This process was enhanced by preferential flow triggered by intense rainfall events. The lysimeter system is suitable for the long-term monitoring of Pb in the soil plant water system. However, the elucidation of the combined effects of preferential flow and particulate leaching requires more intensive sampling, especially after heavy rainfall events, as well as the evaluation of the mass and chemical nature of leached particles and colloids.

A simple parameterization of the dual-porosity model MACRO showed the feasibility of transport models to calculate the short-term behaviour of Pb. However, processes such as particle-bound transport were essential for the prediction of Pb transport at the time scale of the vegetation cycle. Our study indicated that the value of the effective sorption coefficient estimated under dynamic conditions was unrelated to the values measured in conventional batch studies. This indicates that the use of batch studies to derive input values for the sorption coefficient for transport models requires caution. A stochastic analysis showed that the primary control of Pb transport in the long term is the degree of preferential flow in the system, and to a lesser extent the depth of the root system.

To assess the long-term risk associated with Pb contaminated sites with transport models, the plant cycle in relation to production of organic compounds and preferential flow needs to be investigated further.

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