Calculation of zinc transport in a soil contaminated by a brass foundry

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Abstract Soil depth profiles of zinc originating from a long-term pollution by a brass foundry (Dornach, Switzerland) are modelled by combining the deposition history and the advection-dispersion transport model with a linear sorption isotherm. The model input parameters are obtained from laboratory experiments and field data. The model describes the present zinc profiles semi-quantitatively even by neglecting dispersivity effects. Adjusting the dispersivity to 5 cm, which is well in the range of literature values on the appropriate scale, improves the agreement between the calculated and measured profiles. The model was also used to estimate zinc movement in the soils during the next 300 years and to evaluate the long-term effects of possible remediation strategies such as ploughing, soil removal, or soil replacement.

INTRODUCTION

Mining complexes, metal smelters and foundries usually have generated substantial airborne heavy metal emissions in the past and have therefore caused severe soil contaminations nearby (Allaway, 1968; Merian, 1991; Vernet, 1991). The development of effective remediation strategies for such contaminated sites and estimation of their long-term implications on human health requires quantitative understanding of transport of heavy metals in the subsurface zone. The situation, however, differs from the case of weakly sorbing tracers well documented by field experiments (White, 1987; Dagan, 1989; Jardine et al., 1989; Le Blanc et al., 1991). In the case of heavy metals in soils, large retardation factors (100-10 000) lead to very small travel velocities (0.001-1 cm year\(^{-1}\)) and meaningful field experiments with necessary observation times of decades or centuries appear almost impossible to devise. The situation is far from clear, as on such long time scales additional dispersive processes originating from temporal fluctuations of water content, soil temperature, or biological activity may become operational.

Here we propose an alternative approach to the problem. In the present study we discuss a situation where emissions of a brass foundry have polluted nearby soils with mainly zinc and copper down to 10-20 cm. From the well-documented production history of the factory, we estimate the zinc deposition flux on the soil surface which serves as input to a advection-dispersion transport model. This model is used to calculate the observed depth profiles of zinc in soil profiles and to make some tentative future predictions.
INPUT DATA

General description of the site

The site is located in northern Switzerland, south of the city of Basel in Dornach on an eastern slope of the Birs river valley at altitudes between 290-670 m above sea level and includes the village, forests, agricultural fields, and meadows (see Fig. 1). The climate is mild with average temperature of 10°C and prevailing winds from the western direction. The region is contaminated mainly by zinc (but also copper and cadmium) whereby the concentration in about 10 km$^2$ lies above the Swiss guide level for zinc (3 mmol kg$^{-1}$) (Federal Office of Environment, Forests and Landscape, 1986).

The source of this contamination was a brass foundry, which casts metals to brass and argentine since 1895 and has led to air-borne zinc emissions up to 75 t year$^{-1}$. Following Swiss regulations, the factory has installed filters and reduced its emissions below 0.7 t year$^{-1}$. The company now recycles 200-300 t year$^{-1}$ filter powder which is sold as zinc ore. From the map in Fig. 1 and measured depth profiles we estimate that past emissions have caused total zinc deposition of around 900 tons in the region. This number compares rather well with the independent estimate of 1600 tons of the total emitted amount of zinc obtained from the production history of the smelter and current amounts of zinc collected on filters.

The production history of the factory is well documented (dots in Fig. 2) and has initially increased exponentially with a doubling time of about 18 year. We assume that the zinc deposition flux on the soil surface is proportional to the production level of the factory prior to filter installation. During the rather short period of stagnation of the

Fig. 1 Schematic map of the region polluted by heavy metals. Contours of 20, 5 and 2.5 mmol kg$^{-1}$ represent the average zinc concentrations down to 20 cm in the soil (Fröhlicher et al., 1987). The soil profiles (1,2) described in the text are indicated (○). The inset shows the location of the site in Europe.
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Fig. 2 The production rate of the brass smelter (in arbitrary units) as a function of time (years) is represented as points (●). The solid line represents the postulated time dependence of the deposition flux on the soil surface.

Production and the filter installation the deposition flux is taken to be constant. After filter installation was completed, the deposition flux is approximated as being zero (solid line in Fig. 2). The absolute scale of the deposition flux was obtained by estimating total zinc in each profile (see Table 1).

Properties of soil profiles

Parent rock materials are mainly sea sediments with inclusions of loess and alluvial deposits. Two profiles were excavated in locations where we suspect no cultivation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum deposition flux (profile 1)</td>
<td>1650 mol ha(^{-1}) year(^{-1})</td>
</tr>
<tr>
<td>Maximum deposition flux (profile 2)</td>
<td>570 mol ha(^{-1}) year(^{-1})</td>
</tr>
<tr>
<td>Maximum Zn concentration (profile 1)</td>
<td>42 mmol kg(^{-1})</td>
</tr>
<tr>
<td>Maximum Zn concentration (profile 2)</td>
<td>12 mmol kg(^{-1})</td>
</tr>
<tr>
<td>Background Zn concentration</td>
<td>0.7 mmol kg(^{-1})</td>
</tr>
<tr>
<td>Partition coefficient (K_d) (profile 1)</td>
<td>202 l kg(^{-1})</td>
</tr>
<tr>
<td>Partition coefficient (K_d) (profile 2)</td>
<td>38 l kg(^{-1})</td>
</tr>
<tr>
<td>Matrix density</td>
<td>2.61 g cm(^{-3})</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.42</td>
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<tr>
<td>Average rainfall rate</td>
<td>0.87 m year(^{-1})</td>
</tr>
<tr>
<td>Evapotranspiration ratio</td>
<td>0.65</td>
</tr>
<tr>
<td>Best-fit dispersivity</td>
<td>5 cm</td>
</tr>
</tbody>
</table>

Table 1 Summary of parameters for calculation of the soil profiles for the advection-dispersion model with linear sorption isotherm.
practice during the last half century. Here we summarize the main features, details are given in Černík et al. (1994).

Profile 1 is situated in the highly contaminated region near the factory. The soil has developed on calcareous alluvial deposits with a clay loam texture and is classified as Typic Udifluvent. The soil surface is covered with 3 cm of mostly undecomposed, organic litter. The soil in profile 1 is calcareous with pH around 7.5 (0.01 M CaCl₂).

Profile 2 is situated further away from the factory to study a situation with lower contamination levels. The soil is a Typic Eutrochrept which has formed on a calcareous loess deposit. In contrast to profile 1, profile 2 is not covered by a litter layer. The chemical properties of this profile are similar to profile 1 with the exception of lower carbonate content.

Fig. 3 Plot of the zinc adsorption isotherms where a sorbed amount is plotted as a function of a concentration in solution as a double-logarithmic plot. Experimental data points for soils of profile 1 (■) and profile 2 (▲).

Fig. 4 Comparison of measured zinc depth profile 1 (■) with the results based on the pure advective model (dotted line) and the advection-dispersion model for dispersivities of 1 cm (long dashes) and 5 cm (solid line, best fit), respectively. The first point is measured in the undecomposed litter layer. The dispersivity is the only fitting parameter.
For each profile, sorption isotherms and depth profiles were measured for zinc as a key element. Sorption isotherms were determined on soil samples collected from top 10-30 cm of the profile. Suspended soil (0.1 g soil cm\(^{-3}\) in 0.01 M Mg(NO\(_3\))\(_2\)) spiked with appropriate amounts of Zn(NO\(_3\))\(_2\) solution was shaken in contact with atmosphere at 10°C for 24 h. After centrifugation and filtration, samples were analysed for zinc by atomic absorption spectroscopy (see Fig. 3). Zinc depth profiles were determined by sampling 3 to 5 cm layers on plots of 300 cm\(^2\). Extracts with 2 M HNO\(_3\) were measured with atomic absorption spectroscopy (see Fig. 4).

**PRESENT DEPTH PROFILES**

A pollutant deposited on a soil surface will be transported downwards into the soil by rain water and simultaneously retarded by sorption processes. On short time scale (years), the pollutant motion will be strongly influenced by erratic water content variations, but on longer time scales (decades or more) we suspect that these effects result in stochastic perturbations of the steady downwards movement. Their long-time average may result in an effective advection-dispersion description of horizontally averaged pollutant concentration with a possibly enhanced dispersion term. In contrast to a weakly sorbing tracer, the transport of a strongly sorbing tracer depends only on a total water flux but not on the volumetric water content of the soil (Černík et al., 1994). The total water flux can be estimated from the average rainfall rate by taking the measured evapotranspiration ratio into account.

The transport of a linearly sorbing tracer can be deduced from the transport model of a conservative tracer if one rescales the time by the retention factor (Jury & Roth, 1990). The transport of a sorbing tracer, which obeys a convex, nonlinear sorption isotherm, can be approximated by an advection-dispersion model with a linear sorption isotherm with the retention factor obtained from the maximum concentration in the profile (Schweich & Sardin, 1981; Černík et al., 1994). The necessary partition coefficients \(K_d\) are determined from the measured sorption isotherms at points corresponding to the maximum measured concentrations in the profiles. This leads to

![Fig. 5 Comparison of measured zinc depth profile 2 (*) with model results (solid line). No fitting parameters are used.](image-url)
Retention factors around 500-1500.

Zinc depth profile 1 was calculated using such linearized isotherms with parameters summarized in Table 1. In a first approximation, we consider a pure advective model which contains no fitting parameters. Figure 4 shows that this crude model is able to reproduce the present depth profile in an approximate fashion. The agreement with the experimental data can be improved by considering an advection-dispersion model. Figure 4 presents the depth profiles calculated for dispersivities of 1 and 5 cm, respectively. The best fit value of 5 cm is well in the range of dispersivity values obtained from tracer experiments on a comparable field scale (Schulin et al., 1987; Jardine et al., 1989; Gelhar et al., 1992). Profile 2 was calculated with the same parameters as used for calculation of profile 1, using the corresponding deposition flux and the sorption isotherm for profile 2. We are able to predict the depth profile 2 rather well without any fitting parameters (see Fig. 5).

FUTURE DEPTH PROFILES AND REMEDIATION PROCEDURES

The advection-dispersion model can be also used to make tentative projections concerning the zinc translocation in the future. In Fig. 6, we present depth profiles calculated after 100 and 300 years from present. The centre of mass of the zinc pollution moves into the soil with a velocity of ca. 0.9 mm year\(^{-1}\) and reaches a depth of approximately 40 cm after 300 years.

Finally, we have calculated the depth profile 1 after application of four hypothetical remediation procedures of this site (Geiger et al., 1993): (a) no action, (b) plough down to 20 cm, (c) removal of the top 5 cm, and (d) replacement of the top 10 cm by not contaminated soil. Figure 7 shows the zinc distribution in profile 1, 100 years after the remediation applied in the year 2000. Ploughing seems not to be a very effective remediation procedure for a long-term groundwater protection but may prove appropriate as a short-term protection of agricultural production. More effective strategies correspond to reduction the amount of heavy metals by removal or replacement of the contaminated soil.

![Fig. 6](image_url) Calculated zinc depth profile 1 after 100 years (long dashes) and 300 years (short dashes) from today. Present profile is drawn for comparison (solid line) with measured points (■).
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The advection-dispersion model coupled with a linear sorption isotherm discussed here gives rather similar results as a stochastic advective transport model or advection-dispersion model with a nonlinear adsorption isotherm (Černík et al., 1994). This similarity can be explained by the slow variation of deposition flux in time. We suspect that the present approach is able provide a reasonable description near the centre of the pollutant zone with high pollutant concentrations. Regions of substantially smaller contaminations will be much more difficult to model as additional transport mechanisms due to colloids, preferential flow paths, or biological activity may become operational.

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REFERENCES


