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► To cite this version:

F. Mallmann, F.R. dos Santos, P. Cambier, J. Labanowski, I. Lamy, et al.. Using a two site-reactive model for simulating one century changes of Zn and Pb concentration profiles in soils affected by metallurgical fallout. *Environmental Pollution*, 2012, 162, pp.294-302. 10.1016/j.envpol.2011.11.039 . hal-00837996

HAL Id: hal-00837996

<https://hal.science/hal-00837996>

Submitted on 29 May 2020

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Using a two site-reactive model for simulating one century changes of Zn and Pb concentration profiles in soils affected by metallurgical fallout

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ARTICLE INFO

Article history:

Received 5 August 2011

Received in revised form

18 November 2011

Accepted 22 November 2011

Keywords:

Heavy metal

Mathematical model

Hydrus-2D

Metal distribution

Atmospheric deposition

ABSTRACT

Predicting the transfer of contaminants in soils is often hampered by lacking validation of mathematical models. Here, we applied Hydrus-2D software to three agricultural soils for simulating the 1900–2005 changes of zinc and lead concentration profiles derived from industrial atmospheric deposition, to validate the tested models with plausible assumptions on past metal inputs to reach the 2005 situation. The models were set with data from previous studies on the geochemical background, estimated temporal metal deposition, and the 2005 metal distributions. Different hypotheses of chemical reactions of metals with the soil solution were examined: 100% equilibrium or partial equilibrium, parameterized following kinetic chemical extractions. Finally, a two-site model with kinetic constant values adjusted at 1% of EDTA extraction parameters satisfactory predicted changes in metal concentration profiles for two arable soils. For a grassland soil however, this model showed limited applicability by ignoring the role of earthworm activity in metal incorporation.

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1. Introduction

Models that predict flow and metal transport in soils are increasingly applied to address practical problems, aiming at an extrapolation in time and space of experimental laboratory data (Vanderborght et al., 2005). Solute transport models most often consider soil/solution exchanges through reactive surface sites at the solid–liquid interface. With permanent negative charges of 2:1 phyllosilicate minerals, metals form outer-sphere complexes. Such bonds depend to a large extent on the concentration of major cations (Ca, Mg, K, Al) in the soil solution. With variable surface charges (on organic matter, oxy-hydroxides, 1:1 clay minerals), most heavy metals tend to form inner-sphere complexes, which depend more on the pH and the ionic strength of the soil solution. Lead and Cu show high affinities for variable charge sites, especially of organic matter and at neutral or alkaline pH. Zinc and cadmium form both outer- and inner-sphere complexes, with the first type of complexes prevailing in acid soil conditions (Weber et al., 1991). Zn and Cd are considered mobile mainly in dissolved forms (Weber et al., 1991),

whereas Pb is generally considered as low or non-mobile in soils, although Pb migration was demonstrated in association with colloidal particles (Citeau et al., 2003; van Oort et al., 2006).

The adsorption–desorption phenomenon can be represented by mathematical expressions. Many analytical models are based on instantaneous chemical equilibrium, but kinetic models also exist. The absence of equilibrium between soil and solution can be caused by rate-limited sorption (chemical kinetic aspects) or by incomplete mixing of percolating solution with resident water (physical aspects). The two-site model presumes that reactive functional groups in soils can be classified in two types on which (i) instantaneous chemical equilibrium is reached, and (ii) sorption and desorption processes are time-dependent (van Genuchten and Wagenet, 1989; Selim, 1992).

For instantaneous chemical equilibrium (i), a usual approach consists in a simple mathematical relationship between the concentrations in the liquid and the solid phases. Experimental data can be adjusted with a minimum of parameters, following the models of Langmuir, competitive Langmuir, multisite Langmuir, Freundlich, Langmuir–Freundlich, Generalized-Freundlich, Toth, Redlich–Petersen, Dubinin–Raddushkevich, Lineweaver–Burk and Leadie–Hoffstee (Altin et al., 1998; Hinz, 2001; Bradl, 2004). The Freundlich isotherm appeared among the most simple and adapted formalisms for heavy metal adsorption. Its mathematical expression is:

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$$S_{\text{eq}} = K_{\text{F}}C^n \quad (1)$$

where S_{eq} is the fraction of heavy metals retained by the solid phases at instantaneous chemical equilibrium, C is the concentration of metals in soil solution, and K_{F} and n are adjusting parameters which vary with the type and concentration of metals, and with the nature of soil constituents.

For kinetic sites (ii) the most used empirical analytical approaches are Elovich, Power, Langmuir kinetic, Irreversible, Mass transfer and First order. The first model which was incorporated into the convective dispersive equation is the first-order model:

$$\rho \frac{\partial S_{\text{non}}}{\partial t} = \alpha C \theta - \lambda \rho S_{\text{non}} \quad (2)$$

where ρ is the soil bulk density, S_{non} is the fraction of metals retained kinetically by the solid phase, θ is the soil moisture content, α is a forward kinetics constant, λ is a backward kinetics constant, t is the time (Selim, 1992). A mass balance for the two-site model can be calculated from:

$$S_{\text{T}} = S_{\text{eq}} + S_{\text{non}} = \beta S_{\text{T}} + (1 - \beta) S_{\text{T}} \quad (3)$$

where S_{T} is the total sites, and β is the coefficient of the partitioning between the equilibrium and non-equilibrium sites.

Hydrus-2D software can be used to simulate water flow, heat and solute transport in two-dimensional variably saturated media (Šimůnek et al., 1999). Water flow uses Richards equations, and solute transport the Fickian-based advection–dispersion equation. The software uses the generically empirical model that expresses the relationship between the sorbed and dissolved concentration under instantaneous chemical equilibrium conditions, i.e.:

$$S_{\text{eq}} = \frac{KC^n}{1 + mC^n} \quad (4)$$

where m and n are adjusting parameters. For $m = 0$, the equation represents the Freundlich isotherm, for $n = 1$, the Langmuir isotherm, and, for $m = 0$ & $n = 1$ the K_{d} model. With K_{d} defined as the overall distribution coefficient, the sorption rate for instantaneous chemical equilibrium sites becomes:

$$\frac{\partial S_{\text{eq}}}{\partial t} = \beta K_{\text{d}} \frac{\partial C}{\partial t} \quad (5)$$

Similar equations can be obtained with Freundlich and Langmuir parameters.

Sorption on non-equilibrium sites can be written as:

$$\frac{\partial S_{\text{non}}}{\partial t} = \alpha[(1 - \beta)K_{\text{d}}C - S_{\text{non}}] - \lambda S_{\text{non}} \quad (6)$$

where K_{d} can be also substituted by Freundlich and Langmuir parameters (van Genuchten and Wagenet, 1989). Finally, one of the main difficulties for applying such a two-site model is the determination of β and other parameters that describe the rates of metal sorption at kinetic sites. Many experimental approaches can be used to estimate β , but the determination of α and λ would require unreasonable long-term experiments due to the slow sorption mechanisms of metals. Yet, predicting long-term transport of heavy metals in real field situations of contaminated soils faces additional difficulties, notably for the validation of simulations in a context of generally lacking information on historic polluting activity, land use and metal pollutant dynamics.

Such type of information was available for an area contaminated by atmospheric fallout from a former major Zn-smelter complex in production until the 1960's, together with exhaustive pedological, geochemical and physical characteristics of three soils, under

different agricultural management during the 20th century and with different levels of contamination. Considering this wide panel of available data, we attempted in the present study to validate simulations of Zn and Pb redistributions for a past 105-years period in the soils of this area using the Hydrus-2D model. The specific objectives were (i) to test different hypotheses on soil horizon–soil solution exchanges, i.e., complete instantaneous chemical equilibrium or a two-site model with instantaneous equilibrium reactions and kinetic reactions, for describing heavy metal sorption in transport models; (ii) to show that EDTA kinetic extractions can be used for estimating the fraction of exchange sites at instantaneous chemical equilibrium with the soil solution, whereas the time constants of kinetic exchanges obtained from laboratory experiments need to be adapted to the field conditions.

2. Materials and methods

2.1. Location and characteristics of soil profiles

The study was conducted on three sites within an agricultural region contaminated by heavy metals, located at Mortagne du Nord, in Northern France (50°30'14"N–3°27'30"E). The soil profiles are classified as Eutric Cambisols (FAO, 2006), with loamy-sand textures. They developed in comparable parent material derived from Tertiary marine Ostricourt sand deposits, containing predominantly quartz, feldspar and glauconite sand grains. The clay mineralogical composition was dominated by illite and smectite, illite-montmorillonite interstratified minerals, with some kaolinite.

The three soil profiles are located at increasing distances from a former industrial complex, under the dominant wind direction. This industrial complex produced mainly zinc parts, as well as lead parts and sulfuric acid, between 1902 and 1963 with some interruptions (Hardy, 1970). Exhaustive geochemical survey on the former industrial site (Thiry et al., 2002) showed that the industrial metal bearing waste products generated by this metallurgy plant contained primarily sulfates and sulfides. Under alternating humid and dry soil conditions, such metal bearing phases are geochemically unstable and rapidly alter in the soil surface horizons (Bataillard et al., 2003). Consequently, and mobilized metals are redistributed among reactive soil constituents such as organic matter, clays, and iron oxides. In addition, pedo-geochemical survey and spatial distribution mapping of Zn and Pb contents in the 0–30 cm surface horizons of surrounding farmland and forest land (van Oort et al., 2009) showed that metal concentrations decreased rapidly with increasing distance to the former zinc smelter complex, guiding the selection of study sites.

The first site, located at approximately 750 m from the former smelter complex, is under conventional arable land use, moderately contaminated (445 mg kg⁻¹ of Zn and 97 mg kg⁻¹ of Pb in the surface horizon), and referred to as CA⁽⁺⁾. Its profile presents four distinct horizons: Ap (0–33 cm depth), B1 (33–45 cm), B2 (45–80 cm) and C (80–100 cm). For all horizons, physical characteristics required to determine water flow parameters are known, as well as chemical characteristics such as Zn and Pb total concentration, organic carbon, pH and kinetic extractions data by EDTA (Citeau et al., 2003; Labanowski et al., 2008).

The two other sites, one under arable land, the other under permanent pasture for about 100 years, referred to as CA⁽⁺⁾ and PP⁽⁺⁾, are located at 3100 and 2750 m from the industrial complex, respectively. The surface horizons of CA⁽⁺⁾ and PP⁽⁺⁾ contain 111 and 75 mg kg⁻¹ of Zn and 59 and 47 mg kg⁻¹ of Pb, respectively. Macro and micromorphological characteristics, physicochemical data and metal distributions in these soils were extensively studied by Fernandez et al. (2007, 2008, 2010). Although they received equivalent atmospheric deposition loads, the two soils currently present different morphologies, behaviors and metal concentration profiles, due to the different long-term land use. Both soils showed five horizons within the first meter but with clear diverging characteristics, summarized in Table 1. For each horizon, total Zn and Pb concentrations and the main physical parameters that guide water flow in soils (sand, silt, clay and organic carbon contents, bulk density) were available (Fernandez et al., 2007). When compared to the CA⁽⁺⁾ soil, the PP⁽⁺⁾ soil profile showed higher organic matter contents in the first three surface horizons (Table 1). The deeper incorporation of organic matter in the grassland soils is related to an import biological activity, notably of earthworms. Such worm activity for the PP⁽⁺⁾ soil was quantified by Nahmani et al. (2003) and Fernandez et al. (2010).

2.2. Water flow and transport simulation

2.2.1. Physical parameters

Using Hydrus-2D, we considered the vertical two-dimensional flow in a rectangular flow domain, following the van Genuchten water retention model and the van Genuchten–Mualem hydraulic conductivity equation (Šimůnek et al., 1999). For each horizon, the residual soil water content (θ_{r}), the saturated soil water content (θ_{s}), α_{VG} and n parameters of the soil water retention function, as well as the

Table 1
Physical and chemical parameters of arable land soils (CA⁽⁺⁺⁺⁾ and CA⁽⁺⁺⁾) and permanent pasture soil (PP⁽⁺⁾) required for simulation by Hydrus-2D model.

Parameters ^a	CA ⁽⁺⁺⁺⁾ , layers (cm)				CA ⁽⁺⁺⁾ , layers (cm)					PP ⁽⁺⁾ , layers (cm)				
	Ap (0–33)	B1 (33–45)	B2 (45–80)	C (80–100)	Ap (0–26)	B1 (26–44)	B2 (44–72)	Cg1 (72–87)	Cg2 (87–100)	A11 (0–6)	A12 (6–26)	AB (26–53)	ACg (53–76)	Cg2 (76–100)
Soil:														
pH	6.51	6.6	6.7	6.8	6.4	6.3	6.6	6.6	6.7	5.6	5.7	5.7	5.9	6.3
Clay g kg ⁻¹	98	121	172	116	59	57	45	52	280	89	86	67	64	184
Silt g kg ⁻¹	367	366	246	297	179	206	188	202	103	209	213	214	201	118
Sand g kg ⁻¹	535	513	582	587	762	737	767	746	618	702	701	719	735	698
OC g kg ⁻¹	14.5	3.6	2.0	1.0	9.5	2.6	1.7	1.2	1.6	22.3	14.3	4.5	1.4	2.2
Bd g cm ⁻³	1.43	1.53	1.55	1.65	1.43	1.68	1.55	1.64	1.78	1.15	1.48	1.45	1.46	1.65
K _s cm dia ⁻¹	51.8	37.1	42.6	37.5	36.59	15.16	19.79	13.25	6.47	84.58	24.57	25.07	20.91	8.10
θ _s cm ³ cm ⁻³	0.391	0.364	0.373	0.333	0.3940	0.3262	0.3573	0.3366	0.3263	0.4825	0.3880	0.3882	0.3866	0.3675
θ _r cm ³ cm ⁻³	0.053	0.062	0.085	0.060	0.0293	0.0217	0.0245	0.0236	0.0304	0.0476	0.0356	0.0327	0.0340	0.0431
α _{VG} cm ⁻¹	0.0412	0.0477	0.0512	0.0519	0.0104	0.0124	0.0075	0.0077	0.0018	0.0099	0.0112	0.0065	0.0047	0.0115
n ₁	1.3690	1.4334	1.5141	1.5478	1.4023	1.3952	1.4644	1.4571	1.9034	1.3751	1.3777	1.4719	1.5409	1.3162
l	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Zinc:														
Total mg kg ⁻¹ ^b	35.0	21.0	21.0	32.0	35.0	21.0	21.0	21.0	32.0	35.0	21.0	21.0	21.0	32.0
Solution μg l ⁻¹	27.07	25.75	22.69	37.88	41.59	45.37	35.85	40.36	47.91	85.70	54.33	80.50	92.94	71.35
β	0.41	0.37	0.07	0.01	0.27	0.36	0.22	0.13	0.01	0.36	0.33	0.39	0.39	0.02
λ · 10 ⁻³ day ⁻¹	1.4	8.5	7.6	10.6	3.1	3.8	4.0	4.6	1.2	1.9	2.5	4.7	1.8	0.3
K _F	7.54	4.68	5.08	5.54	5.71	3.24	3.77	3.49	4.76	3.57	2.88	2.23	2.03	3.67
n	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Lead:														
Total mg kg ⁻¹ ^b	16.0	7.0	7.0	12.0	16.0	7.0	7.0	7.0	9.7	16.0	16.0	7.0	7.0	4.4
Solution μg l ⁻¹	1.19	0.69	0.64	0.79	1.31	0.90	0.69	0.69	0.76	2.58	2.37	1.49	1.26	0.69
β	0.51	0.10	0.06	0.05	0.18	0.11	0.12	0.15	0.04	0.68	0.48	0.28	0.27	0.21
λ · 10 ⁻³ day ⁻¹	0.5	2.0	4.7	1.1	5.5	4.9	4.0	4.2	6.6	4.2	3.92	10.1	8.7	1.4
K _F	780.55	540.23	580.80	828.20	720.8	434.7	540.2	540.2	689.1	403.8	434.2	281.5	325.4	340.8
n	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.85

^a Bd = bulk density; OC = organic carbon; K_s = hydraulic conductivity; θ_s = saturated water content; θ_r = residual water content; α_{VG} and n₁ = water flow parameter; l = pore-connectivity factor; β = fraction of the heavy metals adsorbed at instantaneous chemical equilibrium; λ = time constant kinetic for 1 - β; K_F and n = parameters of the Freundlich isotherm for β sites.

^b Local geochemical background estimated for 1900 (Fernandez et al., 2007).

saturated hydraulic conductivity (K_s) were estimated using the Rosetta V1.0 software (USDA-USSL, Riverside, California), based on clay, silt and sand contents, bulk density, and water content at potential of -33 and -1500 kPa (Schaap et al., 1998; Schaap and Leij, 1998). The water contents were estimated by pedotransfer function by using clay, silt and organic carbon content and the soil bulk density (Bruand et al., 2004). The pore-connectivity factor used for simulations was 0.5 and considered similar for all horizons.

The top boundary condition was considered atmospheric time-variable. Daily precipitation and potential evapotranspiration were estimated from local meteorological data for the period between 01/01/1995 and 31/12/2004, provided by Météo France. The mean rain precipitation is 867 mm year $^{-1}$, and the mean potential evapotranspiration is 740 mm year $^{-1}$. The mean of minimal and maximal temperatures are 7.0 °C and 15.1 °C, respectively. For the 105 year of simulation we used a repetition of 10.5 periods, supposed meteorologically identical to 1995–2004. We used a constant pressure of -10 kPa for bottom boundary condition. The initial water flux conditions were of -330 kPa and -10 kPa in the top and bottom of the soil, respectively.

2.2.2. Metal concentration data

Total Zn and Pb contents within each horizon of the three soil profiles, before starting of metallurgical activity, corresponding to the local geochemical background (LGCB, Table 2), were taken from Fernandez et al. (2007). These authors estimated the LGCB from Zn/Fe and Pb/Fe relations, established for low and uncontaminated soils similar to the CA^{+++} , CA^{+} and PP^{+} soils, using the data base set compiled by Gaultier et al. (2002). All total metal concentrations presented in this work were measured on soil samples after tri-acid digestion (HF, HClO₄, HCl), following standard methods (NF X31-147, Afnor, 1996). The data used here, as well as technical aspects of chemical analyses were presented by Fernandez et al. (2007) and Labanowski et al. (2008).

Since the available data on metal concentrations for the soil solution was less abundant than for the soil, we tested different published equations to obtain such data for all horizons of the three soil profiles. We adopted the multiple regression Equations (7) and (8) proposed by Sauvé et al. (2000), because they offered the best fits with respect to data of Zn and Pb concentrations determined in the soil solution of the CA^{+++} profile by field monitoring work of Citeau (2004):

$$\log Zn_{\text{solution}} (\mu\text{g l}^{-1}) = 3.68 - 0.55 \text{ pH} + 0.94 \log Zn (\text{mg kg}^{-1}) - 0.34 \log CO(\%) \quad (7)$$

$$\log Pb_{\text{solution}} (\mu\text{g l}^{-1}) = 1.81 - 0.37 \text{ pH} + 0.56 \log Pb (\text{mg kg}^{-1}) \quad (8)$$

These equations use total or pseudo-total soil metal contents, because more complete and homogeneous data sets are often available for total metal contents in soils, contrarily to data on more or less well defined 'labile' fractions. Nevertheless, the improvement in prediction of metal solubility in soils when using labile metal pools, instead of total metal contents, is often small (Sauvé et al., 2000; Degryse et al., 2009).

For running Hydrus, at first, the equilibrium between total soil metal contents and total metals in solution was forced following Freundlich-type Equation (1). From

broad literature on estimations of Freundlich parameters for Zn, we retained 0.65 for the n exponent (Arias et al., 2005; Lair et al., 2006). For Pb, we retained $n = 0.85$, the mean value obtained by Buchter et al. (1989) on 8 soils. Then, we calculated K_f values from the corresponding equation (1), using the available data on total metal contents in soil horizons and the dissolved metal amounts calculated by Equations (7) or (8), in order to obtain an internal consistency between all calculated and measured variables for the recent time. All selected and/or calculated parameters obtained by this approach are summarized in Table 1.

In addition, in order to introduce kinetics in soil–solution exchange, samples of all horizons were submitted to kinetic extractions following Bermond et al. (1998). EDTA extractions (0.05 M, with a soil:solution ratio of 1:10, and pH 6.6) were carried out on samples of all horizons (Labanowski et al., 2008). Concentrations of Zn and Pb were determined after different extraction times: 5, 15, 30 min and 1, 2, 8, 16, 24 h. Then, two metal fractions were defined and their parameters were fitted according to the 2-site kinetic modeling (Fangueiro et al., 2005):

$$Q = Q_1 (1 - e^{-\kappa t}) + Q_2 (1 - e^{-\lambda t}) \quad (9)$$

where Q (mg kg $^{-1}$) = extracted metal at time t ; Q_1 = fraction of readily extractable metal, associated to the rate constant κ ; Q_2 = fraction of less extractable metal, associated to rate constant λ . The EDTA non-extractable metal fraction (Q_3) was calculated from the total metal concentration (Q_T) – Q at $t = 24$ h.

For simulations of the vertical transport of Zn and Pb with Hydrus-2D, the Q_1 fraction was considered at instantaneous equilibrium, due the high value of κ , and β defined by Equation (3) was set equal to the ratio Q_1/Q_T .

The remainder of the metal ($Q_2 + Q_3$) was considered adsorbed to functional groups governed by kinetic adsorption/desorption model, following a kinetic constant (λ). As it is not possible to determine the real value of λ under field conditions, it was in a first approach assumed that 1 min of extraction with EDTA corresponds to one day in the scale of simulation with Hydrus-2D.

The amounts of Zn and Pb deposits on the surface of the three soil profiles were calculated from the difference between the content determined in the soil profile in 2005 and the local geochemical background. Considering the small concentrations in deep horizons, fairly comparable to estimated LGCB levels (Fernandez et al., 2007), metal transfers to the groundwater were assumed negligible during the period of simulation. The CA^{+++} soil received deposits of 256 g m $^{-2}$ of Zn and 44.2 g m $^{-2}$ of Pb. The CA^{+} and PP^{+} soil received 51.6 and 51.0 g m $^{-2}$ of Zn and 19.4 and 17.3 g m $^{-2}$ of Pb, respectively (Table 2).

The temporal repartition of Zn and Pb deposits on the soils was supposed to follow the historical production activity of zinc by the industrial complex (Fig. 1; compiled after Hardy, 1970). Such an approximation was possible because the processed ore type and the used technology for ore processing did not change consistently during the period of activity.

In Hydrus-2D simulations, the amounts of Zn and Pb deposited on the soil's surface by atmospheric deposition were incorporated in the surface horizon and diluted in rain water, considering total and instantaneous solubility. After 1963, the input of Zn by rain precipitation was considered negligible but for Pb, an input of 2.7 $\mu\text{g Pb l}^{-1}$ by rain water was used (Citeau, 2004).

Using these sets of parameters with Hydrus-2D, the transport of zinc and lead was simulated for a period of 105 years (31/12/1900–31/12/2005), in the three soils following three hypotheses for heavy metal reactivity:

- 100% of the amount of metal present in each horizon was considered in instantaneous chemical equilibrium with the solution;
- the fraction of metals at equilibrium with the solution was assumed to be the readily EDTA extractable fraction, and the remaining metal at soil matrix was

Table 2

Zinc and lead stock at each horizon and in total profile of the (CA^{+++}), (CA^{+}), and (PP^{+}) soils. Values estimated for 1900 by the local geochemical background and measured in 2005.

Soil	Horizon	Zinc, g m $^{-2}$		Lead, g m $^{-2}$	
		LGCB ^a 1900	Measured 2005	LGCB ^a 1900	Measured 2005
CA^{+++}	Ap	16.52	210.23	7.55	45.82
	B1	3.86	44.45	1.29	3.18
	B2	11.39	30.60	3.80	7.70
	C	10.56	13.07	3.96	4.13
	Total	42.32	298.35	16.59	60.83
CA^{+}	Ap	13.01	41.23	5.95	21.86
	B1	6.35	19.32	2.12	3.69
	B2	9.11	16.32	3.04	4.47
	Cg1	5.17	6.64	1.72	2.21
	Cg2	7.40	9.16	2.24	2.24
	Total	41.05	92.68	15.07	34.48
PP^{+}	A11	2.42	5.14	1.10	3.21
	A12	6.22	23.50	4.74	15.42
	AB	8.22	22.98	2.74	6.85
	ACg	7.05	18.60	2.35	2.72
	Cg2	12.67	17.31	1.74	1.74
	Total	36.58	87.53	12.67	29.94

^a Local geochemical background estimated for 1900 (Fernandez et al., 2007).

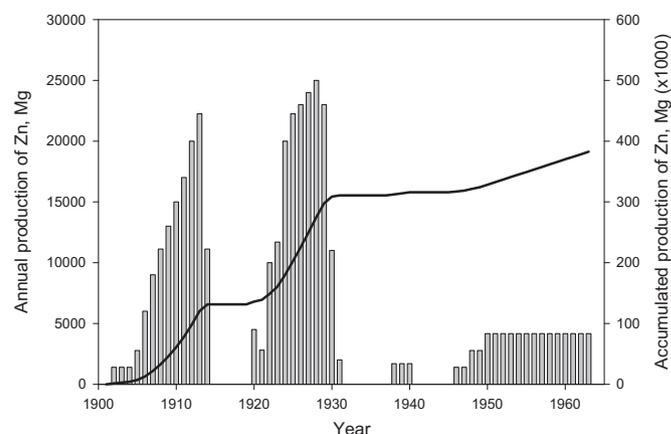


Fig. 1. Annual and accumulated production of zinc by the zinc smelter complex, located at northern France, from 1902 to 1963 (adapted from Hardy, 1970).

supposed to undergo a kinetic adsorption–desorption process according a given rate constant (λ),

- (iii) the fraction of metals at instantaneous chemical equilibrium was still defined by EDTA extractions, but the remaining metal at soil matrix was assumed as taking part of a kinetic adsorption–desorption process in which the λ values were adjusted to conform the field distributions of metal in the recent years.

3. Results and discussion

3.1. Changes of Zn and Pb concentration profiles in CA^{+++} and CA^{++} under hypothesis (i) and (ii)

When testing hypothesis (i) of 100% instantaneous equilibrium, the estimated Zn concentrations for 2005 in the soil horizons of CA^{+++} and CA^{++} profiles showed consistent differences with the measured Zn distributions in 2005 (Table 3). Almost all Zn added to the soil by atmospheric deposition remained in the surface layer, explaining an overestimation of its concentration in the Ap horizons: 131.4 mg kg⁻¹ (29.5%) for CA^{+++} and 60.6 mg kg⁻¹ (54.7%) for CA^{++} . Consequently, the estimated Zn concentrations for 2005 in subsurface horizons of these soils were found fairly similar to those estimated for 1900, consistently lower than the measured ones in 2005.

For Pb, simulations showed a similar behavior as observed for Zn: almost 99% of Pb added to the soil by atmospheric deposition was immobilized in the surface horizon. However, for Pb the differences between the measured and estimated contents were <12.5 mg kg⁻¹ in all horizons (Table 3), consistent with the low mobility of Pb in contaminated soils (Costa et al., 2007). Moreover, the simulated loss of Pb for depths >1 m for the period of 105 years reached only 0.3 kg ha⁻¹, in agreement with findings of Fernandez et al. (2007) and van Oort et al. (2009) who noted that Pb losses from the metal contaminated soils in this area were negligible, even in acid forest soils.

Contrarily to Zn, for Pb the model with the hypothesis of 100% of metals adsorbed at instantaneous chemical equilibrium was found efficient for estimating the changes of Pb concentration profiles in

the CA^{+++} and CA^{++} soils. Minor differences observed between the measured and simulated data in 2005 (Table 3), may be explained by a small but yet real Pb transfer in B1 and B2 horizons. Some migration of Pb was mentioned, via colloidal transport (Citeau et al., 2003), or by mechanical incorporation via biological activity (Fernandez et al., 2010). In that case, the model was unable to predict such mechanisms of metal migration in soils.

Under hypothesis (ii), introducing experimental β and λ values from EDTA extractions in the two-site adsorption model, the obtained simulations for the changes of Zn and Pb concentration profiles in the CA^{+++} and CA^{++} , showed little differences compared to simulations with hypotheses (i). This suggests that the used rate constants of the kinetic sites were too high to produce any difference with the equilibrium conditions. The metal sorption rates clearly smaller in the field than those estimated by chemical extraction in laboratory. EDTA is known as a strong extractant, clearly stronger than water or complexing agents present in the soil solution. Lowering the value of rate constants, besides being more realistic, is also justified by the inclusion of the fraction not extracted by EDTA (Q_3) in the fraction able to be desorbed as Q_2 . Therefore, the testing of the third hypothesis consisted in reducing of rate constants by a constant factor.

3.2. Changes of Zn and Pb concentration profiles in CA^{+++} and CA^{++} under hypothesis (iii)

For simulations using the two-site model with adjusted λ values, we first tested different proportions of the measured rate constants λ deduced from EDTA extractions e.g., 50, 25, 10, 5, 2, 1, 0.5 or 0.1% of the values presented in Table 1. We obtained best fits with the 2005 metal determinations when using a ratio of 1%.

With λ set at 1%, the two-site model produced good estimates of the Zn distributions for the soils under arable land management. In the CA^{+++} soil, the estimated results were fairly similar to the measured ones in 2005 (Table 3). For Ap and B1 horizons, the difference between measured and estimated Zn concentrations in

Table 3
Total zinc and lead concentrations in horizons of the (CA^{+++}) and (CA^{++}) soils in 1900 (LGCB), measured in 2005 and simulated with Hydrus-2D model in 2005 under two hypotheses: 100% adsorbed at chemical instantaneous equilibrium and a two-site model adsorption with adjusted λ values.

Hypothesis/Horizon	Zinc				Lead			
	LGCB ^a (1900) Mg kg ⁻¹	Measured (2005) Mg kg ⁻¹	Simulated (2005) Mg kg ⁻¹	Difference ^b Mg kg ⁻¹ %	LGCB ^a (1900) Mg kg ⁻¹	Measured (2005) Mg kg ⁻¹	Simulated (2005) Mg kg ⁻¹	Difference ^b Mg kg ⁻¹ %
Agricultural moderately contaminated soil (CA^{+++})								
100% at equilibrium								
Ap (0–33)	35.0	445.5	576.9	131.4 29.5	16.0	97.1	109.6	12.5 12.9
B1 (33–45)	21.0	242.1	21.0	-221.1 -91.3	7.0	17.3	7.4	-9.9 -57.5
B2 (45–80)	21.0	56.4	19.8	-36.6 -64.8	7.0	14.2	7.0	-7.2 -50.6
C (80–100)	32.0	39.6	30.2	-9.4 -23.8	12.0	12.5	11.8	-0.7 -5.2
Two-site model with adjusted λ values								
Ap (0–33)	35.0	445.5	435.2	-10.3 -2.3	16.0	97.1	109.6	12.5 12.9
B1 (33–45)	21.0	242.1	287.1	45.0 18.6	7.0	17.3	7.3	-10.0 -57.8
B2 (45–80)	21.0	56.4	52.8	-3.6 -6.3	7.0	14.2	7.0	-7.2 -50.6
C (80–100)	32.0	39.6	30.6	-9.0 -22.6	12.0	12.5	11.9	-0.6 -5.1
Agricultural low contaminated soil (CA^{++})								
100% at equilibrium								
Ap (0–26)	35.0	110.9	171.5	60.6 54.7	16.0	58.8	68.2	9.4 15.9
B1 (26–44)	21.0	63.9	21.2	-42.7 -66.9	7.0	12.2	7.1	-5.1 -41.9
B2 (44–72)	21.0	37.6	21.9	-15.7 -41.6	7.0	10.3	7.1	-3.2 -31.4
Cg1 (72–87)	21.0	27.0	20.9	-6.1 -22.6	7.0	9.0	7.0	-2.0 -22.4
Cg2 (87–100)	32.0	39.6	27.3	-12.3 -31.0	9.7	9.7	9.4	-0.3 -3.1
Two-site model with adjusted λ values								
Ap (0–26)	35.0	110.9	155.9	45.0 40.6	16.0	58.8	68.1	9.3 15.8
B1 (26–44)	21.0	63.9	38.1	-25.8 -40.4	7.0	12.2	7.1	-5.1 -42.1
B2 (44–72)	21.0	37.6	23.4	-14.2 -37.8	7.0	10.3	7.1	-3.2 -31.2
Cg1 (72–87)	21.0	27.0	20.4	-6.6 -24.3	7.0	9.0	7.0	-2.0 -22.1
Cg2 (87–100)	32.0	39.6	29.3	-10.3 -26.1	9.7	9.7	9.5	-0.2 -2.5

^a Local geochemical background estimated for 1900 (Fernandez et al., 2007).

^b Difference between the value obtained by simulation for 2005 and the real one, measured in 2005.

2005 was -10.3 mg kg^{-1} (-2.3%) and 45.0 mg kg^{-1} (18.6%), respectively. In B2 horizon, the model estimated an increasing Zn concentration from 21.0 to 52.8 mg kg^{-1} , close to the 56.4 mg kg^{-1} measured in 2005 (-6.3%).

For the $\text{CA}^{(+)}$ soil, the model also predicted transfer of Zn down to the B2 horizon. Compared to measured 2005 Zn distributions the model overestimated its concentration in the Ap horizon by 45.0 mg kg^{-1} , and underestimated it in the B1 (25.8 mg kg^{-1}), B2 (14.2 mg kg^{-1}), Cg1 (6.6 mg kg^{-1}) and Cg2 horizon (10.3 mg kg^{-1}) (Table 3). Although slightly diverging from the 2005 measured metal concentrations, the estimated distribution showed a fairly similar trend, much closer than simulations under the hypothesis of 100% instantaneous equilibrium. In addition, the loss of Zn towards depth ($>1 \text{ m}$) over the 105 years was small (1.34% of the total Zn amount in the profile).

The evolution of metal loads in the Ap horizon of the $\text{CA}^{(++)}$ soil, predicted under hypotheses (i) and (iii) are shown in Fig. 2. The model under the hypothesis (i) estimated that the Zn concentration in the soil solution, in equilibrium with the solid phase, would reach a maximum of 2.82 mg l^{-1} , in 1930, whereas the two-site model set with a 1% λ value (hypothesis (iii)) showed larger concentrations values, especially during the period of metallurgical activity, with a maximum of 6.98 mg l^{-1} in 1930, but also after the end of the production. The ratio between the two maxima is 0.40, i.e., about the β value. Indeed the concentration of Zn in solution is in equilibrium with the first fraction of sites in the two-site model. These sites are less numerous than in the complete equilibrium model, but become more filled with Zn. The second fraction, the kinetic sites, progressively filled up but was still minor in 1930 (Fig. 2). Between 1963 (end of industrial activity) and 2005, the difference of Zn concentration in solution between hypotheses (i) and (iii) supposed different rates of decrease of total Zn amounts in the Ap horizon (the water flow was the same): hypothesis (i) led to a small decrease, contrarily to hypothesis (iii) showing a significant reduction of the Zn in the solid phase, especially of the metal fraction in equilibrium, promoting buffering of the solution. In

addition to a higher transfer of soluble Zn from the Ap down into deeper horizons, there was also a gradual transfer from the equilibrium to the kinetic fraction, which regularly increased during the simulated period (Fig. 2).

The two-site models assume that, for the kinetic fraction, the process of metals adsorption and desorption to soil is time-dependent (van Genuchten and Wagenet, 1989). So, with a metal sorption rate in the kinetic fraction much lower than in the fraction at equilibrium, Zn remained at larger proportions and for a longer time in solution, favoring its transfer to subsurface horizons.

Fig. 3 presents the estimated Zn concentrations in the soil solution for the 105 years simulation period. It remained negligible in the C and Cg2 horizons of the $\text{CA}^{(++)}$ and $\text{CA}^{(+)}$ soils, explaining the low Zn transfers to the groundwater (14.9 and 12.5 kg ha^{-1} , respectively). Despite its mobile character, Zn transfer from atmospheric deposition at the soil's surface to the C horizons appeared strongly limited (Fig. 3). Concentrations of leachable metals are highly pH dependent as underlined by Hanna et al. (2009) using PHREEQC simulations. In the $\text{CA}^{(++)}$ and $\text{CA}^{(+)}$ soils, the near neutral soil pH (6.3 – 6.8) drastically reduce the metal concentration in the soil solution. By contrast, for acid ($\text{pH} < 4.5$) forest soils in the same study area, van Oort et al. (2009) demonstrated that 40 years after cessation of industrial emissions, more than 80% of the deposited Zn had been leached out of the soil towards the groundwater. Finally, for the $\text{CA}^{(++)}$ and $\text{CA}^{(+)}$ soils, simulations showed that, although most of Zn deposition occurred before 1931, the increase of Zn in the soil solution of the B1 horizons started only after 1955 and 1945, respectively (Fig. 3).

For Pb, despite satisfactory simulations of its content in soil horizons by the models under hypotheses (i) and (iii), a great difference for its concentrations in the soil solution was observed (Fig. 2): the Pb concentration I under hypothesis (iii) was approximately two-fold higher than that under hypothesis (i), yet not enough to induce a significant Pb transfer to subsurface horizons. This is explained by comparing the estimates of Pb concentrations in soil solution with those estimated by simulation under hypothesis (iii) (Figs. 2 and 3), which presented values around 500 times

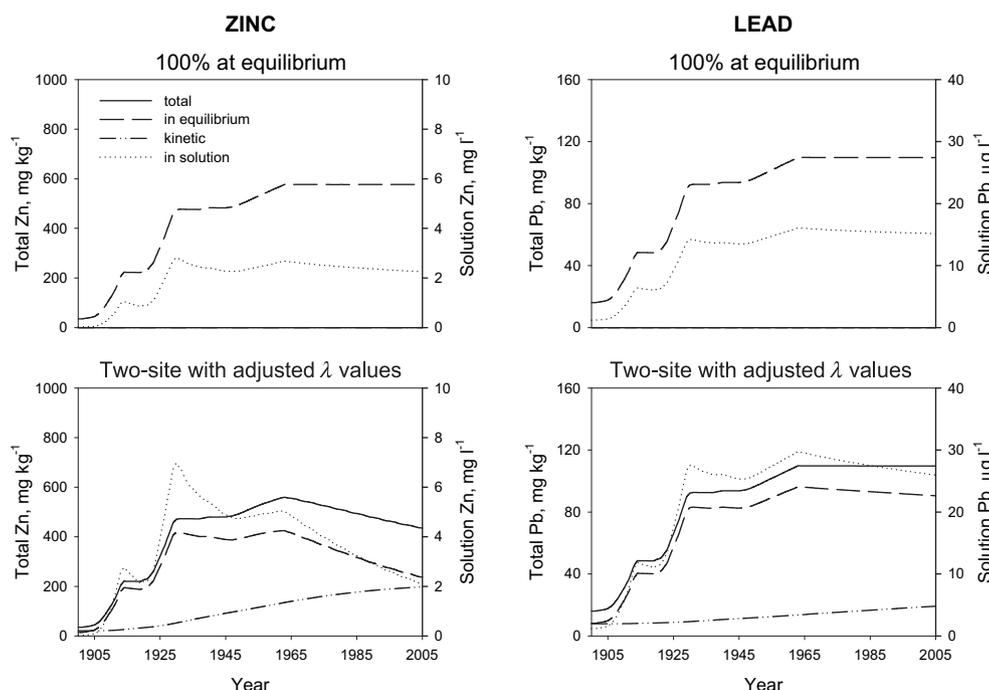


Fig. 2. Total and fractionated Zn and Pb concentrations in the soil and in the solution of the Ap horizon of the $\text{CA}^{(++)}$ soil between 1900 and 2005, estimated by Hydrus-2D under two hypotheses: 100% adsorbed at chemical instantaneous equilibrium; two-site model adsorption with adjusted values of λ .

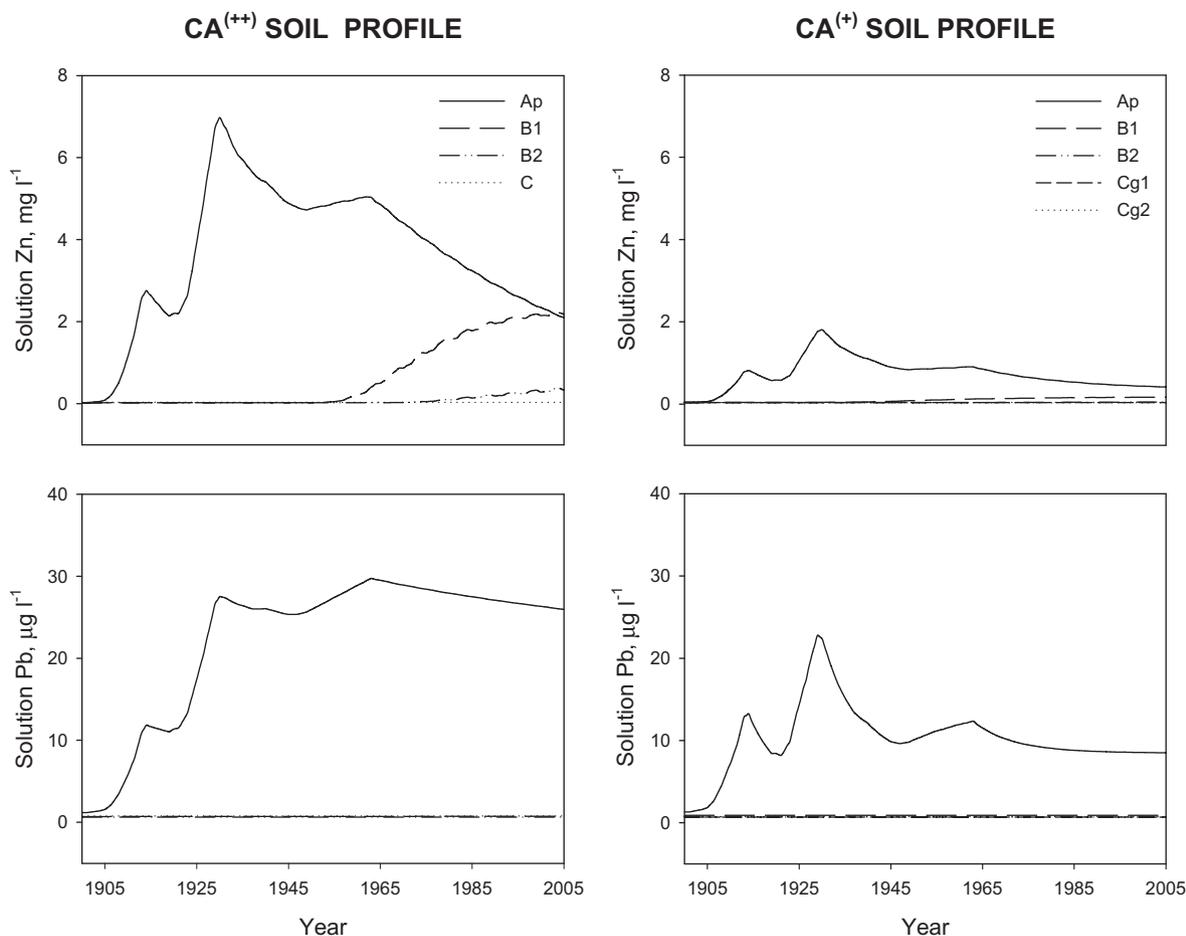


Fig. 3. Zinc and lead concentrations in soil solution for horizons of the $CA^{(++)}$ and $CA^{(+)}$ soils between 1900 and 2005, estimated with Hydrus-2D using the two-site model with adjusted λ values.

larger than those of Pb. In the $CA^{(++)}$ and $CA^{(+)}$ soils, the Pb distributions estimated by the model under the hypothesis (iii) or (i) were practically the same.

No variation of Pb concentrations in the soil solution in subsurface horizons was observed (Fig. 3). Consequently, the amount of Pb transferred to the groundwater was negligible (0.05 and 0.09% of the total Pb stored in $CA^{(++)}$ and $CA^{(+)}$ profiles, respectively), related to high values of K_F for Pb (Table 1), and the great affinity of Pb for organic and mineral colloidal soil particles (McBride, 1994). Therefore, using the arguments already mentioned when discussing hypothesis (i) (3.1.), the model under the hypothesis (iii) was also found efficient to predict Pb distributions in the $CA^{(++)}$ and $CA^{(+)}$ soils as well as its absence of transfer to the groundwater.

3.3. Changes of Zn and Pb concentration profiles in $PP^{(+)}$ under hypothesis (i) and (iii)

For the $PP^{(+)}$ soil, simulations under hypothesis (i) predicted Zn incorporation into 2 subsurface horizons (A2, AB), unlike the findings for the soils under arable land use (Tables 3 and 4). Such different incorporation can be ascribed firstly to different K_F values in the $PP^{(+)}$ soil, low in the two upper horizons (3.57 and 2.88, respectively), compared to $CA^{(++)}$ (7.54 and 4.68, respectively) and $CA^{(+)}$ (5.71 and 3.24, respectively) (Table 1). Besides, the surface horizon of $PP^{(+)}$ soil profile is thinner than those of the other profiles. Moreover, the estimated Zn contents under hypothesis (i)

significantly differed from measured field concentrations (+92.8, +59.9, -16.6, -64.2 and -29.7%, in the A11, A12, AB, Cg1 and Cg2 horizons).

Simulation under hypothesis (iii) predicted the incorporation of Zn to greater depth than under hypothesis (i), including the ACg horizon (Table 4), as well as a Zn loss of 18.8 kg ha⁻¹ (2.15% of total) out of the soil to the groundwater. However, the simulated distribution of this metal in the soil profile in 2005 was different from measured field concentrations profiles. The total Zn concentration of the surface horizon was overestimated by 46.5 mg kg⁻¹ (+62.4%), and underestimated in the ACg and Cg2 horizons (-47.9% and -27.2%, respectively).

For Pb, no simulation satisfactory described its vertical distribution. Estimated distributions for 2005 of anthropic Pb either with hypothesis (i) or (ii) in the upper 50 cm (A11, A12, AB horizons), clearly diverged from the measured values (>400% in the A11 horizon, Table 4). The estimations corresponded to almost 90% of the anthropogenic Pb stock in A11, 10% in A12 and about 1% in AB. By comparison, calculated estimation by Fernandez et al. (2007) reached 12% in A11, 61% in A12, and 18% in AB. According to Cernik et al. (1995), the prediction of metal distribution in little-contaminated soils meets great difficulties, related to the existence of several mechanisms of metal migration other than in dissolved form in the soil solution, such as colloidal transport or mechanical incorporation by biological activity. The latter mechanism is likely to play a significant role in the $PP^{(+)}$ soil, considering the work of Nahmani et al. (2003) who quantified the earthworm

Table 4

Total zinc and lead concentrations in the horizons of the PP⁽⁺⁾ soil in 1900 (LGCB), measured in 2005 and simulated with Hydrus-2D model in 2005 under two hypotheses: 100% adsorbed at chemical instantaneous equilibrium and a two-site model adsorption with adjusted λ values.

Hypothesis/Horizon	Zinc				Lead					
	LGCB ^a (1900) Mg kg ⁻¹	Measured (2005) Mg kg ⁻¹	Simulated (2005) Mg kg ⁻¹	Difference ^b Mg kg ⁻¹ %	LGCB ^a (1900) Mg kg ⁻¹	Measured (2005) Mg kg ⁻¹	Simulated (2005) Mg kg ⁻¹	Difference ^b Mg kg ⁻¹ %		
Permanent pasture low contaminated soil (PP ⁽⁺⁾)										
100% at equilibrium										
A11 (0–6)	35.0	74.5	143.6	69.1	92.8	16.0	46.5	246.3	199.8	429.6
A12 (6–26)	21.0	79.4	127.0	47.6	59.9	16.0	52.1	20.4	-31.7	-60.9
AB (26–53)	21.0	58.7	49.0	-9.7	-16.6	7.0	17.5	7.2	-10.3	-59.0
ACg (53–76)	21.0	55.4	19.9	-35.5	-64.2	7.0	8.1	7.0	-1.1	-14.2
Cg2 (76–100)	32.0	43.7	30.7	-13.0	-29.7	4.4	4.4	4.4	0.0	1.0
Two-site model with adjusted λ values										
A11 (0–6)	35.0	74.5	121.0	46.5	62.4	16.0	46.5	236.0	189.5	407.5
A12 (6–26)	21.0	79.4	99.3	19.9	25.0	16.0	52.1	22.9	-29.2	-56.0
AB (26–53)	21.0	58.7	65.5	6.8	11.5	7.0	17.5	7.2	-10.3	-59.0
ACg (53–76)	21.0	55.4	28.9	-26.5	-47.9	7.0	8.1	7.0	-1.1	-13.9
Cg2 (76–100)	32.0	43.7	31.8	-11.9	-27.2	4.4	4.4	4.4	0.0	0.7

^a Local geochemical background estimated for 1900 (Fernandez et al., 2007).

^b Difference between the value obtained by simulation for 2005 and the real one, measured in 2005.

density in this soil, reaching almost 400 individuals per m² for PP⁽⁺⁾, including about 50 adult endogeic worms, compared to only 50 individuals per m² for CA⁽⁺⁾ with only 9 adult endogeic worms. Such great earthworm activity in the PP⁽⁺⁾ soil was confirmed by optical microscopy work (Fernandez et al., 2010), quantifying the recognizable worm-worked groundmass to 56, 25 and <10% of the analyzed soil surface of the A12, AB and ACg horizons, respectively. A high biological activity facilitates the migration of particulate material in the soil profile, since it increases the total porosity, the number of macropores and their interconnectivity. In addition, earthworm activity promotes soil homogenization–bioturbation (Zorn et al., 2005), tending to make uniform the metal contents in the groundmass of the worm-worked soil depth.

The software Hydrus-2D was fed with Zn and Pb kinetic parameters, determined by EDTA extractions, and earthworm activity was shown to increase metal availability and particularly the amounts of EDTA extractable metals (Cheng and Wong, 2002; Wen et al., 2004; Sizmur and Hodson, 2009; Fernandez et al., 2010). Thus, effects of biological activity on metal transport were partially and indirectly taken in consideration in our simulations using the two-site models. However, this was not sufficient to obtain a satisfactory simulated concentration profile for Pb and Zn in the soil under permanent grassland, suggesting that effects mechanical incorporation by earthworms plays a large role. Such transfer of solids and sorbed substances by means of bioturbation has been described in some models as a particular diffuse process (McLachlan et al., 2002), but not considered in our two-site model here.

3.4. Other neglected factors influencing metal dynamics in soils

The two-site Hydrus-2D model considers sorption–desorption chemical processes, their kinetics as well as soil water transport dynamics. These aspects are certainly major factors driving metal movement in soils, but other intrinsic and external parameters are also known to play a role in metal mobility. In our simulations, metal uptake by plants, and enhanced leaching of fine particles due to annual plowing of cultivated soils were not considered in our work. Moreover, the general physicochemical characteristics of soils, such as pH, bulk density and organic matter content, were assumed constant during the simulated period of 50 years. Liming and phosphate fertilization are known to reduce heavy metal concentrations in the soil solution, and their migration to deeper horizons (Delolme et al., 2004); such agricultural practices were not considered here. Finally, due to the quasi-plane topographical

position of the studied sites and their sandy texture, lateral water losses due to runoff were ignored.

4. Conclusions

The model based on hypothesis of instantaneous chemical equilibrium was found inadequate to estimate vertical Zn transport and redistribution in the three agricultural soils. However, simulated Pb distribution profiles with this model were found consistent with Pb accumulation in the surface horizon of soils under arable land use. Using a two-site model with the repartition coefficient issued from laboratory EDTA extractions and kinetic parameters proportionally adjusted to field conditions, it was possible to predict efficiently the vertical zinc and lead distributions in two cultivated moderately and little metal contaminated soil profiles. This model also predicted a small Zn transfer to groundwater by leaching.

For the soil under permanent pasture none of the three used models produced metal concentration profiles in agreement with the observed concentrations in 2005. Such a lack of correspondence was mainly ascribed to metal dynamics related to biological activity, notably of earthworms, not well considered by the models.

Among the broad range of thermodynamic and phenomenological models, a two-site model with adjusted kinetic constants can be used to predict the sorption/desorption processes of heavy metals in soil and, consequently, to assess risks of the solute transport to the groundwater.

Acknowledgments

The authors greatly acknowledge Sebastien Breuil of INRA-Versailles for help with soil sample collection and preparation, François Lafolie of INRA-Avignon, Dalvan José Reinert-UFSM/Brasil for much constructive discussion on water fluxes in soils, and J. Šimůnek for advices and encouragements concerning the use of Hydrus-2D software.

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