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Kinetics of lead release from soils at historic mining and smelting sites, determined by a modified electro-ultrafiltration

Anto Jelecevic[1]*, *Dietmar Horn*[2], *Herbert Eigner*[3], *Manfred Sager*[4], *Peter Liebhard*[1], *Karl Moder*[1], *Daniel Vollprecht*[5]

[1]*University of Natural Resources and Life Sciences Vienna, Vienna, Austria*
[2]*BGD Bodengesundheitsdienst GmbH, Ochsenfurt, Germany*
[3]*AGRANA Research & Innovation Center GmbH, Tulln, Austria*
[4]*Bio Forschung Austria, Vienna, Austria*
[5]*Montanuniversitaet Leoben, Leoben, Austria*
**Corresponding author: jelazp_20@hotmail.com*

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Abstract: Within a pilot study, after pedological and mineralogical characterization, various kinetic models were tested to fit lead (Pb)-mobilization kinetics from soils at historic mining and smelting sites. Pb mobilization was obtained by modified electro-ultrafiltration (EUF) after addition of diethylenetriaminepentaacetic acid (DTPA) at variable conditions of extraction. 10 fractions were sequentially produced, under mild conditions at 20°C/200 V (to simulate an initial release) for fractions 1–5, and subsequently harder conditions at 80°C/400 V (to simulate a long-term release) for fractions 6–10. The special samples treated within this work yielded higher extraction rates within the first runs. Closest fits in terms of the coefficient of determination (R^2) were obtained from the 2nd order polynomial model $y = a + bt + ct^2$, and in terms of re-calculated results by the parabolic equation $y = a + b\sqrt{t}$. The fitted constants obtained by the modified EUF method correlated better with soil pH than with organic carbon and clay contents. From this, it remains open, whether the dissolution of the Pb-minerals in the electric field or concentration resp. diffusion of the DTPA is rate-determining.

Keywords: heavy metal; toxic element; metal mobility; contamination; soil testing

High levels of lead (Pb) are frequently encountered near still operating or already closed mining and smelting sites. In ore veins, Pb usually occurs in Pb-bearing sulfides, preferably galena PbS. In many cases, Pb accumulations occur in upper layers, because Pb gets sorbed from metalliferous products like slags or fly ashes, or by atmospheric deposition, but it hardly migrates downwards (Gaisberger et al. 2003). In case metal-bearing phases are dissolved the released Pb might impose hazards due to its toxicity, whereas it's level of essentiality (< 0.045 mg/kg for rats; Reichlmayr-Lais and Kirchgessner 1993) is so low that this is hardly considered. However, a part of the released Pb is trapped in secondary $PbCO_3$ cerussite and $PbSO_4$ anglesite.

Sequential leaching of soils containing largely original Pb ore grains revealed just 10% of total Pb as reducible by hydroxylamine, 3–6% oxidizable by H_2O_2, and 81–85% residual. If cerussite formation has occurred, however, Pb gets mobile in dilute acetic acid (Lee et al. 2012).

Apart from detailed knowledge of the respective minerals, a dynamic method to fit the actual release rate should be an adequate method to estimate plant uptake and digestibility of a given substrate and to yield predictions of environmental cycling of metals more precisely than from simple snapshot methods (Dang et al. 1994).

Electro-ultrafiltration (EUF) has been established as an analytical tool to determine the dynamics of plant-available nutrients in arable soils (Németh 1980). Aqueous soil suspension is put into a cell containing semi-permeable membranes, and during application of an electric field, charged particles migrate towards the respective anode or cathode within the soil suspension. Solutes pass the semi-permeable membranes and can be sampled outside the soil suspension (Németh 1982, Horn 2006). If a complexing agent is added, metals are also kept in solution, thus extending the use of the EUF method also for investigations of metal mobilities (Horn 2006). EUF has been already used for technical soil cleaning. In this case, a soil suspension is kept between graphite electrodes and filters, charged contaminants like Pb^{2+} can be removed from soil suspensions by migration in an electric field at a gradient of 2.3 V/cm (Weng et al. 1999).

Complexation is an approach to simulate so-called 'available' fractions during EUF (Sager 1992, Alloway 2013). Diethylentriaminepentaacetic acid (DTPA) and its various metal complexes have been intensely investigated in pure aqueous solutions of ionic strength 0.1 (KCl) to improve complexometric titrations concerning ethylenediaminetetraacetic acid (EDTA) (Anderegg et al. 1959). Most stability constants of metal-DTPA complexes have been determined by re-complexations of the given cation with the Hg-DTPA complex via pH and polarographic determination of free mercury (Hg). Stability constants with trivalent cations were determined by re-complexation of tri-ß-aminoethylthylamine and Cu-DTPA or Zn-DTPA complexes (Table 1). Contrary to EDTA, beneath 1 + 1 complexes MZ^{3-}, also MHZ^{2-} can be formed in acid solution, or M_2Z complexes in the presence of excess metals (Anderegg et al. 1959). DTPA as a complexing or more precisely chelating agent possesses the ability to extract exchangeable, carbonate and organically bound metal fractions, i.e. potentially mobile and phytotoxic fractions in soils. During EUF addition of DTPA attacks, both Fe-oxides, humics, and clay minerals to release co-precipitated Pb (Slavek et al. 1982, Miller et al. 1986).

In Austria, due to construction works, high amounts of excavated soils and subsoils do not meet the requirements for recycling and have to be landfilled (Jelecevic et al. 2018). This work aims to classify the Pb contents of selected soils sampled at historic mining and smelting sites in the Province of Styria (Austria) by application of EUF modified by the addition of DTPA, in order to get additional information about Pb mobilities and release rates. The release of Pb gets fitted by mathematical models to quantify future availability and transport, which should help to estimate the hazard potential of Pb accumulations more precisely.

MATERIAL AND METHODS

Experiments were performed at the Justus Liebig Laboratory of the Südzucker AG Company, situated at Rain am Lech (Germany). As test substrates, arable soil sampled at or close to former mining sites of mainly galena (PbS) in Styria were selected. In the past, also smelting and further processing and manufacturing had been done on site. The onset of respective mining activities dates back to the middle ages and lasted for centuries. Four of the sampled sites have been termed as contaminated, and a further one as non-contaminated, acting as a control. The soil samples were cored at 5–30 cm depth dried at 40°C and sieved minor 2 mm (ÖNORM L 1056, 2004).

The soil pH was determined in 0.01 mol/L $CaCl_2$ (ÖNORM EN 15933, 2012), the clay-silt-sand distribution by the pipette method (ÖNORM L 1061-2, 2002), the total organic carbon (TOC) by combustion (ÖNORM L 1080, 2013), and the pseudo-total contents by inductively coupled plasma optical emission spectrometry (ICP-OES) after digestion with *aqua regia*.

The mineralogical composition of the samples was determined by X-ray diffraction at the Graz

Table 1. Stability constants of diethylenetriamine-pentaacetic acid (DTPA) complexes and solubility product of the hydroxides (Anderegg et al. 1959, Vogel 1961)

Log H^+	DTPA				Lp hydroxide
	10.58/8.00/4.27/2.64/1.5				
	K^H_{MHZ}	K^M_{MHZ}	K_{MZ}	K^M_{MZ}	
Mg^{2+}	–	–	–	–	–
Ca^{2+}	6.11	6.42	10.89	1.98	–
Mn^{2+}	4.64	8.63	15.60	2.09	14.2
Fe^{2+}	5.35	10.71	15.97	2.98	–
Co^{2+}	4.74	13.43	19.27	3.51	–
Ni^{2+}	5.62	15.26	20.22	5.41	–
Cu^{2+}	–	–	21.6	–	19.2
Zn^{2+}	5.43	13.40	18.55	4.36	16.35
Cd^{2+}	4.06	12.79	19.31	2.96	14.0
Pb^{2+}	4.52	12.81	18.87	3.41	15.7
Hg^{2+}	4.24	20.36	26.70	–	–
Fe^{3+}	3.56	19.48	27.50	–	37.4
Ce^{3+}	< 3	–	20.40	–	

$$K^H{}_{MHZ} = \frac{[MHZ]}{[H][MZ]} \qquad K^M{}_{MHZ} = \frac{[MHZ]}{[M][HZ]}$$

$$K_{MZ} = \frac{[MZ]}{[M][Z]} \qquad K^M{}_{MZ} = \frac{[M_2Z]}{[M][MZ]}$$

Table 2. Selected kinetic models

Kinetic model	$f(x)$	Release rate = dy/dt
Linear function	$y = a + bt$	$dy/dt = b$
Elovich equation	$y = a + b \ln(t)$	$dy/dt = b/t$
Power function	$\ln y = a + b \ln(t)$	$dy/dt = b/t \times (a + b \ln(t))$
Parabolic equation	$y = a + b\sqrt{t}$	$dy/dt = b/\sqrt{t}$
2nd order polynomial	$y = a + bt + ct^2$	$dy/dt = b + 2c \times t$

y – measured concentration at time t; a, b, c – fitted constants

University of Technology (Panalytical XPert Pro, step size 0.001° 2 Theta, K_α = 1.78901 Å, 409 mA, 40 kV). Rietveld refinement for phase quantification was conducted using the automated mode, which includes refinement of the scale factors, the background, the zero shift, the lattice parameters, and the peak shape parameter W.

5.00 g of samples were suspended, put into the EUF chamber, and sequentially fractionated, 3 replicated each. Within the original procedure, soluble nutrients get extracted by two subsequent portions of desalinated water of 5 min each, and finally, a 3rd fraction containing released metals can be obtained after addition of a complexant after 35 min. Within this work, this procedure was modified by the addition of 0.002 mol/L DTPA.

As at least 2 different release mechanisms can be expected, it is justified to apply mild conditions at first to simulate an initial reaction, and finally to change to harsher conditions to simulate a long-term release. At first, 200 V and up to 15 mA at 20°C were applied, to obtain an 'Initial' release rate (fraction 1–5). Then, 400 V and up to 150 mA at 80° were applied to obtain a 'long-term'-release rate (fraction 6–10). Each fraction (fraction 1–10) was sampled after 5 min i.e. the extraction of 10 fractions lasted 50 min. Experiments were done in triplicate.

After each extraction, filtrates obtained at cathode and anode were weighed. Final determinations were done by ICP-OES. Cumulated released amounts of Pb (y) were fitted versus time (t) by the use of mathematical models given in Table 2. Fitted constants b and c (2nd order polynomial) represent the slope whereas a represents the intercept of the fitted curves.

The constant a represents the fitted initial concentration at the beginning of the experiment when $t = 0$.

Apart from the linear fit, which assumes a constant release rate, other kinetic models due to Mengel and Uhlenbecker (1993) and Finžgar et al. (2007) were applied. The exponential function reflects the mere dissolution of the mineral as the rate-determining step, expressed in the form of a logarithm (linearized form) and termed as a power function.

RESULTS AND DISCUSSION

Metal content and soil properties. The limit values from the Austrian Landfill Ordinance (BMLFUW 2008) for soil excavation material are often used to evaluate the hazardous potential of metals in soils (Jelecevic et al. 2018). From this, the Pb contents reached from rather high (800 mg/kg) to ambient levels (21 mg/kg) (Table 3) with exceeding the limit values at Soil 1 and Soil 2 (for both columns). Soil 4 has an extremely high content of Cu (1870 mg/kg) and also significant As values (170 mg/kg). The cadmium content exceeded the relevant limit values only in Soil 2.

Table 3. Pseudo-total metal content in the investigated soils

Total content	Soil (mg/kg)					Landfill ordinance*	Landfill ordinance**
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5		
As	19	12	35	170	8.6	50	200
Cd	1.8	2.6	0.26	0.31	0.20	2	4
Cr	27	75	61	18	24	300	500
Cu	47	45	46	1870	31	100	500
Ni	42	51	46	19	24	100	500
Pb	340	800	130	120	21	150	500

*Limit values for metals in soil excavated material (BMLFUW 2008); **If the metal content from soil excavated material is geogenic, then the last column is applicable

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Table 4. Main characteristics of soils investigated

Parameter	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Soil type	Eutric Camibisol	Eutric Gleysol	Dystric Cambisol	Eutric Gleysol	Eutric Cambisol
pH	6.9	7.4	6.2	5.9	7.3
Total organic carbon (%)	2.8	5.4	4.1	14	4.6
Clay (%)	13	10	8	11	9
Silt (%)	41	64	63	29	47
Sand (%)	46	26	30	60	44
Pb – H_20 1:10 (mg/kg)	0.61	0.95	0.35	0.37	0.07

The investigated soils cover a range from slightly acid (pH 5.9) to slightly alkaline (pH 7.4). TOC seems rather high, but this might be due to charcoal residues from smelting (Table 4).

Soil mineralogy. X-ray diffraction patterns of individual soil samples indicate that the soil samples are quite similar concerning mineralogical composition. Quartz, muscovite, chlorite, and feldspars are the main minerals in all the soils (Table 5). Larger amounts of feldspars (about 10 wt% to 30 wt%) suggest that final stages of weathering where all feldspars have been transformed to clay minerals have not yet reached. Concerning Pb, only in Soil 3 a stoichiometrically Pb-bearing mineral phase, litharge (PbO), could be identified in traces. No other Pb minerals like galena, cerussite or anglesite could be detected. This is due to the low detection limit (about 2 wt%) of X-ray diffraction (XRD) compared to the Pb contents which are < 0.1 wt%. However, the presence of large amounts of layered silicates yields a large amount of surface area which might be relevant for Pb adsorption.

Release of lead. The release of Pb in the EUF reactor can by most plausibly modeled as a flow-through reactor, at an inflow of zero. Until the steady state has been reached, depending on the reactor volume over the velocity of flow; therefore, the first fraction may not be typical (Lasaga 1998). The release rate from the solid resembles

$$dc/dt = R - v \times c/V$$

Where: R – chemical reaction rate (mol/m^2/s); v – flow (L/s); c – measured concentration in the outflow (mol/L); V – reactor volume (L).

The chemical reaction rate is governed by the dissolution of the mineral, and the subsequent transport respectively complexation of the free Pb^{2+} by the electric field or DTPA. If the dissolution of the mineral is the rate determining step, a first-order reaction like a radioactive decay is expected, because the back-reaction is prohibited by the electric field and the complexant. The second elementary reaction between the free Pb^{2+} and the DTPA can be assumed second order, but approaches first order also, if DTPA is large enough to be constant.

Figure 1 shows the cumulative amounts of Pb released during the modified EUF procedure, as the means of the determinations in triplicate. Though

Table 5. Mineralogical composition of soils investigated

Mineral	Soil (wt %)				
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Quartz, α-SiO_2	25	31	28	39	40
Muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$	51	30	27	39	14
Albite, $NaAlSi_3O_8$	15	9	23	12	31
Anorthite, $CaAl_2Si_2O_8$	–	–	1	–	–
Kalifeldspar, (Microcline), $KAlSi_3O_8$				1	9
Chlorite, $(Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$	6	27	21	9	6
Rutile, α-TiO_2	4	2	–	–	–
Calcite, $CaCO_3$	–	2	–	–	–
Koninckite, $(Fe,Al)PO_4{\cdot}3\ H_2O$	–	nq	nq	–	–
Litharge, PbO			1	–	–

nq – not quantified

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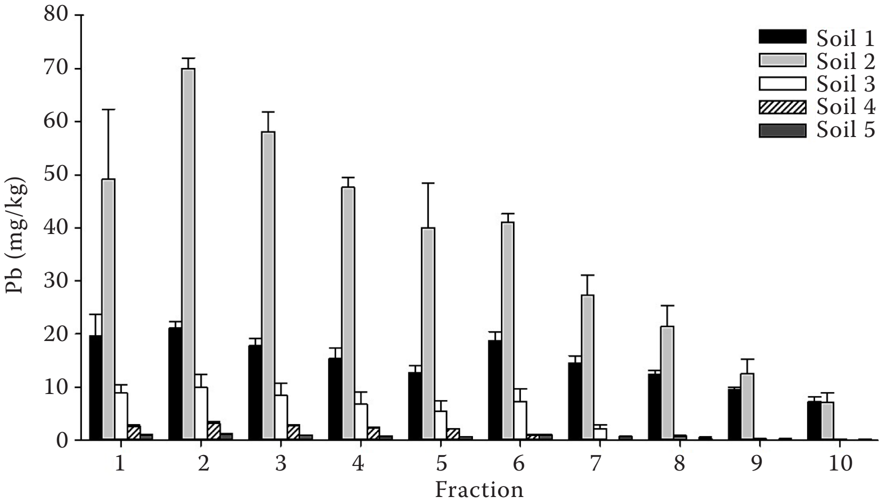

Figure 1. Release of lead (Pb) from soils within 10 fractions: fractions 1–5) 200 V, < 15 mA, 20°C; fractions 6–10) 400 V, < 150 mA, 80°C

conditions for fractions 6–10 were made substantially harsher, released concentrations decreased further.

The first 5 fractions were termed as the initial release (IR), because they contain more soluble and mobile parts. Fractions 6–10 were termed as the long-term release (LR). Even after 10 extracts, the amounts got by *aqua regia* have been not reached by far (Table 6), and the proportion of released was quite different, indicating different stages of weathering of the Pb minerals encountered. Large differences between initial and long-term release occurred, from about equal to 13-fold. Concerning *aqua regia*, least mobile Pb was found in Soil 4, which carries the maximum of TOC also. This suggests that Pb is present in a stable mineral phase, but this could not be verified by XRD due to insufficient detection limits. Whereas for Soil 1, the release rate under both conditions was about equal, the release rate at harsher conditions was less for the others, though they should contain more soluble and mobile parts, which indicates some exhaustion.

Mathematical fitting of cumulative Pb-release. Different extraction conditions justify two different graphs and fitting procedures (Figure 2). Thus release within fractions 1–5 are shown left hand (initial release), and release within fractions 6–10 are shown right hand (long-term release). As the criterium for the goodness of fit of the cumulative curves, the coefficient of determination (R^2) was selected (Mengel and Uhlenbecker 1993).

The resulting constant values from cumulative curves of 5 mathematical functions are presented in Table 7. The values of the linear fit, which assumes a constant release rate, which can be most easily interpreted with soil properties.

Table 8 shows the percentage of the fitted versus experimental values as well as the correlation coefficient (*r*) of the constant *b* with the main soil parameters. Four of five functions fitted sufficiently well. The greater difference between the fitted values versus the experimental ones and the lower coefficient of determination showed that the linear function was not so good at reflecting Pb release in the second release phase (LR). In general, the coefficient of determination decreased in the second release phase, suggesting that there were some discontinuities in the cumulative curve after

Table 6. Experimental cumulative lead (Pb)-release during the modified electro-ultrafiltration procedure

Parameter	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
IR (Σ 1–5 fraction mg/kg)	86.6	264.9	39.4	13.0	4.20
LR (Σ 6–10 fraction mg/kg)	62.3	109.4	10.5	0.99	2.16
Aqua regia (mg/kg)	340	800	130	120	21
IR (% of *aqua regia*)	25.5	33.1	30.3	10.8	20.0
LR (% of *aqua regia*)	18.3	13.7	8.1	0.8	10.3

IR – initial release; LR – long-term release

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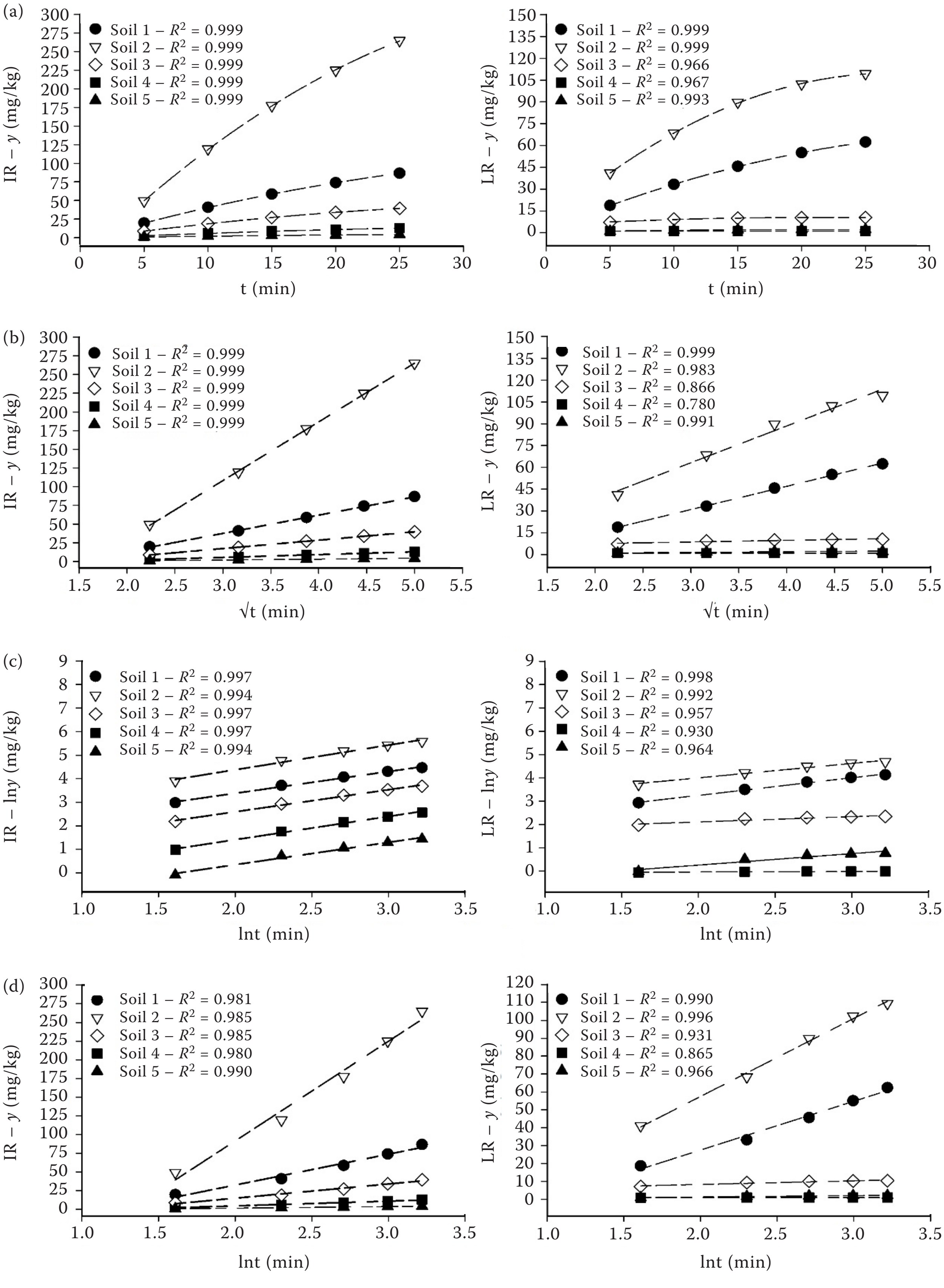

Figure 2. Description of cumulative lead (Pb)-release – initial release (IR) and long-term release (LR) with mathematical functions: (a) 2nd order polynomial; (b) parabolic equation; (c) power function, and (d) Elovich equation

Table 7. Values of the constants from five kinetic models

Kinetic model	Release phase	Constant	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Linear function	IR	*a*	5.79	5.97	2.73	0.47	0.30
	IR	*b*	3.34	10.74	1.53	0.51	0.16
	LR	*a*	10.24	31.01	7.27	0.95	0.94
	LR	*b*	2.18	3.41	0.15	0.001	0.06
Elovich equation	IR	*a*	−50.24	−175.37	−23.14	−8.12	−2.48
	IR	*b*	41.34	133.41	19.02	6.35	2.04
	LR	*a*	−26.97	−29.77	4.34	0.92	−0.15
	LR	*b*	27.25	43.62	2.00	0.02	0.75
Power function	IR	*a*	1.53	2.27	0.72	−0.57	−1.55
	IR	*b*	0.93	1.05	0.94	0.99	0.95
	LR	*a*	1.74	2.75	1.66	−0.08	−0.73
	LR	*b*	0.76	0.62	0.23	0.02	0.50
Parabolic equation	IR	*a*	−35.47	−127.23	−16.26	−5.87	−1.73
	IR	*b*	24.37	78.51	11.19	3.75	1.19
	LR	*a*	−16.99	−12.66	5.27	0.93	0.18
	LR	*b*	16.00	25.30	1.12	0.01	0.43
2nd order polynomial	IR	*a*	−3.181	−29.32	−2.541	−0.873	−0.341
	IR	*b*	4.986	16.79	2.433	0.744	0.272
	IR	*c*	−0.055	−0.201	−0.030	−0.007	−0.004
	LR	*a*	1.497	6.355	5.119	0.922	0.216
	LR	*b*	3.682	7.639	0.516	0.007	0.180
	LR	*c*	−0.050	−0.140	−0.012	−0.0002	−0.004

IR – initial release; LR – long-term release

Table 8. Comparison of fittings and correlation coefficient (r) of the constant b with main soil parameters (only for linear fit, b equals the reaction rate; Table 2)

Function	Release phase	Mean	Standard deviation	pH	Total organic carbon	Clay
		(%)		*b*		
Linear function	IR	102.0	0.64	0.56	−0.24	0.12
	LR	101.2	0.42	0.62	−0.37	0.42
Elovich function	IR	98.7	0.48	0.56	−0.24	0.12
	LR	100.3	0.69	0.62	−0.37	0.41
Power function	IR	100.5	0.74	0.26	0.37	−0.06
	LR	101.2	0.71	0.84	0.77	0.41
Parabolic equation	IR	99.8	0.23	0.56	−0.24	0.12
	LR	100.2	0.40	0.62	−0.37	0.42
2nd order polynomial	IR	101.8	1.99	0.56	−0.24	0.11
	LR	100.7	0.71	0.62	−0.34	0.29

IR – initial release; LR – long-term release

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temperature increase. Best correlations between fitted slope constants *b* and soil properties were achieved with soil pH. The constant *b* (except for IR of the power function) correlates positively with the pH and clay and negatively with the organic carbon.

Possible reaction mechanisms. The fit of kinetic equations can be used to elucidate or to exclude mechanisms of reaction, in case the overall process can be parted reasonably into elementary reactions. The EUF process resembles the dynamics of a flow-through reactor with no input, but a constant flow of charged particles due to the electric field applied. Table 7 shows that the Elovich- and the parabolic equation give a very bad fit of the initial concentrations because they cannot be below zero.

The mineralogical bonding could not be identified for four of the five samples (where Pb is present as litharge, PbO). This is why we assume that $PbCO_3$ is present in the other samples and its dissolution is the first elementary reaction which yields Pb^{2+} + CO_3^{2-}. This dissolution is like decay and therefore, first order.

$$\ln[PbCO_3] = \ln[Pb^{2+}] = \ln\,[PbCO_3]_o - k_1 \times t \quad (1)$$

Where: $[PbCO_3]_o$ – original lead carbonate; k_1 – first order reaction constant.

If this step is rate-determining, the fit would be due to the power equation, which is a modified exponential function. Contrary in Soil 3 a hydration or carbonation of litharge to secondary phases like hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, can be suggested but is not further considered for kinetics.

In a second step, the free Pb^{2+} is transported by the electric field and reacts with DTPA to yield the Pb-DTPA complex, to prevent hydroxide precipitation at the cathode or within the cathodolyte chamber.

$$d[PbDTPA]/dt = k_2 \times [Pb^{2+}] \times [DTPA] \quad (2)$$

Where: ${}_o\int^t$[PbDTPA] has been measured as 'x'; k_2 – second order reaction constant.

Now we can substitute $[Pb^{2+}]$ in the second equation by the expression obtained in the first one, and assume a dependency of DTPA from the originally present concentration $[DTPA]_o$ versus time *t*. If [DTPA] is a constant, because its concentration is large enough that is not consumed immediately, integration yields an equation simplified to $y = a + b \times t + c \times t^2$.

The fitted constant *b* contains $k_2 \times$ [DTPA], and the fitted constant *c* contains $k_1 \times [PbCO_3]_o$. Linearity is only approached if $k_1 \times [PbCO_3]_o$ gets very small, or DTPA gets large.

If actual [DTPA] declines linear with time because of transport in the electric field.

$$[DTPA] = [DTPA]_o - b' \times t \quad (3)$$

Again, a quadratic equation results in the simplified form $y = a + b \times t + c \times t^2$.

The fitted constant *c* contains $k_1 \times k_2[PbCO_3]_o$ $([DTPA]_o - 1)$, and the fitted constant *b* contains k_2.

If the reacting [DTPA] is diffusion controlled.

$$[DTPA] \times t = q \times D \times [DTPA]_o \quad (4)$$

Where: *q* – cross section; D – diffusion coefficient.

Substitution and integration yield a simplified equation $y = a + b \times \ln(t)$, where the fitted constant '*a*' is an integration constant, and fitted '*b*' the reaction constant, the diffusion coefficient of DTPA and the original concentrations of the reactants. This is like the Elovich equation in Table 7.

Explanations for the parabolic equation have not been found. Nevertheless, the fitting of the re-calculated results was best. But because the functions fitted sufficiently well, conclusions about rate determining steps from the 5 points each can hardly be done.

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