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Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate

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Kinetically defined metal fractions mimic mobility aspects of heavy metals.

Abstract

Kinetic EDTA and citrate extractions were used to mimic metal mobilization in a soil contaminated by metallurgical fallout. Modeling of metal removal rates vs. time distinguished two metal pools: readily labile (Q_{M1}) and less labile (Q_{M2}). In citrate extractions, total extractability ($Q_{M1} + Q_{M2}$) of Zn and Cd was proportionally higher than for Pb and Cu. Proportions of Pb and Cu extracted with EDTA were three times higher than when using citrate. We observed similar Q_{M1}/Q_{M2} ratios for Zn and Cu regardless of the extractant, suggesting comparable binding energies to soil constituents. However, for Pb and Cd, more heterogeneous binding energies were hypothesized to explain different kinetic extraction behaviors. Proportions of citrate-labile metals were found consistent with their short-term, *in-situ* mobility assessed in the studied soil, i.e., metal amount released in the soil solution or extracted by cultivated plants. Kinetic EDTA extractions were hypothesized to be more predictive for long-term metal migration with depth.

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Keywords: Kinetic extraction modeling; Heavy metals; EDTA; Citrate; Metal mobility; Soils

1. Introduction

Fate of heavy metals in soils is of great environmental concern. They represent major risks regarding contamination of natural waters after release by metal-bearing soil constituents and migration *via* the soil solution downward to the water table (van Oort et al., 2006). Studying soil solution collected *in situ* from different horizons in metal polluted soils, Denaix et al. (2001) and Citeau et al. (2003) reported the presence of metals either as predominantly mobile, water-soluble forms (Zn, Cd) or as colloidal forms (Pb, Cu). Incorporation of metal pollutants in soils generally leads to changes in chemical

speciation. Liberated metal ions are variously trapped by a wide range of reactive soil constituents, i.e. organic matter, iron and manganese oxides and hydroxides, phyllosilicates, phosphates, carbonates. A fraction of these metals can thereafter be (re)mobilized, either in dissolved or colloidal form before migrating downward. Mobilization is defined here as the potential capacity of metals to be transferred from the solid phase into the soil solution. It depends on the various links between metals and reactive sites of solid phase surfaces.

Numerous operational chemical extraction methods, including one-step extractions (Chaignon et al., 2003; Feng et al., 2005) and sequential extraction procedures (McGrath, 1996; Gleyzes et al., 2002; Krishnamurti et al., 2002), have been developed to estimate the extractable metal pools in relation to the metal-bearing soil phases. Although informative, such extraction procedures generally suffer from lacking

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selectivity with respect to the targeted chemical forms of metals. Alternatively, several authors have hypothesized that kinetic metal extraction data might better reflect dynamics of metals in soils (Gutzman and Langford, 1993; Bermond et al., 1998; Lo and Yang, 1999; Bermond et al., 2005) and in sediments (Fangueiro et al., 2002, 2005; Gismera et al., 2004). For a given chemical agent, the kinetic extraction approach generates two kinds of data: (i) the proportion of metals extracted with respect to the total metal content of the soil sample; and (ii) the kinetic behavior of metals. It has been suggested that such kinetic extractions can be modeled by two first-order reactions, so-called TFOR model, which empirically define two different pools. Although chemical extractants used for experiments do not perfectly mimic natural conditions, the first pool of readily extracted metals, called “labile” by Fangueiro et al. (2005), and the second pool of more slowly extracted metals, called “less labile”, might be reasonably attributed to potentially “mobile” and/or “bioavailable” metal pools (Bermond et al., 2005). In this view, Degryse et al. (2006) showed that the proportion of labile metals was well-correlated with metal uptake in plants. Particularly for sandy textured soils, the distinction of two types of extractability with time is hypothesized to provide a good expression of the diversity of metal-soil constituent interactions, i.e., to various chemical bond stabilities. In soils with strong aggregation phenomena (i.e., clay soils), disaggregation phenomena due to chemical agents or physical stirring may, however, influence the extraction of discrete kinetic pools.

Naidu and Harter (1998) stated that metals extracted by a mixture of organic acids are well-correlated with the mobile metal fraction in the soil solution. Organic acids are likely to be more representative of a mobile metal fraction that is available for biota. Low molecular weight organic acids, naturally exuded by plant roots or produced by microbial activity (Fox and Comerford, 1990), have been hypothesized to influence nutrient mobilization (van Hees et al., 2002) or translocation of metals in soil profiles (van Hees and Lundström, 2000; Li et al., 2006). Ethylene diamine tetraacetic acid (EDTA) is a well-known strong chelating agent and has been widely used in agronomy for estimating the total extractable metal pool (Alvarez et al., 2006; Manouchehri et al., 2006). EDTA was reported to remove metals organically bound, occluded in oxides, and associated with secondary clay minerals (Payà-Pérez et al., 1993). In contrast, citrate has been reported to be one of the dominant organic acids in the soil solution (van Hees et al., 2002). Among the low-molecular-weight organic acids used to simulate metal mobilization, citrate presents a moderate metal complexation strength compared to EDTA, according to thermodynamic data from Sillen and Martell (1964) and Lindsay (1979) shown in Table 1.

The present study aimed at estimating the labile fractions of different trace metals (Zn, Pb, Cu, and Cd) by applying kinetic EDTA and citrate extractions on samples from a moderately metal-contaminated agricultural soil (Labanowski et al., 2007). Comparison of EDTA and citrate extractions was used to quantify metal mobilization and to assess relationships between the energy of metal binding and the strength of the

Table 1
Formation constants ($\log K_f$) for metal-EDTA and metal-citrate complexes at 0.1 M ionic strength

	Zn	Pb	Cd	Cu
Me[EDTA] ²⁻	16.3	18.2	16.5	18.8
Me[citrate] ⁻	4.9	4.0	3.8	5.9
Me ₂ [citrate] ₂ ²⁻	—	—	—	13.2
Me[citrate] ₂ ⁴⁻	6.5	6.1	5.4	8.1

The $\log K_f$ values presented in this table are derived from those of Sillen and Martell (1964) and Lindsay (1979). They are recalculated to the same ionic strength.

used chemical extractant. By expressing the data in terms of metal removal rates vs. time, we first checked the pertinence of fitting kinetic extractions with a TFOR model. Parameters provided by this modeling were then used to compare the different kinetic metal pools with results on metal mobility obtained from field studies (Citeau et al., 2003) and pot experiments (Mench et al., 2007) conducted on the same soil.

2. Materials and methods

2.1. Site conditions and soil sampling

The site selected for this study was an agricultural field located about 750 m from a former metallurgical complex in northern France (Elsass et al., 2002; Labanowski et al., 2007). From 1901 to the late 1960s, the activity of a Zn smelter produced major atmospheric fallout (Thiry and van Oort, 1999), affecting agricultural land over an area of 3500 ha. The study site was a corn field representative of the most metal-contaminated agriculture areas, with reported total metal contents of 384–489 mg Zn kg⁻¹, 89–124 mg Pb kg⁻¹, 16.6–18.9 mg Cu kg⁻¹, and 3.5–3.8 mg Cd kg⁻¹ (Chartier, 1998; Elsass et al., 2002; van Oort et al., 2002). For understanding overall soil development, behavior, and metal distribution patterns, a large soil pit was dug and carefully sampled according to characteristic soil horizons as well as systematic sampling at 10-cm depth increments. For the present study, focusing on the plow layer, representative bulk samples of several kilograms between 0 and 28 cm were air-dried, sieved to <2 mm and homogenized before analyses.

2.2. Soil analyses

Characteristic physico-chemical parameters of the plow layer (particle size distribution, pH, CaCO₃ content, CEC using cobaltithexamine) were determined by INRA's national soil analysis laboratory using standard methods (AFNOR, Agence Française de Normalisation, 1996). Total carbon content (Total C) was measured using NC 2500 C/H/N analyzer (NC Instruments). Total metal concentrations in the sample were determined by atomic absorption spectrophotometry (AAS), either flame or furnace (Varian SpectrAA 220) after HF/HNO₃ (1:3, v:v) acid digestion under microwave heating (CEM MarsX) according to the digestion applications manual (CEM, 1998). HF (40%) and HNO₃ (68%) were of analytical grade. Total metal concentrations were also measured on samples from subsurface horizons. Quality control included triplicate analyses, blanks and a standard reference soil (CRM 7001, CMI, Prague, Czech Republic). Measured concentrations of elements from the reference material always were <5% from certified values. Metal concentrations in blanks were below the detection limit.

2.3. Extraction kinetics

Extraction kinetics by EDTA or citrate were used on soil samples to study: (i) the maximal potential metal extraction capacity after 24 h; and (ii) the

Table 2
Selected physico-chemical parameters of the studied soil (plow layer)

Particle size distribution (g kg ⁻¹)					pH	CEC (cmol kg ⁻¹)	Total Org. C (g kg ⁻¹)	CaCO ₃ (g kg ⁻¹)	Total metals (mg kg ⁻¹)			
Clay	Fine silt	Coarse silt	Fine sand	Coarse sand					Zn	Pb	Cu	Cd
98	76	291	449	86	6.6	6.7	14.8	2.5	411	100	16.7	3.6

extraction rates of metals released as a function of time (between 0 and 24 h). For this, 1 g of soil was shaken with 10 ml of extracting solution for different periods (5, 15, and 30 min; 1, 2, 5, 11, 17, and 24 h) and then immediately filtered on a 0.45- μ m cellulose membrane. For extractions >1 h, suspensions were centrifuged 5 min at 16,786 g before filtration. All EDTA and citrate extractions were made in three replicates and yielded 54 samples. Preliminary studies (not shown here) were conducted to optimize the experimental conditions. Finally, a 0.05 M Na₂H₂-EDTA and a 0.1 M (NH₄)₂H-citrate solution were found optimal for assessing the maximum extractability of the metals. Since many of the reactions with the extracting agents were pH dependent, all extracting solutions used in this work had a pH adjusted to 6.6 (soil pH) by adding adapted amounts of NaOH. Fangueiro et al. (2002) showed that a pH of about 6 guaranteed minimal variations of pH during extraction and hence, prevented competitive extraction by H⁺. Metal contents were determined as described above.

3. Results and discussion

3.1. Soil physico-chemical characteristics

The plow layer of the studied soil showed a slightly acidic pH and very low calcium carbonate content (Table 2). Other parameters, i.e., total carbon content (14.8 g kg⁻¹) and CEC (6.7 cmol kg⁻¹), were found to be typical for such sandy cultivated soils. Total metal concentrations reached 411 mg Zn kg⁻¹, 100 mg Pb kg⁻¹, and 3.6 mg Cd kg⁻¹. These values were much higher than those of the local geochemical background of the soils, estimated at 35, 16 and 0.2 mg kg⁻¹ for Zn, Pb, and Cd, respectively (Fernandez et al., 2007). The content of Cu (16.7 mg kg⁻¹) did not point to a marked industrial pollution. However long-term effects of fertilization and application of herbicides and fungicides may have contributed to the addition of anthropogenic Cu to the soil surface.

Distribution of total Zn, Pb, Cu, and Cd concentrations between the Ap and the C horizon (Fig. 1) clearly showed their dominant accumulation in the plow layer. Below the Ap horizon, the concentrations of Zn and Cd decreased progressively

indicating their migration until about 80-cm to depth, whereas Pb and Cu concentrations varied little. Such metal distribution patterns with depth are in agreement with comparable studies on other cultivated soils in the same area (Fernandez et al., 2007).

3.2. Proportion of metal extracted after 24 h

Examination of metal extraction evolutions with time showed that equilibrium was almost reached after 24 h (Fig. 2), except for Pb and to a lesser extent for Zn and Cd, when extracted with EDTA, which still showed some minor metal release at the end of the experiment. The percentages of extracted Zn, Pb, Cu, and Cd by EDTA were always higher than those extracted by citrate, although divergences were more marked for Pb and Cu than for Zn and Cd. These latter two elements can be considered as easily extractable metals, since both strong and moderately-strong chemical extracting agents were able to mobilize them in similar proportions, i.e., 45–55% for Zn and about 70–80% for Cd (Fig. 2). These results corroborate general statements that classify these two metals among the most mobile in soils, occurring frequently in appreciable amounts in the soil solution (Gray et al., 2003; Citeau et al., 2003). For Pb and Cu, however, the extracted amounts differed, depending on the strength of the used extractant (Fig. 2). With EDTA, about 90% of Pb was removed from the soil. Such a value is in agreement with other works which frequently report lead extractions >60% with EDTA (Lestan et al., 2005). Yet Pb is widely considered to be a low-mobility or immobile metal in soils. This apparent contradiction clearly highlights the discrepancy between metal-“mobilization” studied in laboratory conditions and metal-“mobility” observed in field conditions. Solubilization of a metal with a chemical extractant therefore does not imply its mobility in the soil, but means that the metal is potentially mobile under certain physicochemical conditions.

3.3. Kinetic aspects

In order to check the pertinence of the application of any first order model to kinetic extractions, the experimental results were expressed firstly in terms of metal removal rates per time unit. The amount of metal *M* extracted per weight unit of soil between *t_i* and *t_{i-1}*, *M* (mg kg⁻¹), can be defined as:

$$M_{(t_{i-1} < t < t_i)} = \frac{[C_M(t_i) - C_M(t_{i-1})]V}{m} \quad (1)$$

where *C_M(t)*, *V* and *m* represent the metal concentration at time *t*, the volume of extractant solution and the sample

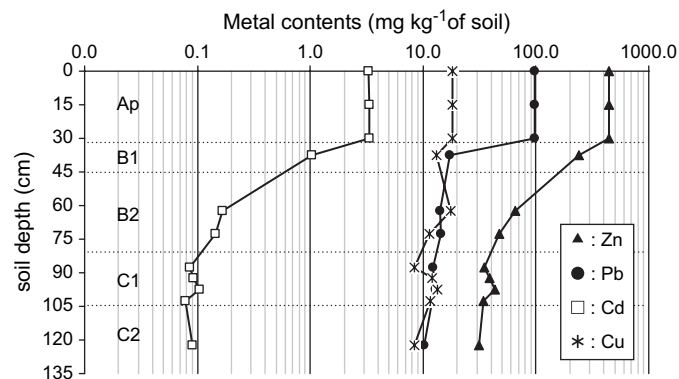


Fig. 1. Metal distribution patterns with depth in the studied soil profile (van Oort, unpublished data).

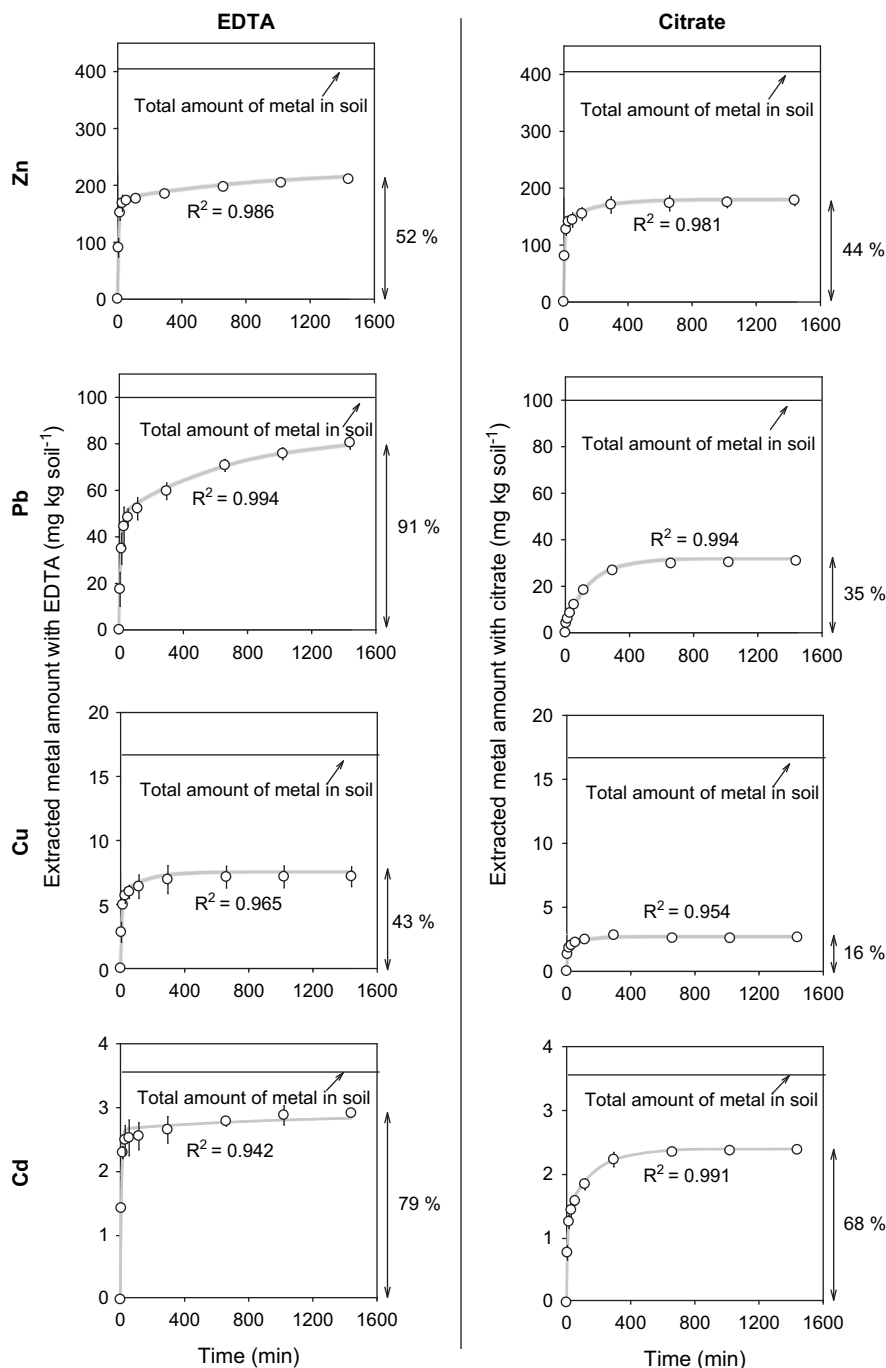


Fig. 2. Evolution of cumulative extracted amounts of Zn, Pb, Cu, and Cd metal vs. time with EDTA and citrate. Open circles: average of the results obtained from three replicates; error bars represent the 95% confidence level ($\bar{x} \pm s.t_{(v=2; \alpha=0.05, \text{bilateral})}/\sqrt{3}$). Thick grey line: modeled values (see text for details).

mass, respectively. Then, the average removal rate per time unit, $A_M(t)$, between t_i and t_{i-1} , for a given metal can be written as:

$$A_{M(t_{i-1} < t < t_i)} = \frac{M_{(t_{i-1} < t < t_i)}}{t_i - t_{i-1}}, \quad (2)$$

Practically, the values $A_M(t)$ were computed for each lag time of the three independent replicates. The mean values and the 95% confidence intervals were calculated and plotted in a semi-log diagram (Fig. 3), which was another way for

representing the data originally reported in Fig. 2. It appeared that the evolution of $A_M(t)$ generally occurs as two distinct linear segments with different, non-null slopes and different intercepts on the Y-axis. Such clear differences of behaviour through time allow the variable $A_M(t)$ to be modelled by the sum of two distinct pools occurring simultaneously, each of them following an exponential decreasing function:

$$A_M(t) = A_{M1}(0)e^{-\lambda_{M1}t} + A_{M2}(0)e^{-\lambda_{M2}t}, \quad (3)$$

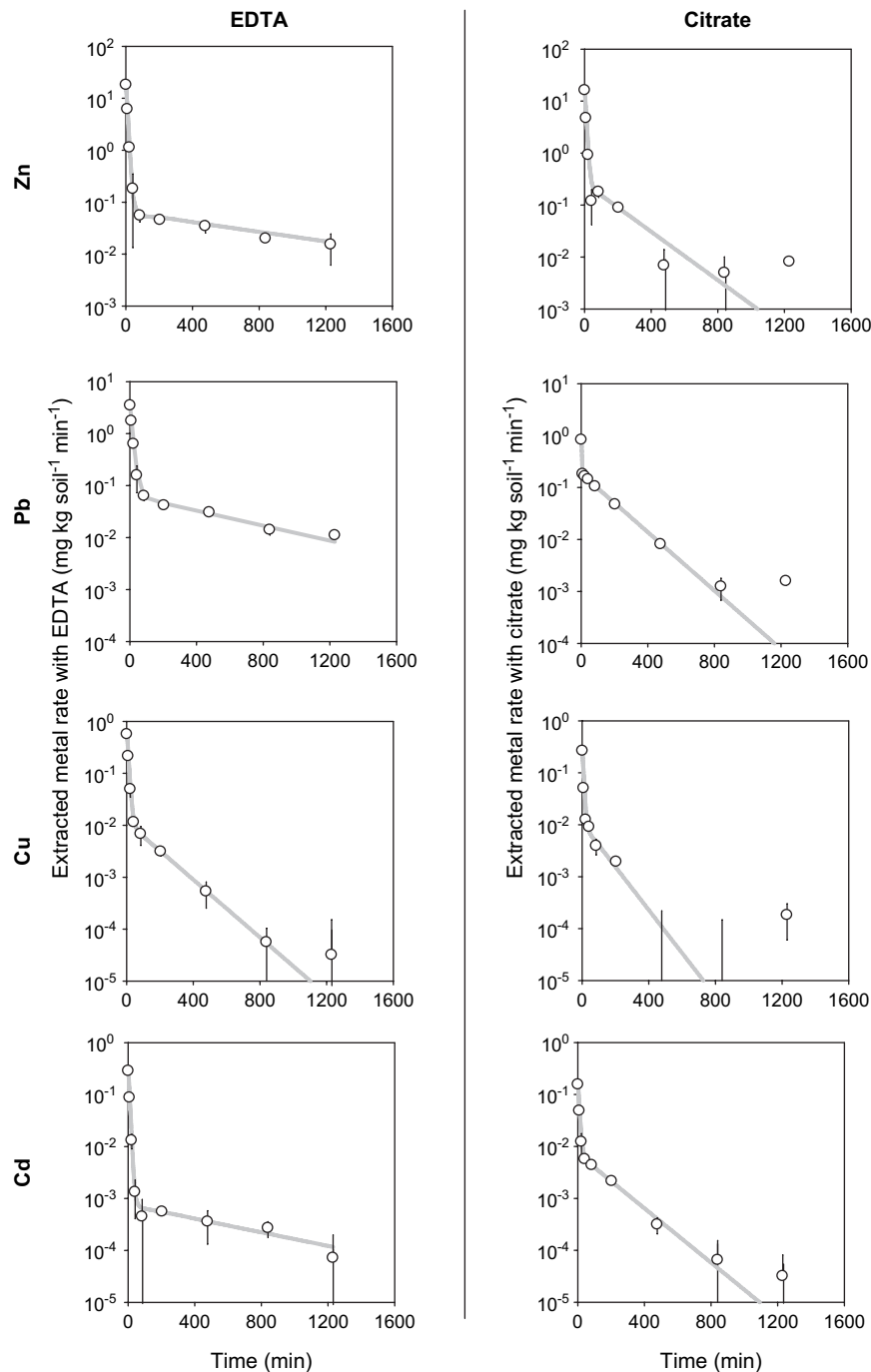


Fig. 3. Evolution of Zn, Pb, Cu, and Cd removal rate vs. time after with EDTA and citrate. Open circles: average of the results obtained from three replicates; error bars represent the 95% confidence level ($\bar{x} \pm s.t_{(v=2; \alpha=0.05, \text{bilateral})}/\sqrt{3}$). Thick grey line: modeled values (see text for details).

where $A_{M1}(0)$ and $A_{M2}(0)$ are the initial removal rates (at $t = 0$) of the metal M of the two pools and λ_{M1} and λ_{M2} are their apparent rate constants.

The extracted metal amounts gradually increased up to the end of the experiments with EDTA (Fig. 2) but quickly level off with citrate. Hence, it would have been tempting to model these latter using a single first order equation. As it can be seen in Fig. 3, and more particularly for extractions involving citrate, the representation using extraction rates vs. time reveals

more clearly the presence of two metal pools than using cumulative amounts of extracted metals (Fig. 2). The metal removal rates appeared to be high at the start of the extraction, dominated by the parameter $A_{M1}(0)$ characteristic of the first pool, but the contribution of this first pool decreased quickly to become insignificant (exponential decrease governed by λ_{M1}) (Fig. 3). Then, after a while, the contribution of the second pool became preponderant, with a clear slower extraction rate which still decreased with time (following λ_{M2}).

At time t , the total amount of metal extracted corresponds to the equation:

$$Q_M(t) = \int_0^t A_M(t) dt \quad (4)$$

and, after integration:

$$Q_M(t) = \frac{A_{M1}(0)}{\lambda_{M1}}(1 - e^{-\lambda_{M1}t}) + \frac{A_{M2}(0)}{\lambda_{M2}}(1 - e^{-\lambda_{M2}t}) \quad (5)$$

Let us denote Q_{M1} by $A_{M1}(0)/\lambda_{M1}$ and Q_{M2} by $A_{M2}(0)/\lambda_{M2}$. Then Eq. (5) can be written as:

$$Q_M(t) = Q_{M1}(1 - e^{-\lambda_{M1}t}) + Q_{M2}(1 - e^{-\lambda_{M2}t}) \quad (6)$$

Application of Eq. (6) to metal-extraction kinetics distinguishes two pools of metal, previously defined by Fangueiro et al. (2005) as Q_{M1} corresponding to the readily extractable metal fraction, called labile, associated with the apparent rate constant λ_{M1} , and Q_{M2} corresponding to the less readily extractable metal fraction, called less labile, associated with the apparent rate constant λ_{M2} . In addition, the total non-extractable metal fraction, Q_{M3} , must also be considered. It corresponds to the difference between the total amount of metal in soil (Q_{tot}) and the above mentioned pools:

$$Q_{M3} = Q_{tot} - Q_{M1} - Q_{M2} \quad (7)$$

Calculations of kinetic parameters diverge to some extent from those proposed by Bermond et al. (1998) and Fangueiro et al. (2005); both authors computing the parameters from the cumulative amount of metal extracted through time (Eq. (6)). In the present study, the parameters $A_{M1}(0)$, λ_{M1} , and $A_{M2}(0)$, λ_{M2} , were computed separately from both linear segments (Fig. 3). Each value was first weighted by using the inverse of its relative standard deviation, calculated on the basis of the three replicates. The parameters $A_M(0)$ and λ_M were drawn from the Y -axis intercepts and the slopes, respectively by linear fitting to Eq. (3). From their standard deviations provided by Statistica 6.0 for Windows, a 95% confidence interval was calculated (given that two degrees of freedom were lost by each linear fitting). Then, the parameters Q_M were obtained by

dividing $A_M(0)$ and λ_M . Their 95% confidence intervals were calculated by combining individual errors (Tables 3 and 4).

The metal amounts extracted by citrate after about 400–800 min were very low so that the subtraction $C(t_i) - C(t_{i-1})$ performed in Eq. (1) became inaccurate (Fig. 2). Therefore, the results for $t = 1440$ min were discarded for modelling citrate data. Besides, Pb extracted with citrate seemed to fit a single exponential decrease, even though the first extract was notably enriched by comparison to the general trend (Fig. 3). Consequently, this Pb case was treated as an instantaneous extraction pulse followed by a single exponential decrease. Finally, the total amounts of metal extracted with time have been simulated using Eq. (5) and compared to experimental observations (Figs. 2 and 3) (we obtained 5 degrees of freedom for EDTA extractions because two times two degrees of freedom are lost by linear fittings, and 4 for citrate extractions because the last extract was discarded). R -square values were calculated on this basis. They provided an indication of how well the model fitted the data. All R^2 were closed to unity, indicating that almost all of the variability has been accounted for with the variables specified in the model (Tables 3 and 4).

Comparison between results of the two kinetic extraction methods indicated that both the labile and less labile metal pools were generally greater for EDTA than for citrate (Tables 3 and 4). Only Cd does not fit this scenario since the less-labile fraction represented about 30% of the total Cd with citrate vs. about 10% with EDTA. A second general trend is that the labile metal fraction was generally greater than the less labile fraction for both extractants ($Q_{M1}/Q_{M2} > 1$), except for Pb (Tables 3 and 4). The Q_{M1}/Q_{M2} ratios of Zn and Cu were fairly similar for EDTA and citrate extractions, in spite of significantly different total amounts of metals extracted after 24 h. This suggests that the extracted fractions of Zn and Cu were bound to soil constituents with fairly homogeneous binding strengths for each metal.

On the contrary, mobilization of Cd and Pb was markedly related to the extraction strength (i.e., the intensity of complexation measured by the $\log K_F$ values, Table 1), notably in terms of proportion of labile and less labile pools. For Pb, the relative prevalence of the less-labile pool with citrate extractions (clearly highlighted by Fig. 3) suggests a slow and

Table 3
Initial extraction rates, $A_{Mi}(0)$, kinetic parameters, λ_{Mi} , and amounts, Q_{Mi} , of metal extracted with EDTA per kg of soil for the two pools defined by the TFOR kinetic model

	$A_{M1}(0)$ (mg kg ⁻¹ min ⁻¹)	λ_{M1} (min ⁻¹)	Q_{M1} (mg kg ⁻¹) (% of total)	$A_{M2}(0)$ (mg kg ⁻¹ min ⁻¹)	λ_{M2} (min ⁻¹ , ×10 ⁻³)	Q_{M2} (mg kg ⁻¹) (% of total)	R^2	Q_{M1}/Q_{M2}	Q_3 (mg kg ⁻¹) (% of total)
Zn	21.5–25.5	0.128–0.138	160–192 ~45%	0.058–0.068	0.9–1.2	51–67 ~15%	0.986	~3	~175 ~40%
Pb	3.7–4.1	0.076–0.082	46–52 ~50%	0.055–0.075	1.4–1.9	30–47 ~41%	0.994	~1.3	~10 ~10%
Cu	0.72–0.79	0.118–0.126	5.7–6.5 ~35%	0.011–0.012	6.3–6.5	1.7–1.9 ~10%	0.964	~3.5	~10 ~55%
Cd	0.417–0.423	0.155–0.157	2.6–2.7 ~75%	5.4 10 ⁻⁴ –10 ⁻³	0.8–2.1	0.2–0.8 ~10%	0.941	~7.5	~0.5 ~15%

Values correspond to confidence interval at a level of 95% (see text for details). Q_3 has been evaluated by subtracting Q_{M1} and Q_{M2} from the total metal amount per kg of soil.

Table 4

Initial extraction rates, $A_{M_i}(0)$, kinetic parameters, λ_{M_i} , and amounts, Q_{M_i} , of metal extracted with citrate per kg of soil for the two pools defined by the TFOR kinetic model

	$A_{M_1}(0)$ ($\text{mg kg}^{-1} \text{ min}^{-1}$)	λ_{M_1} (min^{-1})	Q_{M_1} (mg kg^{-1}) (% of total)	$A_{M_2}(0)$ ($\text{mg kg}^{-1} \text{ min}^{-1}$)	λ_{M_2} (min^{-1} , $\times 10^{-3}$)	Q_{M_2} (mg kg^{-1}) (% of total)	R^2	Q_{M_1}/Q_{M_2}	Q_3 (mg kg^{-1}) (% of total)
Zn	18–22	0.127–0.142	133–169 ~35%	0.16–0.42	3.6–7.0	22–77 ~10%	0.981	~3.5	~200 ~55%
Pb	Almost instantaneous		3.8–4.8 ~5%	0.18–0.19	6.4–6.6	28–29 ~30%	0.994	~0.2	~65 ~65%
Cu	0.28–0.42	0.138–0.167	1.7–2.7 ~15%	$0.8 \cdot 10^{-2}$ – $1.2 \cdot 10^{-2}$	7.4–11	0.6–1.4 ~5%	0.954	~3	~13 ~80%
Cd	0.19–0.22	0.134–0.151	1.3–1.6 ~40%	$5.9 \cdot 10^{-3}$ – $8.6 \cdot 10^{-3}$	5.4–6.7	0.9–1.4 ~30%	0.991	~1.4	~1 ~30%

Values correspond to confidence interval at a level of 95%. Q_3 has been evaluated by subtracting Q_{M_1} and Q_{M_2} from the total metal amount per kg of soil. See text for details about the case of Pb.

low mobilization under moderate extraction-strength conditions, consistent with generally low Pb mobility observed in soils. For Cd, a part of the fraction easily removed by EDTA becomes less labile with citrate (Tables 3 and 4): the configuration Q_{M_1} : 75%, Q_{M_2} : 10% with EDTA turns into Q_{M_1} : 40%, Q_{M_2} : 30%, maybe because, with citrate, more time is necessary to break links between Cd and soil constituents. Yet, at the end of the experiment, both EDTA and citrate have removed comparable amounts of Cd: 85% and 70%, respectively.

In terms of kinetics, the labile pools of Zn, Cu, and Cd are extracted approximately at the same high apparent rate constant: $\lambda_{M_1} \sim 0.11$ – 0.17 min^{-1} whatever the extractants used and the total extracted metal amounts. This means that approximately 10–20% of the remaining labile pool are removed per minute (Tables 3 and 4). Labile Pb seems to be less rapidly removed by EDTA ($\lambda_{M_1} \sim 0.07$ – 0.08 min^{-1}). The calculation with citrate was not done for the reasons mentioned above. The λ_{M_2} constants characterizing the less labile pool are much lower than the λ_{M_1} constants. The λ_{M_2} values of Zn, Pb, and Cd obtained with EDTA are comparable: 0.8×10^{-3} – $2.1 \times 10^{-3} \text{ min}^{-1}$ while a similar homogeneity is observed for these metals, with citrate $\lambda_{M_2} = 3.6 \times 10^{-3}$ – $11 \times 10^{-3} \text{ min}^{-1}$. For both extractants, the λ_{M_2} values of Cu are higher than those of other metals, suggesting that this Cu pool is associated with soil phases with low binding energy.

3.4. Operational use of kinetic extraction data in soil metal mobility studies

As already mentioned above, the two metal pools defined by the TFOR model have been attributed to mobile or bioavailable metal fractions (Bermond et al., 2005; Degryse et al., 2006). Significance of kinetic chemical extractions for providing detailed insight on metal speciation is still questionable yet, because different metal mobilization kinetics are observed following the reagent used. Studies connecting results from the kinetic approach with real-world investigations on metal mobility are cruelly lacking. In the present case, data issued by both approaches are interestingly available since complementary data on metal mobility and

bioavailability were obtained for the soil of our study by experimental field work, and by laboratory pot experiments. Citeau and co-workers collected periodically over three years gravitational soil water by lysimeters placed at the bottom of the Ap horizon, and assumed to explore a soil volume of about 7 L (Citeau et al., 2001, 2003; Citeau, 2004). Results are reported in Table 5. Exposure of different cultivars to metal polluted soil was also studied (Chartier, 1998; Mench et al., 2007). Green salad, carrot and rye grass were cultivated in 3 replicates using 10-kg pots filled with plow layer samples sieved to <5 mm. These cultivars were harvested at the usual growth stage (about 30 days). They were carefully washed with distilled water, dried at 60 °C, ground and analyzed for total metal contents (Mench et al., 2007) (Table 5). Metals display approximately the same behavior in both experiments. Percentages of Zn and Cd extracted monthly from the Ap horizon by soil solutions or plants are remarkably close. They vary only within one order of magnitude or less and are about 10–20 and 100–200 times higher than those of Cu and Pb, respectively (Table 5). Interestingly, the same pattern is observed for the percentages of readily citrate-labile pools: Zn ~ Cd > Cu > Pb (Table 4). Hence,

Table 5

Experimental data on metal mobility determined in the soil solution and by plant uptake

	Zn	Pb	Cd	Cu
– Average % of total metal extracted from the soil by the soil solution over 1 month*	0.25	0.0005	0.17	0.01
– Average % of total metal extracted from the soil by plant over 1 month**				
Green salad	0.71	0.002	1.54	0.09
Rye grass	1.39	0.008	1.05	0.42
Carrot	0.26	0.001	0.25	0.05

*Mean values compiled from lysimeter data of metal amounts in, and volumes of gravitational water ($n = 31$) leaching out of the Ap horizon (from Citeau, 2004); **mean values compiled from pot experiment data on metal-uptake by three cultivars with replicates ($n = 3$) (from Chartier, 1998; Mench et al., 2007). Metal extraction was expressed as a percentage of total metal content in the bulk sample.

labile metals extracted by citrate might be representative of short-term metal dynamics (solid-liquid transfer, plant-availability). In contrast, there is less resemblance of behavior between the readily labile pools using EDTA and real-world experiments, in particular for lead. This can be ascribed to the high extraction strength of EDTA (Table 1) which appears out of proportion with respect to natural soil conditions. As a consequence, EDTA rather provides an upper limit of metal mobility and can be a valuable parameter to predict long-term transfer in soils.

4. Conclusion

The representation of EDTA and citrate kinetic extractions in terms of removal rate confirmed the existence of two kinetic metal pools, a labile and a less-labile pool, which can be modeled by two first order reactions. Zn and Cu showed similar kinetic behaviors (in terms of Q_{M1}/Q_{M2} ratios) regardless of the extraction strength, contrarily to Cd and Pb which were markedly related to the used extractant. These results suggest that Zn and Cu have a more homogeneous binding strengths (with one or more soil constituents) compared to Cd and Pb.

Q_{M1} -citrate values were considered to be a good indicator for short-term metal mobility as they mimic metal mobilization in field and experimental conditions and are consistent with the frequently observed mobility scheme: Zn \sim Cd > Cu > Pb. EDTA extracted greater amounts of metals from the soil compared to citrate. It may therefore provide an indication for the maximum potential metal extractability, helpful for the prediction of long-term risks.

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