Kinetics as a tool to assess the immobilization of soil trace metals by binding phase amendments for *in situ* remediation purposes

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ABSTRACT

Many soil remediation techniques consist in decreasing the mobility of trace metals by means of adding trace metal binding phases. For this study, whose aim is to assess the efficiency of soil remediation method by binding phase amendment, a kinetic fractionation method that provides the labile and slowly labile trace metal amounts in soil has been introduced. Manganese oxides (vernadite) and insolubilized humic acids (IHA) have been used as binding phases for the remediation of four heavily polluted soils. Vernadite amendments are effective for lead and cadmium remediation, whereas IHA amendments are only effective for copper remediation. In most cases, the labile metal fractions decrease dramatically in amended soils (up to 50%); on the other hand, the amounts of total extracted metal near the point of thermodynamic equilibrium often show no significant difference between the amended soil and the control soil. These results highlight the utility of kinetic fractionation in assessing the efficiency of soil remediation techniques and, more generally, in evaluating trace metal mobility in soils and its potential advantages compared to extraction schemes performed under equilibrium conditions. In the future, this kinetic method could be considerably simplified so as to consume much less time allowing its routine use.

1. Introduction

Given the increasing numbers of soils contaminated by trace metals, a wide array of techniques aimed at reducing environmental risks have already been developed and tested. Three main approaches will be briefly described herein. The first consists of removing soil trace metals by washing with one or more suitable reagents, such as chelating agents [1]. These techniques are very effective yet remain expensive and may be destructive for the treated soil, thus complicating their use in applications to agricultural soils. The second approach is the phytoextraction, i.e. the extraction of soil metals by hyperaccumulator plants. It has become very widespread over the past few years [2]. The third approach consists in decreasing trace element mobility and hence trace element migration towards crops or groundwater; it entails a soil amendment of compounds known for their ability to bind trace metals. A large number of various inorganic or organic binding phases have already been tested [3].

Regardless of the remediation technique employed, an assessment of its efficiency may be derived by comparing trace metal contents in crops grown on rehabilitated soils vs. contents in crops from non-rehabilitated soils. Although this approach seems to be the most efficient, it is still difficult to extrapolate the results obtained for a given crop species to other species, which explains the need for chemical testing (i.e. the chemical extraction of bioavailable forms). The efficiency of *in situ* remediation techniques may be determined through metal extraction using a single chemical reagent. Single extraction schemes have been proposed, based in particular on the Measurement and Testing Programme of Community Bureau of Reference (BCR) [4], in order to assess the bioavailable metal fraction. These schemes however are performed under equilibrium conditions, and the information output on species distribution and bioavailability provided by thermodynamic considerations alone is of limited application.

Several studies conducted in soils have demonstrated that measurements of effective metal concentration using DGT (diffusive gradients in thin-films) generally correlate very well with metal concentrations in plants grown on the same soil [5]. The diffusion layer of DGT in fact controls the uptake flux over a range that appears to be compatible with the uptake fluxes of plants. DGT directly mimics the supply from solution as well as the kinetically limited release from the solid phase that accompanies this solution depletion. The high level of correlation with plant uptake and modelled depletion at both the DGT and plant surface reveal that the kinetics of supply is significant. Moreover, several authors [6,7] consider that an accurate approach to the mobility and bioavailabil-

Table 1
Physicochemical parameters and total concentrations of cadmium, copper and lead in the Couhins, Pierrelaye, P8 and YLM8 soils.

Soil	Couhins	Pierrelaye	P8	YLM8
Texture	Sandy	Sandy	Loamy sand	Loamy sand
pH	7.1	7.1	5.8	7.1
Carbonates	/	3%	/	/
Organic matter content (g kg^{-1} dw)	22.2	57.4	48.3	24.8
CEC (cmol kg^{-1} dw)	2.8	5.6	9.3	6.0
Cd (mg kg^{-1} dw)	94.9	2.2	5.8	1.6
Cu (mg kg^{-1} dw)	45.3	125.3	26.9	15.3
Pb (mg kg^{-1} dw)	44.8	178.3	139.0	56.0

ity of metals in soils could be derived by studying the kinetics of metal extraction with a single reagent. Application of the multiple first-order kinetic model to experimental results allows establishing metal fractions with different labilities, thus making it possible to assess soil trace metal bioavailability. Moreover, EDTA is one of the most widely used chelating agents for such studies. Indeed, use of multiple first-order kinetic model with EDTA as extractant is already well developed and has been validated after determination of optimal experimental conditions [8,9]. Furthermore this kinetic method has been compared to other well-developed methods like one-step extraction procedure [10] and sequential extraction [11]. In this previous study, the labile fraction was correlated with available metal. This kinetic fractionation method was also applied for the heavy metal speciation of two BCR reference materials which have been specifically developed as materials to evaluate the validated BCR three-step sequential extraction method [12]. When compared with the sequential extraction data, it seemed that the lability of an element determined with this kinetic method was positively correlated to the first step extraction fraction. With this kinetic method, Bermond et al. [13] found a significant correlation between the labile concentration of cadmium in ten unpolluted soils from Burgundy (France) and the concentration in wheat shoots.

In this study, our aim has been to study the relevance of this kinetic fractionation method, i.e. the multiple first-order reaction model, in order to determine the efficiency of soil remediation techniques using binding phase amendments. Two binding phases were selected for the soil remediation tests carried out on four heavily polluted soils.

2. Materials and methods

2.1. Soil samples

For soil remediation tests with the selected binding phases, four heavily polluted French soils were chosen. The P8 and YLM8 soils were from Mortagne (northern France) and polluted by output from an industrial complex. The Pierrelaye soil (Paris region) has been polluted by wastewater spreading since 1899. Lastly, the Couhins soil (Bordeaux area) was polluted by the spreading of sewage sludge. The total contents of cadmium, copper, lead and certain physicochemical parameters are listed in Table 1.

2.2. Binding phases

The trace metal binding capabilities of various binding phases using the kinetic fractionation method have been evaluated in another study [14]; among them, two binding phases were selected for the present study:

- insolubilized humic acids (IHA) were prepared from humic acids (HA) (supplied by the Sigma–Aldrich company) by heating at 330 °C for 1 h under a nitrogen atmosphere. This thermal treatment avoids IHA solubilization within the pH range of soils and

then avoids an increase in trace metal mobility through the formation of soluble metal complexes with humic acids. These insolubilized humic substances have never been used elsewhere for remediation purposes. The full set of preparation steps and characteristics regarding them have been presented in other studies conducted by Seki and Suzuki [15] and also by Varrault and Bermond [16];
- a hydrous manganese oxide, vernadite (δMnO_2). Synthetic vernadite was prepared by the rapid oxidation of a 30-mM MnCl$_2$ solution containing an equal volume of a 20-mM KMnO$_4$ solution at pH 10. The dried product appears as black in colour and is composed of crystallite agglomerations [17].

2.3. Principles of the kinetic fractionation method: the two-compartment model

The multiple first-order reaction model was used for fitting the experimental curves of metal cation desorption from soils, whether amended or not, in assuming the existence of just two types of metal cations, i.e. those quickly extracted (called labile cations) and those less quickly extracted (called slowly labile cations). This assumption may be represented by the two following reactions (Eqs. (1) and (2)) for extracting reagent R and a given metal M:

$$S_1M + R \rightarrow S_1 + MR \quad (k_1) \tag{1}$$

$$S_2M + R \rightarrow S_2 + MR \quad (k_2) \tag{2}$$

where S_1 and S_2 denote the soil binding sites, corresponding respectively to the labile and slowly labile compartments, along with the two kinetic constants k_1 and k_2. Let us keep in mind however that these two compartments are only kinetically defined. In this study, the extracting agent used was EDTA, a strong chelating agent. To apply this model appropriately, the extracting reagent must be in excess, such that desorption reactions can be considered as pseudo-first-order reactions. The kinetic constants associated with this model are respectively k_1 and k_2. According to the multiple first-order reaction model, the desorption rate of a metal cation from soil particles is given by Eq. (3):

$$Q(t) = \sum_{i=0}^{n} Q_i(1 - e^{-k_i t}) \tag{3}$$

where Q_i denotes the metal content bound to site i, which is expressed in micrograms of metal per gram of dry soil sample ($\mu g\,g^{-1}$ dw); k_i denotes the kinetic constant related to the metal extracted from site i (min^{-1}); $Q(t)$ is the extracted metal content at time t which is expressed in micrograms of metal per gram of dry soil sample ($\mu g\,g^{-1}$ dw).

By applying the first-order reaction model according to our hypothesis (i.e. only labile and slowly labile compartments from reactions (1) and (2)), then Eq. (3) may be simplified as:

$$Q(t) = Q_L(1 - \exp^{-k_L t}) + Q_{SL}(1 - \exp^{-k_{SL} t}) \tag{4}$$

where Q_L and Q_{SL} denote the labile metal and slowly labile metal contents, respectively; k_L and k_{SL} denote the kinetic constants

related to metal extracted from labile and slowly labile compartments, respectively; a fifth parameter, Q_{NE}, which represents the non-extracted amount, is derived by calculating the difference between the total amount of metal contained in the soil and the $Q_L + Q_{SL}$ sum.

In order to calculate the four constants introduced in Eq. (4), a nonlinear regression programme using the Levenberg–Marquardt algorithm was applied to the experimental results, yielding these four constants plus a set of statistical parameters that allow estimating the quality of the fit.

2.4. Soil remediation efficiency assessment using kinetic fractionation

The efficiency of each binding phase has been assessed using the kinetic fractionation method on both amended and non-amended soils. The following procedure was performed:

- 100 mg of a given binding phase and 10 g of soil (1%, w/w) were mixed and stirred for 6 weeks in a 40-ml NaNO₃ 0.1 M solution;
- After stirring, this solution was centrifuged (3000 × g, 30 min) and supernatant was stored at 4 °C until determination of the trace metal content. The solid was oven dried at 30 °C for 1 week.

A kinetic study was conducted on the solid sample obtained above via the following procedure:

- Batch experiments were initiated by mixing 1 g of oven-dried sample with 30 ml of extracting solution (EDTA 0.0166 M at pH 6.5) in a 60-ml polyethylene tube;
- The mixtures were kept shaken by using an end-over-end shaker. After the selected extraction time (3, 5, 10, 15, 30, 60, 120, 180, 300 and 1,440 min), solutions were immediately filtered (0.45 μm) and stored at +4 °C until the metal determination step.

For each soil sample, a control was carried out in accordance with this protocol and without including the binding phase. All these experiments were performed in triplicate.

2.5. Reagents

Only chemicals of analytical quality were employed. Deionised water was prepared using a Milli-Q water system (Millipore). Polyethylene containers were cleaned with a 1:1 laboratory reagent grade HNO₃ for 24 hrs and then rinsed four times with Milli-Q water. Analytical solutions were also prepared using Milli-Q water and stored in polyethylene bottles.

Table 2
Variation in amount of cadmium in each fraction of both the control sample and after binding phase amendment for the four test soils, and variation in each fraction compared to the control sample (nsv: no significant variation).

	Binding phase	Cadmium amount ($\mu g\,g^{-1}$) and relaxation times for each fraction of the control sample and after binding phase amendment for the four test soils, and variation (%) in each fraction compared to the control	
		P8	Pierrelaye
Q_L (ug g^{-1})/t_L(min)	Control	3.26/1.1	1.62/2.1
(ΔQ_L (%))	Vernadite	1.92/2.5 (−41%)	1.03/1.8 (−36%)
Q_{SL} (ug g^{-1})/t_{SL}(min)	Control	0.84/50	0.53/65
(ΔQ_{SL} (%))	Vernadite	1.81/90 (+116%)	1.17/140 (+119%)
Q_{NE} (ug g^{-1}) (ΔQ_{NE} (%))	Control	1.68	0.07
	Vernadite	2.04 (+21%)	0.02 (−71%)
pH in supernatant	Control	7.8	7.2
	Vernadite	7.8	7.4

2.6. Determination of trace metal concentrations

Metal concentrations in solution were measured in AAS with a Varian Spectra 250 Plus atomic absorption spectrometer using an air-acetylene flame and external standards. Under these conditions, the relative standard deviations obtained for extraction results using the given reagents, including soil sample variability, were satisfactory and ranged from 2% to 4%. Total metal content in the soil samples was determined after hydrofluoric acid mineralisation and then measured by means of graphite furnace atomic absorption spectrometry (Varian Spectra A 400 with Zeeman effect background corrector and equipped with an autosampler). Cadmium was determined at 228.8 nm, lead at 283.3 nm and copper at 324.7 nm. The spectral bandwidths were 0.5 nm for cadmium and 0.7 nm for lead and copper. Ten microliters of sample was introduced into the pyrolitically coated graphite tubes for metals determinations. The peak areas of the analytical signals were measured. Three measurements were done with a standard deviation of less than 5%.

3. Results and discussion

3.1. Soil remediation tests

The kinetic study was carried out on all four amended soils. For each sample, this study was also conducted on the non-amended soil to serve as a control sample. The variations in labile, slowly labile and non-extracted contents, compared with the controls, are summarised in Tables 2–4 for cadmium, copper and lead respectively. Any variations in these contents of less than 20% were considered insignificant. pH values in the supernatant measured at

Table 3
Variation in amount of copper in each fraction of both the control sample and after binding phase amendment for the four test soils, and variation in each fraction compared to the control sample (nsv: no significant variation).

	Binding phase	Copper amount ($\mu g\,g^{-1}$) and relaxation times for each fraction of the control sample and after binding phase amendment for the four test soils, and variation (%) in each fraction compared to the control		
		P8	YLM8	Couhins
Q_L (ug g^{-1})/t_L(min)	Control	9.0/2.8	4.4/2.3	22.0/2.2
(ΔQ_L (%))	IHA	5.6/2.0 (−38%)	2.4/2.8 (−45%)	15.9/2.2 (−28%)
Q_{SL} (ug g^{-1})/t_{SL}(min)	Control	17.9/180	10.9/220	20.2/105
(ΔQ_{SL} (%))	IHA	18.6/220 (nsv)	9.9/230 (nsv)	23.5/135 (nsv)
Q_{NE} (ug g^{-1}) (ΔQ_{NE} (%))	Control	0.3	0.5	3.1
	IHA	3.0 (+900%)	3.4 (+580%)	8.0 (+158%)
pH in supernatant	Control	7.8	6.9	7.6
	IHA	7.4	6.7	7.3

Table 4
Variation in amount of lead in each fraction of both the control sample and after binding phase amendment for the four test soils, and variation in each fraction compared to the control sample (nsv: no significant variation).

	Binding phase	Lead amount ($\mu g\,g^{-1}$) and relaxation times for each fraction of the control sample and after binding phase amendment for the four test soils, and variation (%) in each fraction compared to the control			
		P8	Pierrelaye	YLM8	Couhins
Q_L (ug g^{-1})/t_L(min)	Control	47.1/4.2	85.6/5.3	26.1/7.8	21.6/1.7
(ΔQ_L (%))	Vernadite	35.4/11 (−24%)	41.0/4.1 (−52%)	14.4/8.4 (−45%)	12.2/3.2 (−43%)
Q_{SL} (ug g^{-1})/t_{SL}(min)	Control	78.4/240	59.9/150	22.7/40	19.7/160
(ΔQ_{SL} (%))	Vernadite	84.4/190 (nsv)	108.4/160 (+81%)	33.0/74 (+44%)	33.2/190 (+68%)
Q_{NE} (ug g^{-1}) (ΔQ_{NE} (%))	Control	13.5	33.1	7.1	3.5
	Vernadite	19.3 (+43%)	28.7 (nsv)	8.6 (nsv)	−0.6/
pH in supernatant	Control	7.8	7.2	6.9	7.6
	Vernadite	7.8	7.4	7	7.8

the end of the six week stirring period are also listed in Tables 2–4. In all cases, trace metal concentrations in the supernatant at the end of the six week stirring period were below the detection limit of our analytical method and then represent less than 1% of the total metal amounts in all soils considered in this study. Relaxation times values t_L (=$1/k_L$) and t_{SL} (=$1/k_{SL}$) are also summarised in Tables 2–4. Values of relative standard deviation for each kinetic parameter have been calculated and are systematically lower than 5% for labile and slowly labile metal amounts and systematically lower than 15% for relaxation times. These relatively low values indicate the good fitting of experimental values by the two-compartment model. Compared with the controls, the values of t_L are not clearly influenced by binding phase amendment whereas the t_{SL} values seem to be generally slightly higher in amended soils.

As an example of the metal desorption rate from soils, the desorption rate of lead bound to Pierrelaye soil vs. extraction time either with or without a vernadite amendment is presented in Fig. 1. The lead desorption is expressed as a fraction of the total soil metal content. In this example, the relaxation time values obtained with or without amendment are respectively 4.1 and 5.3 min for the labile compartment and reach 160 and 150 min for the slowly labile compartment. Labile metal is thus nearly completely extracted during the first 30 min of EDTA extraction, whereas slowly labile metal is extracted in roughly 10 or 20 h. The non-extracted metals during the 24 h extraction time represent here between 15 and 20% of the total soil metal amount.

3.1.1. The vernadite amendment

In comparison with non-amended soils, the labile contents of lead in vernadite-amended soils decreased sharply for all tested
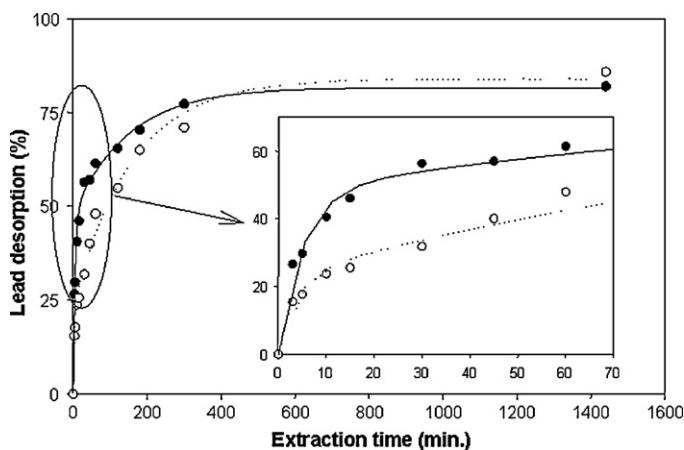

Fig. 1. Desorption rate of lead bound to Pierrelaye soil, both without an amendment (experimental points (●), fitted curve (—)) and with a vernadite amendment (experimental points (○), fitted curve (….)).

soils, from 24% for P8 to 52% for Pierrelaye. In most cases, the decrease in labile lead content in amended soils resulted in a similar increase of the slowly labile fraction. For the P8 soil, it results also in an increase in the non-extracted fraction (+43%).

The labile contents of cadmium decreased by about 40%, but only for the P8 and Pierrelaye samples. In the case of P8, this decrease in labile fraction produced an increase in the slowly labile fraction (+116%) as well as in the non-extracted fraction (+21%).

For copper, the vernadite amendment proves ineffective towards decreasing the labile contents of the four soils tested.

The binding capability of vernadite has already been highlighted in other desorption studies conducted on this type of compound [18]. Furthermore, for ten unpolluted soils from Burgundy, a significant negative correlation ($p < 0.01$) was found between the labile fraction and the manganese oxide content [14]. These results suggest that manganese oxides are able to bind trace metals tightly in soils, especially cadmium and lead.

3.1.2. The IHA amendment

The IHA amendment is effective only in the case of copper for the P8, YLM8 and Couhins soils, given that labile fractions decreased precipitously, by as much as 45%. However no significant variations in the slowly labile fraction could be observed. As a result, in all cases, an increase of the non-extracted fractions was observed. For the other metals, the IHA amendment does not significantly decrease the labile fractions. The limited effectiveness of the IHA amendment in the case of cadmium may be explained by the relatively weak affinity of cadmium for humic substances. Also, the good results obtained for copper are easily explained since it is well-known that copper has a very strong affinity for humic substances [19].

3.1.3. Responsible mechanisms of the labile fraction decrease following binding phase amendment

From these results, it appears difficult to determine the mechanisms responsible for the labile fraction decrease in metal after soil amendment with the binding phase. During the 6-week stirring period, we hypothesize that metal cations bound to sites from where they are quickly desorbed migrate towards binding phase sites from which their desorption is slower, thus explaining the labile fraction decrease and slowly labile fraction increase. Furthermore, it is possible for the binding phases to gradually cover those soil sites initially in contact with the solution. Such a coating could then prevent trace metal extraction during the kinetic study. For copper, this could constitute the main reason for the labile fraction decrease, which gives rise to an increase not in the slowly labile fraction but in the non-extracted fraction. Indeed, the copper binding capability of EDTA is actually higher than that of humic substances; consequently, copper bound onto the binding phase surface should be totally extracted at thermodynamic equilibrium. Nevertheless, this coating is probably not the sole

reason why the labile copper fraction decreases; otherwise, IHA would also be efficient for cadmium and lead remediation. Another possible mechanism to explain the labile fraction decrease is the intraparticle diffusion [20]. Indeed, some sorption sites within particle interiors could be reached only by intraparticle diffusion of metals during the six-week stirring period. In consequence, metals bound to these sites would become not extractable by EDTA at least during the first hour of extraction. In any case, these labile fraction variations are certainly not due to pH variation during the six-week stirring period (liming effect) since for all four soils, the pH in supernatant does not evolve significantly following amendment (less than 0.2 pH unity).

3.1.4. Benefit of the kinetic fractionation method in assessing trace metal mobility

As observed in Fig. 1, the amount of extracted lead is very similar at or near thermodynamic equilibrium (after 24 h of extraction in the present case) between the amended soil and the control soil. The amounts of lead extracted for both the amended and control soils differ considerably during the first 30 min; this difference then diminishes with time and becomes insignificant beyond 240 min. The distinction between lead extraction rates, and then distinction between lead mobility, can only be derived by the kinetic method. In this study, for both lead and cadmium, even when a measurable effect of the binding phase amendment can be detected on trace metal extractability, no significant overall variation exists in the amount extracted at equilibrium. The only significant effect to be highlighted concerns the extracted amount in the labile compartment, which is very well correlated with the bioavailable soil metals Indeed, in the study of Bermond et al. [13], the relationships between cadmium in plants and labile cadmium concentrations in soils have been studied. The labile cadmium concentrations have been determined exactly with the same methodology than in our study. The relationship between cadmium in plants and labile cadmium is statistically significant at $p < 0.01$. On the opposite, cadmium amounts extracted by $Ca(NO_3)_2$ and EDTA in 24 h are not correlated with cadmium in plants. In the same manner total cadmium is not correlated with cadmium in plants. So, although chemical extractants used for experiments do not perfectly mimic natural conditions, the first pool of readily extracted metals, called "labile" might be reasonably attributed to potentially "mobile" and/or "bioavailable" metal pools.

For almost all trace metal extractions carried out as part of this study, the relaxation time values t_L (=$1/k_L$) and t_{SL} (=$1/k_{SL}$) ranged respectively from 1 to 5 min for the labile compartment and 50 to 300 min for the slowly labile compartment. Labile metal is thus nearly completely extracted during the first 30 min of EDTA extraction, whereas slowly labile metal is extracted in roughly 10 or 20 h. In the future therefore, the kinetic fractionation method could be significantly simplified by retaining just two extraction times (as opposed to ten in this study), the first at 30 min to determine the labile metal fraction and the second at 24 h for the slowly labile metal fraction.

4. Conclusion

In this study, our aim has been to study the effectiveness of a kinetic fractionation method, i.e. the multiple first-order reaction model, in order to assess remediation technique efficiency. The particular technique used in this study consists of soil remediation via the use of either vernadite or insolubilized humic acid amendment. Soil remediation tests were carried out on four

heavily polluted soils; these tests indicated a high efficiency of vernadite amendment for both lead and cadmium-polluted soil remediation, whereas the IHA amendment was only effective for copper. The labile fractions of these metals in all four polluted soils actually decreased by as much as 50%. It should be pointed out however that except for copper, even when the labile metal fraction greatly decreased after binding phase amendment, the total extracted metal amounts near thermodynamic equilibrium were often insignificantly different when comparing the amended and control soils. These results underscore the benefit of the kinetic fractionation method in assessing the efficiency of soil remediation techniques and, more generally, in assessing trace metal mobility in soils. Furthermore, this method could be radically simplified in the future, by proceeding with just two extraction times at 30 min and 24 h, in order to determine the labile metal and slowly labile metal fractions respectively.

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