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A solid–liquid extraction approach to elucidate the chemical availability of metals in soil and sediment assuming Langmuir isotherm behaviour

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Abstract

In an earlier paper (Anal. Chim. Acta 514 (2004) 137) we claimed that the maximal extractability of a metal from soil or sediment for a user-defined extractant, i.e. the chemical availability in that particular extractant, may be biased as a result of inadequate volume to mass (*V*/*m*) ratios. Correcting for that artifact using an implementation of the simple linear isotherm model gave good results although we cautioned the general applicability. In this paper we will theoretically derive the limitations of that approach based on the more general assumption that sorption processes are described by a Langmuir isotherm.

NIST reference material 8704 was extracted with 1 mol l^{-1} NaOAc (adjusted to pH 5) to experimentally verify the applicability of the Langmuir isotherm approach and illustrate the deviations obtained for some metals using the linear isotherm approach. Of the seven metals measured (Cr, Co, Ni, Cu, Zn, Cd, and Ba) only for Cr and Cu severe discrepancies between both approaches were found, which could be traced back to non-linear isotherm behaviour. Moreover, the Langmuir isotherm approach showed that the above mentioned extractability artifact is even more serious than earlier assumed applying the linear isotherm approach.

Keywords: Sediment SRM NIST 8704; Metals; Chemical availability; Extraction; Langmuir isotherm model; Variable volume to mass ratio approach; ICP-MS

1. Introduction

The chemical availability of metals in soil and sediment is generally associated with the sorption between metal ions and surface soil particles and may be derived from extraction processes. Weak extractants relate to a lower chemical availability than strong extractants and therefore the chemical availability is a function of the type of extractant. An extractant such as, e.g. 0.01 mol l^{-1} $CaCl_2$ is thought to resemble the chemical composition of the soil or sediment pore water [1] and as such gives an indication of the possible metal equilibrium concentration in soil or sediment pore water via ion exchange processes. Stronger extractants such as e.g. 1 mol l^{-1} NaOAc (adjusted to pH 5) and 0.5 mol l^{-1} $NH_2OH{\cdot}HCl$ target metals bound to carbonate [2] and iron and manganese oxide phases [3], respectively.

In a previous paper [4] it was reported that the chemical availability of metals in soil determined via the above mentioned procedures may be subject to incomplete extraction due to an insufficient extractant volume (*V*) to soil mass (*m*) ratio. Using 0.1 mol l^{-1} HNO_3 as an extractant it was found that commonly used *V*/*m* ratios in the range of 10–40 ml g^{-1} may give as much as 50% too low extraction yields. A variable volume to mass ratio extraction procedure based on assumption of a linear isotherm was applied to derive the correct chemical availability (=maximal extractability for that particular extractant) for seven metals in an urban soil. However, it is feasible that with other extractant or sample compositions no linear isotherm behaviour is found. Commonly it is assumed that a Langmuir isotherm is able to describe more extreme sorption behaviour [5,6] since a Langmuir isotherm

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takes into account a finite amount of soil or sediment sorption sites, denoted by the capacity of the soil or sediment, whereas a linear isotherm assumes an infinite amount of sorption sites.

A theoretical model will be developed for retrieval of the chemical availability based on assumption of a Langmuir isotherm. The limitations of the earlier developed variable volume extraction approach based on linear isotherm behaviour will be demonstrated. The applicability of the model will be illustrated by determining the chemical availability of seven metals in NIST reference material 8704 (Buffalo river sediment) using 1 mol l^{-1} NaOAc (adjusted to pH 5) as an extractant. The findings will be compared with these obtained when treating the data according to the previous model.

2. Model

In Fig. 1 a generalization of the chemical availability and extractability of a metal in a solid using a variable volume to mass ratio approach is given. The chemically available metal concentration a_0 (mg kg^{-1}) in a solid differs from the total metal concentration a_t (mg kg^{-1}) and is dependent on the extraction conditions used. However, under non-digestive conditions the "inert" metal concentration ($a_t - a_0$) must be attributed to mineralogical parameters. In many instances [7] we notice an extractability dependence with V/m ratio as illustrated by the c_1V/m curve which asymptotically approaches a_0, where c_1 (mg l^{-1}) denotes the metal concentration in the extract after equilibration. This leads to a remaining chemically available metal concentration $a_1 = a_0 - c_1V/m$ (mg kg^{-1}) in the solid which decreases with V/m ratio. High V/m ratios should give an adequate measure of the chemically available metal concentration in the solid; however, this is potentially invalidated by an inmeasurably low metal concentration in the extract.

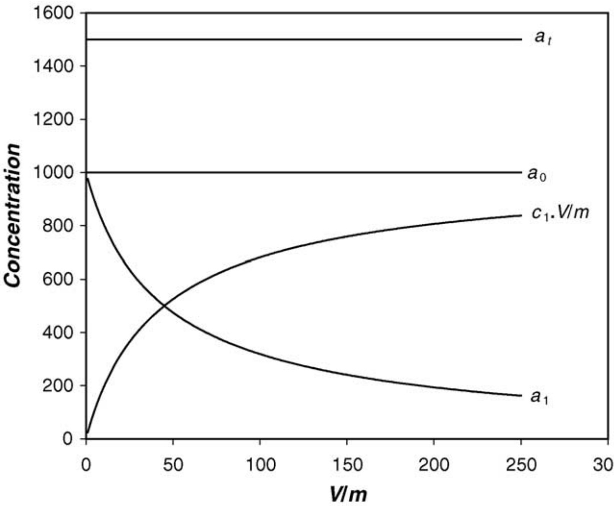

Fig. 1. Generalized concept of chemical availability and extractability as a function of V/m ratio; concentrations are expressed as (corresponding) soil concentrations.

In a previous paper [4] we reported on the successful use of the variable volume to mass ratio procedure based on an linear isotherm approach to retrieve the chemically available concentration. Using the mass balance:

$$ma_0 = c_1V + ma_1 \tag{1}$$

and, after substitution of the linear isotherm relationship $a_1 = K_Dc_1$ into this mass balance, with K_D ($l\,kg^{-1}$) the partitioning coefficient between solid and liquid, the following c_1 versus V/m correlation is obtained

$$c_1 = \frac{a_0}{V/m + K_D} \tag{2}$$

In this paper we will elaborate on the limitations of this approach by assuming a Langmuir isotherm relationship $a_1 = (K_Lc_1a_{cap})/(1 + K_Lc_1)$, with K_L ($l\,mg^{-1}$) the Langmuir coefficient and a_{cap} (mg kg^{-1}) the capacity of the solid. Substitution into the mass balance and solving for c_1 gives the following c_1 versus V/m correlation:

$$c_1 = -\frac{\begin{array}{c} V/m - K_La_{cap} + K_La_0 \\ +\sqrt{(V/m + K_La_{cap} + K_La_0)^2 + 4K_LV/ma_0} \end{array}}{2V/mK_L} \tag{3}$$

3. Experimental

3.1. Materials

Millipore (Milford, MA, USA) Milli-Q-Plus water (18.2 MΩ cm), denoted as MQ water, was used for all preparations of solutions. All chemicals used were at least of analytical reagent grade. A multi-element standard solution with a 1000 ± 10 mg l^{-1} concentration for 23 elements (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn) in 1 mol l^{-1} HNO_3 was purchased from Merck (Merck #11355 Multi-Element-Standard IV). A stable 10 mg l^{-1} stock solution in a poly(propylene) flask was prepared by dilution with 0.1 mol l^{-1} HNO_3. For ICP-MS analysis, working solutions were made fresh by further dilution of the stock solution with 0.1 mol l^{-1} HNO_3 to create calibration curves in the range 0–500 μg l^{-1}. A sediment standard reference material (NIST 8704, Buffalo river sediment) was used in the extraction experiments. Reference concentration values for (most of) the elements under study: Cr, 121.9 ± 3.8 mg kg^{-1}; Co, 13.57 ± 0.43 mg kg^{-1}; Ni, 42.9 ± 3.7 mg kg^{-1}; Zn, 408 ± 15 mg kg^{-1}; Cd, 2.94 ± 0.29 mg kg^{-1}; Ba, 413 ± 13 mg kg^{-1}.

3.2. Extraction procedure

Varying amounts of soil sample (0.1–1.0 g dw) were accurately weighed into 50 ml "Falcon" poly(propylene) centrifuge tubes to give an as even as possible spacing in the

Table 1
ICP-MS operating conditions

Nebulizer	Babington
Spray chamber	Scott, 2 °C
rf power	1300 W
Sampling depth	6.4 mm
Plasma gas flow rate	15.0 l min^{-1}
Auxillary gas flow rate	1.0 l min^{-1}
Nebulizer gas flow rate	1.05 l min^{-1}
Sampler	0.5 mm, Ni
Skimmer	0.5 mm, Ni
Masses measured	^{53}Cr, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{111}Cd, ^{137}Ba
Integration time	0.3 s/channel (three channels per mass)
Repetitions	5

V/*m* range from 25 to 250 ml g^{-1} (for in total ten *V*/*m* ratios). To each tube, 25.0 ml of a 1 mol l^{-1} NaOAc solution (adjusted to pH 5.0) was added (the pH in the tubes did not change with *V*/*m* ratio). A blank containing only this solution was taken through the extraction procedure as well. The tubes were shaken in an end-over-end custom-made shaker (Spes, Slovenia) with a rotation speed of 30 ± 1 rpm for 5 h in a thermostatted room at 22 °C; 5 h is supposed to be sufficient to yield complete extraction of metals from river sediments with the extractant used [8]. After the required shaking time the soil samples were immediately centrifuged at 3200 rpm for 20 min. The solutions were carefully removed with a poly(propylene) pasteur pipette and diluted 1 + 9 with 0.1 mol l^{-1} $\mathrm{HNO_3}$. They were kept in poly(propylene) measuring vials with screw cap and no variation in metal concentrations was found due to storage up to at least one month.

3.3. ICP-MS analysis

The ICP-MS analysis for seven elements (Cr, Co, Ni, Cu, Zn, Cd and Ba) was carried out using a Hewlett-Packard 4500 PLUS ICP-MS spectrometer equipped with a Cetac ASX-500 autosampler. The operating conditions are given in Table 1. Calibration solutions (nine points) were run before and after each sample series consisting of 10–15 samples (including blanks) and in-between calibration checks were performed after each four samples. Metal concentrations in unknown solutions were calculated based on external calibration curves.

4. Results and discussion

4.1. Model calculations for Langmuir isotherm model

In order to visualize the influence of the soil or sediment capacity a_{cap} on the metal extraction behaviour, in Fig. 2A graphs are given for the metal concentration c_1 in an extract as a function of *V*/*m* ratio for several capacities with equal Langmuir coefficients. The capacity range is chosen from 10 to 500% of the chemically available metal concentration a_0. Although a capacity below the chemically available concentration may seem extraordinary from an isotherm point of view, the fact that the extractant is in general much "stronger" than the soil or sediment pore solution may lower the capacity of the soil or sediment drastically, probably below the chemically available concentration. This implies that the fraction given by $(a_0 - a_{\mathrm{cap}})/a_0$ is readily available without being subject to any isotherm. What this means for the extractability $c_1 V/m$ is shown in Fig. 2B, where the lowest capacity logically results in the highest extractability, closest to the chemically available concentration. To illustrate the limitation of the linear isotherm approach the ten data points (for each capacity) in Fig. 2A, which were generated with a Langmuir isotherm, are fitted with a linear isotherm according to Eq. (2) (non-linear least square curve fitting with Origin® 6.1 software, OriginLab Corporation, MA, USA). From Table 2 it can be seen that the largest deviation from the theoretical chemically available concentration of 1000 mg kg^{-1} is found for a capacity of 1000 mg kg^{-1}. To get a better insight into the parameters influencing this deviation, in the next section a generalized concept is given to apply it for all possible situations, i.e. all combinations of a_0, a_{cap} and K_{L}.

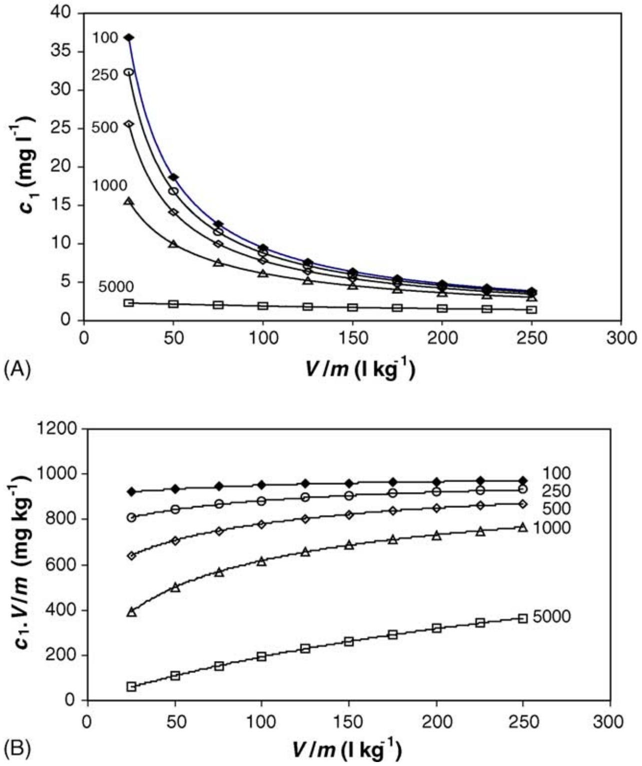

Fig. 2. Illustration of the volume to mass ratio model for a Langmuir isotherm approach assuming a chemically available metal concentration of 1000 mg kg^{-1} and soil or sediment capacities in the range from 100 to 5000 mg kg^{-1}. Both the metal concentration in extract (A) and the corresponding extractability (B) as a function of *V*/*m* ratio are shown.

4.2. Limitations of linear isotherm model

If we assume that a Langmuir isotherm correctly describes metal extraction from a soil or sediment, by definition a linear

Table 2
Results of non-linear least square curve fitting of data generated with a Langmuir isotherm (Fig. 2A) on a linear isotherm (Eq. (2)) to yield the chemically available concentration a_0; the theoretical chemically available concentration was in all cases 1000 mg kg^{-1} and the capacity a_{cap} ranged from 100 to 5000 mg kg^{-1}

a_{cap} (mg kg^{-1})	a_0 (mg kg^{-1})	S.D. (mg kg^{-1})
100	961.20	3.40
250	910.23	7.96
500	845.60	13.91
1000	787.65	19.10
5000	874.77	4.94

Standard deviations represent fitting errors in a_0.

isotherm is not able to accurately fit such extraction data. In order to get a grip on the limitations of the linear isotherm model, which is easy to apply and has shown its potential for certain sample/extractant/metal combinations [4], we have to look at the key parameters affecting linear isotherm behaviour. Linear isotherm behaviour is governed by K_D only and Langmuir isotherm behaviour by both K_L and a_{cap}. We may see the $a_{\text{cap}}K_L$ product as a kind of pseudo-K_D, very closely resembling the K_D in the case of samples which have a high surplus of unsaturated sites. In that instance the capacity of the soil is much higher than the chemical availability ($a_{\text{cap}}/a_0 \gg 1$) and linear and Langmuir isotherms fit extraction data equally well. When the extraction data become sorption-site limited, i.e. when the capacity approaches the chemical availability ($a_{\text{cap}}/a_0 = 1$), a linear isotherm no longer suffices to fit the extraction data. In case strong extractants are used, extracting much more metals than anticipated in soil or sediments pore waters, the capacity goes well below the chemical availability ($a_{\text{cap}}/a_0 \ll 1$). Since both K_D and $a_{\text{cap}}K_L$ approach zero then, this results in extraction data which fit linear and Langmuir isotherms equally well. These qualitative features marking the extraction behaviour discrepancies under linear and Langmuir isotherm behaviour may be quantified in the form of universally valid graphs. To this end, ten c_1 versus V/m data points were generated with a Langmuir isotherm and fitted on a linear isotherm via non-linear least square curve fitting according to Eq. (3). The universally valid fits giving the chemically available concentration a_0 obtained by this fit (related to the theoretical chemically available concentration $a_{0,\text{th}}$, as input for the Langmuir isotherm) as a function of the $a_{\text{cap}}/a_{0,\text{th}}$ ratio for different $a_{\text{cap}}K_L$ products is given in Fig. 3. From this figure we can see that when the capacity of the soil or sediment approaches 0 or infinity, the linear isotherm approach (Eq. (2)) generates similar a_0 data then the Langmuir isotherm approach (Eq. (3)). Furthermore, we see that a lower K_L results in retrieval of higher $a_0/a_{0,\text{th}}$ ratios and thus better linear isotherm behaviour. The dips in the graphs are in all cases positioned at $a_{\text{cap}}/a_{0,\text{th}}$ ratios ≤ 1, closer to 1 for larger K_L values. Fig. 3 may be a good starting point in explaining why certain c_1 versus V/m experimental data point profiles can not be fitted with a linear isotherm approach as given in Eq. (2).

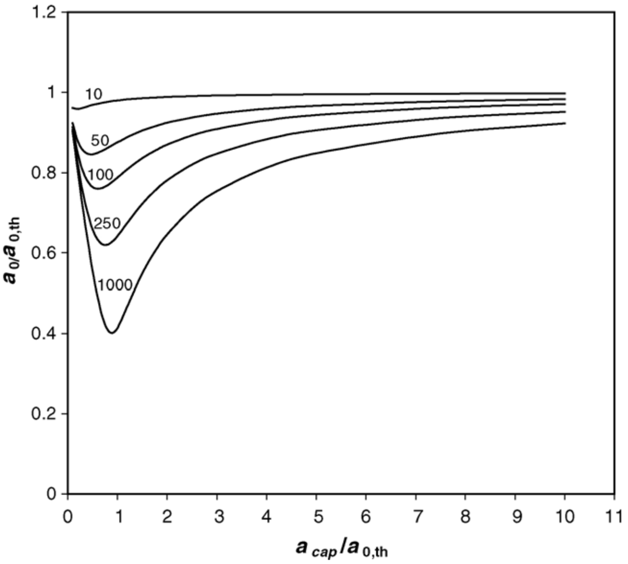

Fig. 3. Demonstration of the limitations of the linear isotherm model for retrieval of a theoretical chemically available concentration $a_{0,\text{th}}$ for c_1 vs. V/m data points generated via a Langmuir isotherm. Plotted is how the $a_{\text{cap}}/a_{0,\text{th}}$ ratio influences the chemically available concentration a_0 deduced via the linear isotherm approach for different $a_{\text{cap}}K_L$ values.

4.3. Application of the Langmuir isotherm model

The experimental c_1 versus V/m extraction data for seven metals (for NIST 8704 extracted with 1 mol l^{-1} NaOAc solution (adjusted to pH 5)) have been fitted on Langmuir and linear isotherms and the results of the fits are given in Table 3. It can be seen that the chemically available concentrations for both approaches yield varying results, depending on the metal; for chromium and copper the worst correlations are obtained, whereas for the other metals the differences are less than ca. 20%, with cobalt and cadmium giving almost identical results. It should be noted that the capacity of the sediment is less than the available concentration for all metals studied; this is in agreement with the hypothesis given above. Looking at the worst correlation (chromium), it is obvious, from the high $a_{\text{cap}}K_L$ product (1468 l kg^{-1}) and a $a_{\text{cap}}/a_0(K_L)$ ratio of 0.88, why the correlation is so bad (see Fig. 3). A plot of the c_1 versus V/m extraction data for chromium is given in Fig. 4A, including the fits obtained with both isotherms. It is clear that the linear isotherm approach gives a fit that considerably deviates from the experimental data whereas the Langmuir isotherm approach gives a near perfect fit. For copper a similar behaviour is observed although not so strong; for the other metals it is very difficult to visualize the difference between the fits. In Fig. 4B the a_1 versus c_1 plots, calculated from $a_1 = a_0$ (Langmuir or linear) $- c_1V/m$, for both approaches are given to illustrate the bad fitting behaviour of chromium on the linear isotherm $a_1 = K_Dc_1$. The Langmuir isotherm $a_1 = (K_Lc_1a_{\text{cap}})/(1+K_Lc_1)$ shows a perfect fit, in line with what we would expect to see, viz. saturation behaviour what contradicts fitting with the linear isotherm approach. The

Table 3
Non-linear least square curve fitting results for experimental c_1 vs. V/m data under assumption of two different isotherms; in parentheses the fitting errors are given, expressed as relative standard deviations in the respective parameters

	Langmuir sorption isotherm			Linear isotherm		Comparison
	a_0 (mg kg^{-1})	a_{cap} (mg kg^{-1})	K_L (l mg^{-1})	a_0 (mg kg^{-1})	K_D (l kg^{-1})	a_0 (linear)/a_0 (Langmuir)
Cr	19.6 (35.8)	17.3 (40.1)	84.8 (55.2)	6.80 (4.9)	23.1 (13.1)	0.347
Co	1.41 (4.5)	0.33 (57.2)	19.4 (179)	1.38 (1.2)	2.51 (16.4)	0.979
Ni	4.10 (21.2)	1.64 (24.4)	18.2 (193)	3.63 (2.9)	5.55 (19.4)	0.885
Cu	31.6 (7.1)	27.8 (6.0)	8.20 (19.8)	20.1 (3.9)	25.0 (10.1)	0.636
Zn	132 (9.9)	48.7 (21.8)	1.27 (62.5)	109 (1.7)	4.83 (13.1)	0.826
Cd	1.68 (3.1)	0.47 (55.2)	12.6 (137)	1.64 (0.9)	2.72 (10.6)	0.976
Ba	32.3 (2.1)	19.8 (3.3)	1.55 (19.5)	28.8 (1.5)	9.17 (6.9)	0.891

chemical metal availability a_0 in 1 mol l^{-1} NaOAc solution (adjusted to pH 5), as derived from the Langmuir isotherm approach, and expressed as a fraction a_0/a_t of the total certified metal concentration in NIST 8704 is as follows for the metal studied: Cr, 16.1%; Co, 10.4%; Ni, 9.56%; Zn, 32.4%; Cd, 57.1%; Ba, 7.82% (for Cu no certified total concentration is given). It should be emphasized that these fractions would have been much lower using the generally accepted V/m ratio of 40 l kg^{-1} [9]; for chromium e.g. only 3.4% would have been found. This is in agreement with the findings in an earlier paper [4], but now even more pronounced because of the fact that the extractability $(c_1 V/m)/a_0$ is governed by the chemically available concentration a_0 which is always higher for the Langmuir isotherm approach than for the linear isotherm approach (see Table 3).

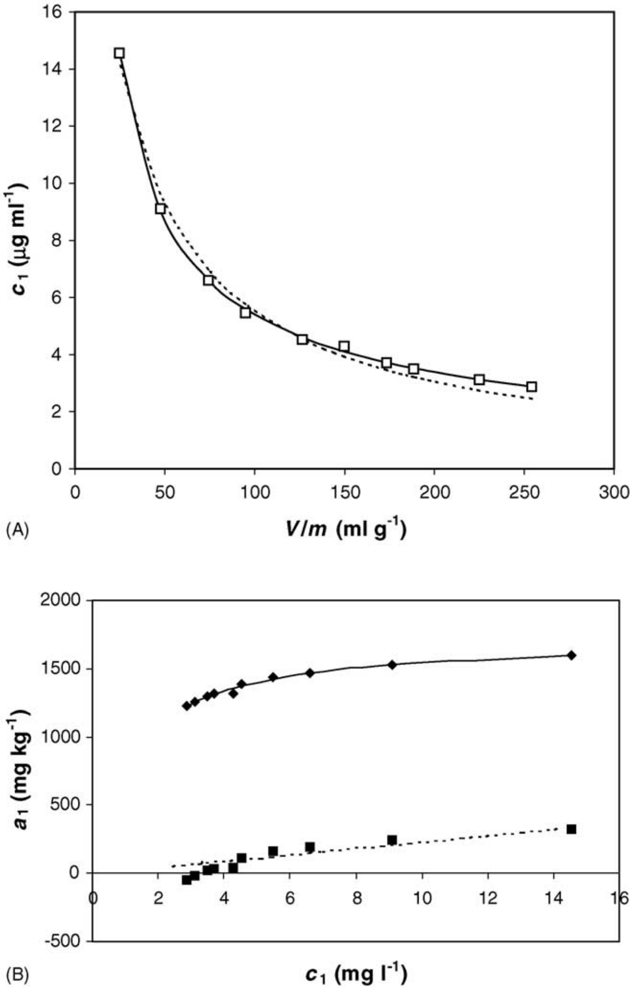

Fig. 4. Langmuir (solid line) and linear (dashed line) isotherm fits on experimental data for chromium extracted from NIST 8794 with 1 mol l^{-1} NaOAc solution (adjusted to pH 5).

5. Conclusions

This work gives a testimony of the strength of the Langmuir isotherm approach, in the form of a variable volume to mass extraction setup (metal concentration in extract versus V/m), for retrieval of the chemically available metal fraction in soil or sediment. At the same time the limitations of an earlier linear isotherm approach could be identified and traced back to soil or sediment saturation behaviour, i.e. a combined effect of a soil or sediment capacity (for a particular extractant) similar to the chemically available metal concentration and a high value for the Langmuir coefficient.

It was shown that the Langmuir isotherm approach yields excellent fits for metal extraction data generated with 1 mol l^{-1} NaOAc solution (adjusted to pH 5) and NIST reference material 8704 (Buffalo river sediment), in contrast to some fits using the linear isotherm approach. Nonlinear isotherm behaviour was especially evident for the metals chromium and copper. Concluding we can say that the Langmuir isotherm approach is more robust than the linear isotherm approach and seems to have a greater validity.

It should be emphasized that the Langmuir isotherm approach, even more than the linear isotherm approach, cautions the use of low V/m ratios in single and sequential extraction protocols.

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