

# 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  $1 \text{ mol l}^{-1}$  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.

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## 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.  $0.01 \text{ mol l}^{-1}$   $\text{CaCl}_2$  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.  $1 \text{ mol l}^{-1}$  NaOAc (adjusted to pH 5) and  $0.5 \text{ mol l}^{-1}$

$\text{NH}_2\text{OH}\cdot\text{HCl}$  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  $0.1 \text{ mol l}^{-1}$   $\text{HNO}_3$  as an extractant it was found that commonly used  $V/m$  ratios in the range of  $10\text{--}40 \text{ ml g}^{-1}$  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  $1 \text{ mol l}^{-1}$  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  $a_0$  ( $\text{mg kg}^{-1}$ ) in a solid differs from the total metal concentration  $a_t$  ( $\text{mg kg}^{-1}$ ) 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  $c_1 V/m$  curve which asymptotically approaches  $a_0$ , where  $c_1$  ( $\text{mg l}^{-1}$ ) denotes the metal concentration in the extract after equilibration. This leads to a remaining chemically available metal concentration  $a_1 = a_0 - c_1 V/m$  ( $\text{mg kg}^{-1}$ ) 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 immeasurably low metal concentration in the extract.

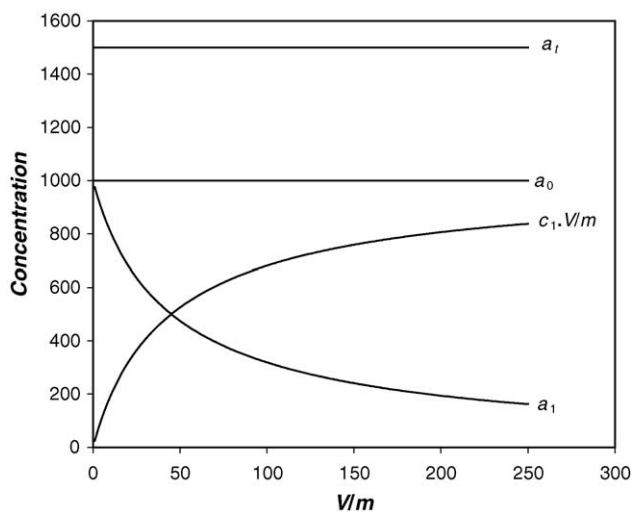


Fig. 1. Generalized concept of chemical availability and extractability as a function of  $V/m$  ratio; concentrations are expressed as (corresponding) soil concentrations.

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

$$ma_0 = c_1 V + ma_1 \quad (1)$$

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

$$c_1 = \frac{a_0}{V/m + K_D} \quad (2)$$

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

$$c_1 = - \frac{V/m - K_L a_{\text{cap}} + K_L a_0 + \sqrt{(V/m + K_L a_{\text{cap}} + K_L a_0)^2 + 4K_L V/m a_0}}{2V/m K_L} \quad (3)$$

## 3. Experimental

### 3.1. Materials

Millipore (Milford, MA, USA) Milli-Q-Plus water ( $18.2 \text{ M}\Omega \text{ cm}$ ), 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  $1000 \pm 10 \text{ mg l}^{-1}$  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  $1 \text{ mol l}^{-1}$   $\text{HNO}_3$  was purchased from Merck (#11355 Multi-Element-Standard IV). A stable  $10 \text{ mg l}^{-1}$  stock solution in a poly(propylene) flask was prepared by dilution with  $0.1 \text{ mol l}^{-1}$   $\text{HNO}_3$ . For ICP-MS analysis, working solutions were made fresh by further dilution of the stock solution with  $0.1 \text{ mol l}^{-1}$   $\text{HNO}_3$  to create calibration curves in the range  $0\text{--}500 \mu\text{g l}^{-1}$ . 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,  $121.9 \pm 3.8 \text{ mg kg}^{-1}$ ; Co,  $13.57 \pm 0.43 \text{ mg kg}^{-1}$ ; Ni,  $42.9 \pm 3.7 \text{ mg kg}^{-1}$ ; Zn,  $408 \pm 15 \text{ mg kg}^{-1}$ ; Cd,  $2.94 \pm 0.29 \text{ mg kg}^{-1}$ ; Ba,  $413 \pm 13 \text{ mg kg}^{-1}$ .

### 3.2. Extraction procedure

Varying amounts of soil sample ( $0.1\text{--}1.0 \text{ g dw}$ ) were accurately weighed into  $50 \text{ ml}$  “Falcon” poly(propylene) centrifuge tubes to give an as even as possible spacing in the

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