

## NOVEL APPROACHES FOR DETERMINATION OF THE CHEMICAL AVAILABILITY OF METAL(LOID)S IN SOIL BASED ON THE $K_D$ CONCEPT

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### Abstract

A theoretical framework is presented to introduce several novel approaches for deduction of the chemically available metal(loid) concentrations in soil. The framework is based on the  $K_D$  concept assuming a linear relationship between the extractable metal(loid) concentration in the solid phase and the metal(loid) concentration in the liquid phase. The approaches introduced include both exact approaches using (radioactive or stable) tracers and approximate approaches using more conventional extraction techniques.

**Key words:** sol, metal(loid)s, chemical availability, partitioning coefficient

### Introduction

The metal(loid) concentration in a soil is generally assessed by complete digestion or destructive analytical procedures. These procedures measure the total concentration of a metal(loid) in a soil; however, the concentration actually available to contribute to the exposure of organisms in soil is quite different. For reasons of clarity we distinguish between the parameters chemical availability and bioavailability.<sup>1,2</sup> The chemical availability of metal(loid)s in soils depends on adsorption-desorption processes, i.e. the dynamic exchange between the metal(loid) in soil particles and soil pore water under environmental conditions. This parameter is mostly estimated by extraction protocols<sup>3</sup> using extractants simulating the soil pore water composition and is governed by the partitioning coefficient,  $K_D$ .<sup>4</sup> The bioavailability describes the proportion of a metal(loid) in soil which is available for uptake by biota under environmental conditions and depends on the chemical availability, the physico-chemical form (speciation) of the metal(loid), transfer mechanism across membranes, etc. Once in the bioorganism a toxic effect may be expressed in the form of e.g. a growth deficiency.

In this communication we will focus on novel approaches to accurately determine the chemical availability of metal(loid)s in soil. Most extraction protocols assume

quantitative recovery of chemically available metal(loid)s for a given extractant; however, this is questionable in many instances.<sup>5</sup> Only when we are able to extrapolate to e.g. an infinite extractant volume, are quantitative recoveries found. Furthermore, it is important to note that the actual chemical availability is only given by the metal(loid) fraction directly related to the solution in the soil pores; extractants having a chemical composition dissimilar from the soil pore solution yield an estimate of the actual chemical availability. Some novel approaches to describe the (actual) chemical availability will be theoretically derived by adopting the  $K_D$  concept.

### Theory

In soil the total metal(loid) concentration may be expressed by

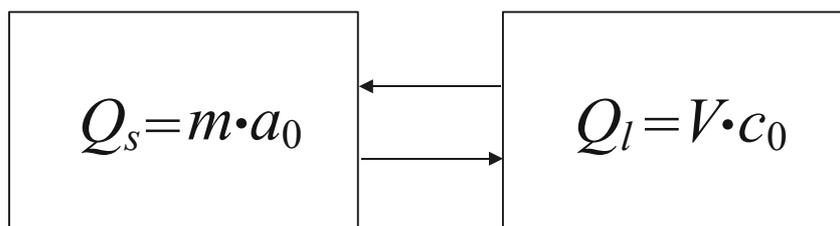
$$a_t = a_0 + a_{\infty} \quad (1)$$

where  $a_t$  is the total metal(loid) concentration,  $a_0$  the chemically available concentration and  $a_{\infty}$  the chemically unavailable concentration; all concentrations in mol kg<sup>-1</sup>. The chemically available concentration  $a_0$  is directly related to the metal(loid) concentration  $c_0$  (in mol L<sup>-1</sup>) in the soil pore solution via the *in situ*  $K_D$ :

$$K_D = \frac{a_0}{c_0} \quad (2)$$

with  $K_D$  in L kg<sup>-1</sup>. This is true when we assume a steady-state equilibrium and linear adsorption isotherm behaviour on one soil adsorption site only. The schematic diagram in Figure 1 reflects this situation in undisturbed soil systems and is given in the form of a 2-compartmental model.

In practical measurement situations it is unavoidable that we disturb the systems measured, but with well-chosen approaches the deviations may be minimized and a pseudo-equilibrated system may be assumed. An exact approach using tracers and more conventional approximate approaches using extraction techniques are discussed below for retrieval of the chemical availability. Where possible the approaches will be illustrated with appropriate examples.



**Figure 1.** Schematic representation of an environmental soil system.  $Q_s$  is the chemically available metal(loid) amount ( $=m \cdot a_0$ ) in the soil and  $Q_l$  the corresponding metal(loid) amount in the soil pore solution ( $=V \cdot c_0$ ), both in moles.  $m$  is the mass of the soil (in kg) and  $V$  is the volume of the soil pore solution (in L).

### Exact approach

An isotopic exchange approach<sup>6,7</sup> yields the closest resemblance to the actual chemical availability. At the sampling site representative soil samples are put into containers and a tracer (stable or radioactive) containing the labelled metal(loid) under study is added and thoroughly mixed. It is essential that the tracer has a “labelled/unlabelled” ratio which is so high that a negligible amount of the unlabelled metal(loid) is added with the tracer. After several weeks of equilibration, and, depending on the sample type, several wet/dry cycles, the soil samples are centrifuged/filtered to separate the phases. The label has distributed proportionally over the accessible fractions (the chemically unavailable metal(loid) is excluded) as follows:

$$\frac{q_s}{Q_s} = \frac{q_l}{Q_l} \quad (3)$$

with  $q_s$  and  $q_l$  the “label amounts” (in arbitrary units depending on the tracer properties) in solid and liquid, respectively, and  $Q_s$  and  $Q_l$  the related “unlabelled amounts” (in moles) in solid and liquid, respectively. Since  $Q_l/V$  and  $Q_s/M$  mimic  $c_0$  and  $a_0$ , respectively,  $K_D$  may be written as

$$K_D = \frac{a_0}{c_0} = \frac{Q_s \cdot V}{Q_l \cdot m} = \frac{q_s \cdot V}{q_l \cdot m} \quad (4)$$

thereby giving a quantitative measure of the *in situ*  $K_D$  via measurement of the “label amounts”  $q_s$  and  $q_l$ , knowing volume  $V$  (in L) and soil mass  $m$  (in kg). When  $c_0$  is measured as well, the chemical availability  $a_0$  may be derived:

$$a_0 = \frac{c_0 \cdot q_s \cdot V}{q_l \cdot m} \quad (5)$$

When e.g. 10000 counts (= count rate in cpm  $\times$  counting time in min) of a metal(loid) radiotracer are added to a system where  $m$  is 0.001 kg and  $V$  is 0.001 L with a measured  $c_0$  of 0.0002 mol L<sup>-1</sup>, and we measure a  $q_s$  of 8333 counts and a  $q_l$  of 1667 counts (after an appropriate equilibration time),  $K_D$  is 5 L kg<sup>-1</sup> and  $a_0$  is 0.001 mol kg<sup>-1</sup>.

### Approximate approaches

The *in situ*  $K_D$  and actual chemical availability  $a_0$  can only be properly estimated by isotopic exchange methods when applied very carefully as described above. Extraction approaches are approximate because the soil pore solution has to be replaced with an extractant which has to mimic the composition of the soil solution (pH,  $E_h$ , ionic strength, etc.) as closely as possible. Often aqueous extractants such as e.g. 0.01 mol L<sup>-1</sup> CaCl<sub>2</sub> are used for that purpose. Then, a fairly accurate estimate of the *in situ*  $K_D$  and  $a_0$  may be obtained under various experimental approaches. After appropriate equilibration and removal of the solid phase by centrifugation/filtration the metal(loid) concentration in the liquid phase is measured.

### Variable volume/mass ratio

To be able to extract the chemically available metal(loid) concentration from a soil, a high  $V/m$  ratio may be required, depending on the  $K_D$ . In that case the resulting metal(loid) concentrations in the extract may become undetectably low. To circumvent this problem the metal(loid) concentration in the extract may be measured as a function of the  $V/m$  ratio from which relationship we may deduce the chemically available metal(loid) concentration in the soil as described below.<sup>8</sup>

When an amount of soil ( $m$ ) containing an chemically available metal(loid) concentration ( $a_0$ ) is contacted with an extractant, after equilibration the following mass balance exists:

$$M \cdot a_0 = c_1 \cdot V + M \cdot a_1 \quad (6)$$

where  $a_1$  is the remaining metal(loid) concentration (in mol kg<sup>-1</sup>) in soil and  $c_1$  the extracted metal(loid) concentration in the extractant (in mol L<sup>-1</sup>). Substitution of the relationship  $a_1 = K_D \cdot c_1$  in Eq. (6) gives

$$\frac{1}{c_1} = \frac{1}{a_0} \cdot \frac{V}{m} + \frac{K_D}{a_0} \quad (7)$$

Thus, by measuring  $1/c_1$  as a function of the  $V/m$  ratio a linear relationship is obtained with a slope of  $1/a_0$  and an intercept of  $K_D/a_0$  (see Figure 2A). Initial successful experiences with this approach have been reported.<sup>9</sup>

### Repetitive extraction

Another approach to obtain insight into the chemically available concentration is by performing repetitive extractions. If we perform enough extractions, finally the chemically available fraction will be completely stripped from the soil. In order not to end up with an extremely high number of extraction steps, in the case of high  $K_D$  values, a relationship between the extraction step and the corresponding metal(loid) concentration in the extract may be established to derive the chemically available concentration by extrapolation. A similar mass balance as given in Eq. (6) is obeyed, but now for each individual extraction step  $p$ :

$$m \cdot a_{p-1} = c_p \cdot V + m \cdot a_p \quad (8)$$

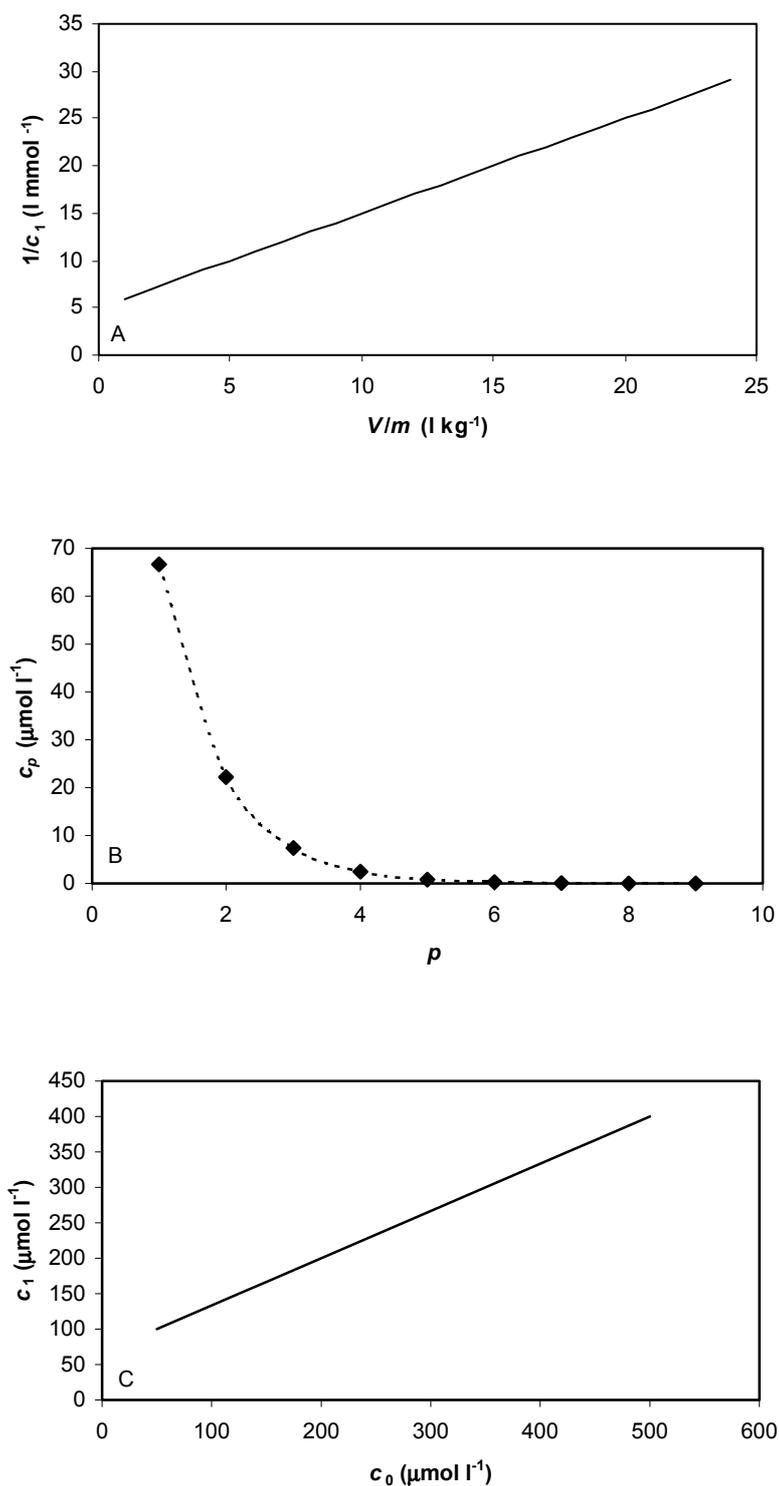
with  $p = 1, 2, 3, \dots$ . For each extraction step  $p$  the following relationship is valid:

$$K_D = \frac{a_p}{c_p} \quad (9)$$

Substitution of Eq. (9) in Eq. (8) for the individual extraction steps gives

$$c_p = \frac{a_0 \cdot K_D^{p-1}}{\left(\frac{V}{m} + K_D\right)^p} \quad (10)$$

Thus, by measuring  $c_p$  as a function of the repetitive extraction step  $p$ ,  $K_D$  and  $a_0$  may be retrieved with a non-linear curve fitting protocol (see the discrete graph in Figure 2B). Initial successful experiences with this approach have been reported.<sup>9</sup>



**Figure 2.** Graphical illustration of the different approaches to derive  $K_D$  and  $a_0$ : variable volume/mass ratio approach (A), repetitive extraction approach (B) and titration approach (C). For all examples  $K_D$  was set to  $5 \text{ L kg}^{-1}$  and  $a_0$  was set to  $0.001 \text{ mol kg}^{-1}$ ; for (B) and (C) the  $V/m$  ratio was set to 10.

### Titration

The method of choice for determination of  $K_D$  is by varying the concentration of the metal(loid) ( $c_0$ ) in the extractant during equilibration with a known amount of soil.<sup>4</sup> Only low  $c_0$  concentrations may be used so as not to jeopardize the linear adsorption isotherm concept; when adsorption sites become saturated the  $K_D$  concept no longer holds. However, this approach may also be applied for retrieval of the chemical availability assuming that the following mass balance exists under equilibrium conditions:

$$c_0 \cdot V + m \cdot a_0 = c_1 \cdot V + m \cdot a_1 \quad (11)$$

Substitution of the relationship  $a_1 = K_D \cdot c_1$  in Eq. (11) gives

$$c_1 = \frac{c_0 \cdot \frac{V}{m}}{\frac{V}{m} + K_D} + \frac{a_0}{\frac{V}{m} + K_D} \quad (12)$$

Thus, by measuring  $c_1$  as a function of  $c_0$  a linear relationship is obtained with a slope of  $(V/m)/(V/m+K_D)$  and an intercept of  $a_0/(V/m+K_D)$  (see Figure 2C).

### Conclusions

Some novel approaches are introduced to derive the chemical availability of metal(loid)s in soils. It is shown that application of the  $K_D$  concept allows for calculation of the chemically available fraction relying upon various experimental approaches. The exact approach using (radioactive or stable) tracers is the closest to estimating the actual chemical availability, whereas the approximate extraction approaches (variation of volume/mass ratios, repetitive extraction and titration) may deliver suitable results as well when the extractant composition matches the soil pore solution as closely as possible. Work is in progress to experimentally evaluate all approaches developed in this communication.

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### Povzetek

Članek obravnava teoretične osnove različnih eksperimentalnih pristopov za določitev okoljsko razpoložljivih koncentracij kovin in polkovin v tleh. Ideja je osnovana na konceptu  $K_D$ , ki predpostavlja linearno adsorpcijsko izotermo, to je linearno razmerje med razpoložljivo koncentracijo kovine/polkovine v trdni fazi in koncentracijo kovine/polkovine v tekoči fazi. Opisane experimentalne tehnike vključujejo tako ekzaktni pristop z uporabo radioaktivnih ali stabilnih sledilcev kot tudi neekzaktni pristop z uporabo konvencionalnih ekstrakcijskih tehnik.