

 Open access • Journal Article • DOI:10.1111/J.1365-2389.2009.01142.X

Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications — a review — [Source link](#)

Fien Degryse, Erik Smolders, David R. Parker

Institutions: University of California, Riverside

Published on: 01 Aug 2009 - European Journal of Soil Science (Blackwell Publishing Ltd)

Topics: Dilution, Dissolved organic carbon, Soil organic matter, Metal ions in aqueous solution and Equilibrium constant

Related papers:

- [Solid-Solution Partitioning of Metals in Contaminated Soils: Dependence on pH, Total Metal Burden, and Organic Matter](#)
- [The solid-solution partitioning of heavy metals \(Cu, Zn, Cd, Pb\) in upland soils of England and Wales](#)
- [Toxicity of trace metals in soil as affected by soil type and aging after contamination: using calibrated bioavailability models to set ecological soil standards.](#)
- [Solubility control of Cu, Zn, Cd and Pb in contaminated soils](#)
- [Sequential extraction procedure for the speciation of particulate trace metals](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/partitioning-of-metals-cd-co-cu-ni-pb-zn-in-soils-concepts-1jm04h2dad>

Degryse F., Smolders E. & Parker D.R. (2009) Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications – a review. *European Journal of Soil Science* 60: 590-612.

Author manuscript

The definitive version is available at www.blackwell-synergy.com.

Running title: Partitioning of metals in soils

Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications – a review

F. DEGRYSE^a, E. SMOLDERS^a & D. R. PARKER^b

^a*Division Soil and Water Management, K.U.Leuven, Kasteelpark Arenberg 20, 3001 Heverlee, Belgium, and* ^b*Department of Environmental Sciences, University of California, Riverside, CA 92521, USA*

Correspondence: F. Degryse. E-mail: fien.degryse@ees.kuleuven.be

Summary

Prediction of the fate of metals in soil requires knowledge on their solid–liquid partitioning. This paper reviews analytical methods and models for measuring or predicting the solid–liquid partitioning of metals in aerobic soils, and collates experimental data. The solid–liquid partitioning is often expressed with an empirical distribution coefficient or K_d , which gives the ratio of the concentration in the solid phase to that in the solution phase. The K_d value of a metal reflects the net effect of various reactions in the solid and liquid phases and varies orders of magnitude among soils. The K_d value can be derived from the solid–liquid distribution of added metal or that of the soil-borne metal. Only part of the solid-phase metal is rapidly exchangeable with the solution phase. Various methods have been developed to quantify this ‘labile’ phase, and K_d values based on this phase often correlate better with soil properties than K_d values based on total concentration, and are more appropriate to express metal ion buffering in solute transport models. The *in situ* soil solution is the preferred solution phase for K_d determinations. Alternatively, water or dilute-salt extracts can be used, but these may underestimate *in situ* concentrations of dissolved metal due to dilution of metal-complexing ligands such as dissolved organic matter. Multi-surface models and empirical models have been proposed to predict metal partitioning from soil properties. Though soil pH is the most important soil property determining the retention of the free metal ion, K_d values based on total dissolved metal in solution may show little pH dependence for metal ions that have strong affinity for dissolved organic matter. The K_d is used as an equilibrium constant in risk assessment models. However, slow dissociation of metal complexes in solution and slow exchange of metals between labile and non-labile pools in the solid phase may invalidate this equilibrium assumption.

Introduction

The solid–liquid distribution of trace metals largely affects their mobility and bioavailability in soils. Leaching of metals from soil to groundwater is related to the dissolved metal concentrations and the amount of metal on the solid phase buffering the metal in solution. The free metal ion is usually considered to be the major determinant of bioavailability. The importance of metal speciation for assessing availability and risk of metals is well recognized, and numerous data on solid–liquid partitioning of metals in soil have been published and compiled (Sauvé *et al.*, 2000a). The distribution coefficient (K_d) varies orders of magnitude among soils for the same metal. The lack of a consistent methodology and terminology complicates the comparison of data and may also confuse readers as to how the results can be interpreted and used.

This paper reviews the methods to measure the solid–liquid partitioning of metals and of models to predict this process in soils. The interpretation and possible use of solid–liquid distribution coefficients is discussed. A selective compilation of existing data on solid–liquid partitioning of trace metals in soil is given.

Metal partitioning in soils: concepts and quantification

There are numerous reactions that affect the speciation of metals in soil. Metal ions adsorb to organic matter, oxyhydroxides and clay minerals. Metals can also be precipitated as pure or mixed solids. In solution phase, metals are present as free ion, as complexes with inorganic or organic ligands, or associated with mineral colloids. The free ion in solution is generally the most reactive species in terms of reaction with the solid phase. Sorption reactions rather than precipitation reactions generally control the ion activity in the liquid phase. For instance, sorption curves of Cd, Co, Cu, Ni, Pb and Zn in four soils suggested that solubility of these metals was controlled by sorption and complexation processes,

rather than precipitation (Welp & Brümmer, 1999). Similarly, McBride *et al.* (1997) found indications that Cd, Cu, Pb and Zn solubility in moderately contaminated soils was controlled by sorption reactions. Although there is sufficient evidence for the presence of metals in pure or mixed solids in contaminated soils (Roberts *et al.*, 2002; Sarret *et al.*, 2004), these phases are unlikely to control the ion activity in soil solution, but are likely present as an inert – or only very slowly reactive – phase. For example, the free ion activity of a divalent cationic metal is usually much less affected by soil pH than the 100-fold change per unit pH that should be observed if carbonates, oxides or hydroxides would control the metal solubility (Salam & Helmke, 1998; Jopony & Young, 1994; Sauvé *et al.*, 1997b, 2000b). In most cases, the decrease in free ion activity, at constant total metal concentration, is between 3- and 15-fold per unit pH increase for divalent metals. This pH dependence can be successfully described assuming sorption of metals on variable charge surfaces (Barrow & Whelan, 1998; Weng *et al.*, 2001a; Tipping *et al.*, 2003).

The partitioning of metals in soil is often quantified by a distribution coefficient or K_d . The K_d expresses the distribution of an element between the solid phase and solution phase:

$$K_d = M_{\text{solid}}/[M], \quad (1)$$

where M_{solid} is the solid phase concentration ('quantity'), expressed on a soil-weight basis, and $[M]$ the (total or free ion) concentration in solution ('intensity'), expressed on a solution-volume basis. Thus, the K_d value has a unit of volume/mass, typically litre kg^{-1} . Depending on the methods used to characterize the solid and liquid phase, different K_d values may be obtained that express partitioning between different pools. Figure 1 illustrates different potential reactions mechanisms involved in the solid–liquid distribution and defines different K_d values. This terminology will be further used in this review. The most complex set of reactions is given in the first scheme. In solution, the metal is present as the free ion (M^{n+}) or as a complex (ML) with organic and/or inorganic ligands (Figure

1a). The free ion can adsorb onto the solid phase, on organic matter, (hydr)oxides or clay minerals. For purpose of illustration, we assume that only the free ion reacts with the solid phase, though some complexes may also adsorb on the soil surface (Bowers & Huang, 1986). Other ions, mainly H^+ , Ca^{2+} , and Mg^{2+} , but also other trace metal ions when present in elevated concentrations, compete for sorption on the surface sites. From the 'labile' pool on the solid phase, metals can be transferred to a non-labile pool ('fixed'). The transfer from labile to non-labile pool is a slow process (reaction time in order of years or longer), whereas the initial adsorption reaction occurs within minutes to hours. Figure 1a also considers an inert pool on the solid phase that does not exchange with other pools, which may be the case for metals present in parent minerals. Similarly, some metal in solution may be equally non-reactive, such as metals in colloidal minerals. The other schemes are progressively more simplified. In Figure 1b, it is assumed that there is rapid equilibrium between the free ion and the labile pool (double arrow). As will be discussed later, equilibrium assumptions are justified if the time scale of the process considered is slow compared with the time scale of the chemical reactions converting a metal species into another. The last, most simplified, scheme shows how the distribution coefficient in soil is usually determined: as the ratio of the 'total' concentration in the solid phase (for instance determined by hot acid extraction) and the total solution concentration (in an actual soil solution or in an extract). Table 1 gives a non-exhaustive overview of methods that have been used to measure the partitioning of metals in soils, and how the measured solid-liquid partitioning relates to the conceptual schemes in Figure 1.

Graphical representation of metal partitioning

Partitioning of metals is often presented by sorption isotherms or sorption curves, which relate the concentration on the solid phase, M_{solid} , to the (total or free ion) concentration in solution, $[M]$. If the sorption curve is linear, it can be described with a constant K_d value. In

reality, sorption curves are often non-linear, and are better described with a Freundlich equation:

$$M_{\text{solid}} = k \cdot [M]^n, \quad (2)$$

with k and n the Freundlich parameters. Extended, more generally applicable, Freundlich-type equations have been proposed that take into account the effect of competing cations such as H^+ and Ca^{2+} ions, or of the sorptive solid phase, namely organic C content or CEC (Temminghoff *et al.*, 1995; McBride *et al.*, 1997; Barrow & Whelan, 1998; Elzinga *et al.*, 1999). This results in equations that take following form when log-transformed:

$$\log M_{\text{solid}} = \log k + n \log[M] + a \text{ pH} + b \log(\text{OM}), \quad (3)$$

where a and b are regression coefficients and OM is the organic matter content of the soil.

Although somewhat simplistic, the constant K_d approach is frequently applied, since it is easily integrated into various models. Moreover, sorption curves are often nearly linear ($n \rightarrow 1$) in the lower concentration range, in which case the use of a constant K_d value is justified. However, at higher metal loadings the sorption curve levels off, as sorption sites become saturated, and the K_d progressively decreases (Hendrickson & Corey, 1981). The opposite effect, an increase in K_d with increasing load, may indicate that precipitation reactions rule the metal solubility, but is rarely observed at relevant metal concentrations in soils, except for Pb (Buchter *et al.*, 1989) or in calcareous soils. An increase in slope of the sorption curve is not necessarily related to precipitation, but has also been reported for elements as Cu (Sposito, 1984) or Hg (Barrow & Cox, 1992) in presence of small amounts of soluble organic ligands. Complexation with the ligand limits the metal adsorption at low metal concentrations, but has little effect at high metal concentrations when the soluble ligand is saturated with the metal. The dependence of K_d on metal load implies that the K_d will be misestimated if they are determined at metal loadings that are beyond

environmental relevant values, a situation that is most critical for metals present at low concentrations such as Cd (Christensen, 1989b).

Sorption is sometimes illustrated by sorption envelopes that show the percentage – or amount – of metal sorbed on the surface as a function of pH. The liquid/solid ratio (L/S; litre kg⁻¹) at which the sorption is measured should always be reported to convert these data to K_d values (Figure 2):

$$\%_{\text{sorbed}} = \frac{K_d}{K_d + L/S} \cdot 100 \quad \text{or} \quad K_d = \frac{L/S}{\frac{100}{\%_{\text{sorbed}}} - 1} \quad (4)$$

However, it is not possible to derive K_d values from graphically presented sorption envelopes with sufficient precision if the sorbed metal fraction is very small or large, as small differences in the fraction of sorbed metal correspond to large differences in the K_d value under these conditions. For example, the difference between 95% (corresponding to $K_d=L/S \times 20$) and 99.5% adsorbed metal (or $K_d=L/S \times 200$) appears minor on an sorption envelope but is a 10-fold difference in metal solubility. Cationic metals often have K_d values well above 200 litre kg⁻¹ corresponding to >95% metal adsorbed at a liquid/solid ratio of 10 litre kg⁻¹. Therefore, sorption data of cationic metals are better presented in terms of solution concentrations or K_d values than in terms of fraction sorbed.

Measurement of the metal partitioning

The K_d can either be determined from the distribution of added metal salt (also termed ‘adsorption K_d ’), or by measuring the distribution of soil-borne metals between the solid and liquid phase. Both approaches are discussed in this section.

Adsorption K_d

Adsorption K_d values measure the partitioning of freshly added metal salt within relatively small time-frames. Therefore, adsorption K_d values classify as K_d^{lab} in our scheme (Figure

1). An adsorption K_d , is usually measured by adding a metal salt to a soil suspended in water or a dilute salt. The suspension is equilibrated, generally for one day to about one week, and the solution concentration is measured after phase separation. The concentration on the solid phase is calculated as the difference between the amount added and the metal amount still present in solution. The background metal should be included in the solid phase concentration as the soil-borne metals are also involved in sorption (Welp & Brümmer, 1999). Failure to take into account the background will lead to an underestimate of the adsorbed metal concentration that buffers the metal concentration in the liquid phase. However, inclusion of the total background concentration in the solid phase concentration may also distort the sorption curve, since some portion of the native solid-phase pool may not be involved in short-term reactions. Only the 'labile' background concentration should be considered. Estimates of labile metal concentrations can be obtained by isotopic dilution, or by extraction with dilute acids or a complexing agent (see below).

The use of non-relevant high metal concentrations in sorption tests should be avoided, as this may result in a saturation of the binding sites and also in a decrease in pH and increase of ionic strength of the solution (Percival *et al.*, 1999; Stevens *et al.*, 2003). The addition of cationic metals at large doses strongly decreases the solution pH due to displacement of specifically bound protons from surfaces. The decrease in soil solution pH and increase in salinity in metal salt amended soils enhances the metal solubility. As a result, metal concentrations in soil solutions are often much larger, even up to 1000-fold, in metal salt spiked soils than in field-contaminated soils with corresponding total metal concentrations (Smolders *et al.*, 2004; Degryse *et al.*, 2007).

Distribution of soil-borne metals: the solid phase (quantity)

Total metal concentrations are usually measured by hot acid digestion. Part of the metals that are extracted by digestion may be present in non-labile form. For example, the element may be present as a pure or mixed solid, in crystal lattices, or in internal pores of sorbents (such as oxides) after intraparticle diffusion. This non-labile metal pool does not contribute to the immediate solid–solution distribution that occurs between the labile pool on the solid phase and the solution phase (See Figure 1b-c). Therefore, it is more appropriate to express the solid–liquid distribution with respect to the labile metal pool in soil (Welp & Brümmer, 1999; Degryse *et al.*, 2003), and to base transport calculations on this labile pool instead of the total metal content (Streck & Richter, 1997).

Of course, this binary classification in labile and non-labile solid phase pools is an oversimplification. However, a more sophisticated approach, such as a continuous distribution of sorption kinetics, would often be impractical to deal with. Moreover, isotopic dilution studies suggest that there is a reasonably distinguishable labile and non-labile pool, as the isotopically exchanged metal generally changes little with isotope equilibration time, beyond 2 days of equilibration (Young *et al.*, 2007). The labile pool may therefore be operationally defined as the amount of metal that equilibrates with the solution phase within a few days (usually between 1 and 7 days).

Isotopic dilution is conceptually the most attractive method to measure labile metals in soil, as it represents the fraction of metals that is in dynamic equilibrium with metals in the solution phase within a certain timeframe. The use of radio-isotopes is not suitable for routine measurements, hence the need for other methods to determine ‘labile metal’. Welp & Brümmer (1999) calculated the labile concentration from an adsorption experiment at low doses. The labile metal in the soil at background is calculated from the increase in solution concentration when adding a small amount of metal salt to a soil suspension, in

the assumption that the partitioning of the labile metal remains unaffected by the addition of the metal salt. This approach is essentially the same as calculating the labile background pool from the negative intercept of a sorption curve of added metal (Barrow, 2008). While conceptually sound, this method has practical drawbacks, since the solution composition may be altered by addition of the metal salt, in which case the assumption of equal partitioning of labile metal for the unamended and amended sample will be violated. Young *et al.* (2000) proposed extraction of the labile Cd pool with 1 M CaCl₂, as labile Cd is solubilized through complexation by Cl⁻ and competition for surface sites by Ca²⁺, while it is unlikely that fixed Cd (occluded in minerals, etc.) will be dissolved by CaCl₂. Extraction with 1 M CaCl₂ has indeed been found to give good estimates of isotopically exchangeable Cd (Young *et al.*, 2000; Gray *et al.*, 2003). A single extraction is methodologically attractive, but the selection of an extractant that completely and exclusively extracts the metal fraction that is in equilibrium with the solution phase is often impossible. Ahnstrom & Parker (2001) found that none of fractions of a sequential extraction procedure, nor any combinations of fractions, corresponded to the isotopically exchangeable concentration. Nakhone & Young (1993) measured *E* values (the isotopically exchangeable amount) and EDTA-extractable Cd for 33 soils (EDTA 0.05 M, L/S=3 litre kg⁻¹). These parameters correlated well ($r=0.98$), but EDTA-extractable amounts were (on average 63 %) larger than *E* values, indicating that the EDTA extract released non-exchangeable Cd. Nevertheless, EDTA, in appropriate concentrations, may be the best choice when trying to estimate the labile pool of several metals using a single extractant (Welp & Brümmer, 1999; Tongtavee *et al.*, 2005; Gäbler *et al.*, 2007). We suggest that EDTA extracts appear the most appropriate choice to approximate the labile metal content, when applied in a concentration of *c.* 50 to 100 mmol EDTA per kg soil, since smaller concentrations may not completely extract the labile amount and larger concentrations will possibly release considerable amounts of the non-labile metal pool

(Degryse *et al.*, 2004). In addition, dilute mineral acids (0.43 M HNO₃ or 2 M HNO₃) have been suggested to extract the labile metal pool (Tipping *et al.*, 2003; Weng *et al.*, 2001a). However, the Zn concentration extracted with 0.43 M or 2 M HNO₃ is often larger than the isotopically exchangeable Zn, especially in calcareous soils (Sinaj *et al.*, 2004; own unpublished data). We hypothesize that non-exchangeable Zn that is occluded in carbonate minerals is released because of the solubilization of these minerals by the acid extract. The HNO₃ extractable Zn was also much larger than the *E* value for some non-calcareous, heavily contaminated soils with a small fraction of labile Zn (Sinaj *et al.*, 2004; unpublished data). These soils were presumably contaminated with sparingly soluble Zn-containing minerals that solubilize under acid conditions.

Several studies have used isotope dilution to measure labile fractions of metals (mostly Cd and Zn) in field-collected soils. The %*E* values (labile versus total metal content) generally range between 40 and 80 % for Cd and between 10 and 60 % for Zn, though lower values are observed, for instance in mine spoil soils (Young *et al.*, 2000; Degryse *et al.*, 2004). Less information is available about the lability of other metals in soils. The available data suggest that Pb is often for the largest part in labile form, as %*E* values were larger than 40% even in field contaminated soils (Tongtavee *et al.*, 2005; Degryse *et al.*, 2007). For Cu, %*E* values ranged between 4 and 52% (average 20%) in uncontaminated or field-contaminated soils (Nolan *et al.*, 2004). In 16 naturally and anthropogenically Ni-rich soils, the *E* values (extrapolated to 3 months of isotope equilibration time) ranged between 0.1 and 50% of total Ni concentration in soil, with low labile fractions in soils with significant amounts of crystalline Fe-oxides (Massoura *et al.*, 2006). Gäbler *et al.* (2007) measured labile concentrations of several metals by stable isotope dilution on 115 unpolluted soil samples, and found following order of lability (median *E* value relative to median total content in brackets): Pb (33%) ≥ Cd (25%) > Cu (10%) > Zn (5%) ≥ Ni (4%).

Distribution of soil-borne metals: the liquid phase (intensity)

Solution isolation. Aqueous metal concentrations can either be measured in an *in situ* soil solution (pore water) or in a soil extract. Soil solutions are mostly obtained by centrifugation, or by using special samplers such as Rhizon samplers (Meijboom & van Noordwijk, 1992) or hollow-fibre samplers (Litaor, 1988). The composition of soil solutions isolated from high pH soils differs from the *in situ* soil solution; CO₂ degasses after separation of the solution from soil because of the higher CO₂ partial pressure in the soil atmosphere than in the ambient atmosphere (Suarez, 1986). This CO₂ degassing results in an increase in solution pH, thereby biasing solution metal speciation data obtained on these solutions. Isolation of soil solution is a laborious method, and it is difficult to obtain large volumes, which may be necessary for certain analyses. Soil extracts are often used instead, the assumption being that the solution concentration in the extract is a good estimator of that in *in situ* soil solution. The pH and composition of an extract is, however, different from that of the *in situ* soil solution. A dilute salt extract with similar ionic strength as the soil solution will probably give the best approximation to the soil solution composition. For many soils, the ionic strength of 0.01 M CaCl₂ solution approximates that of the soil solution. Data of de Groot *et al.* (1998), however, show that metal concentrations in a 0.01 M CaCl₂ extract (L/S=10 litre kg⁻¹) may differ considerably from those in the soil solution. For Cd and Zn, the differences between concentrations in the dilute salt extract and in soil solution were relatively small (mostly within a factor of 5). However, concentrations in the soil solution and in a CaCl₂ extract differed up to 30-fold for Ni and Pb, and up to 140-fold for Cu. Total concentrations in the soil solution were mostly larger than in a 0.01 M CaCl₂ extract for these metals, which was probably related to a lower degree of complexation with dissolved organic matter (DOM) in the extract than in the soil solution. Complexation is less significant in a CaCl₂ extract because DOM

concentrations are often lower as a result of dilution (Yin *et al.*, 2002), and coagulation and sorption of Ca-DOM complexes on the solid phase (Römken *et al.*, 1996).

The K_d measured in a soil suspension depends on the composition of the extract (Gerritse & Van Driel, 1984). Naidu *et al.* (1994) studied the effect of ionic strength, varied with NaNO_3 , on Cd adsorption by soils, and found that Cd adsorption decreased with increasing ionic strength in the normal pH range (at pH values above the zero point of charge). Temminghoff *et al.* (1995) studied the effects of ionic strength and Ca concentration on cadmium adsorption by a sandy soil. At the same pH, the cadmium adsorption was 60 to 80% smaller in a 0.01 M $\text{Ca}(\text{NO}_3)_2$ solution than in a NaNO_3 solution with same ionic strength, which was attributed to competition between Cd and Ca. Figure 3 also illustrates the effect of changing Ca concentration (at constant ionic strength) on metal concentrations in a soil extract ($\text{L/S} = 10 \text{ litre kg}^{-1}$) for a low-pH and a neutral-pH soil. In both soils, Zn concentrations increase with increasing Ca concentrations, suggesting Ca competition for sorption on the surface sites. The same effect was observed for Cd. Concentrations of Cu, however, decrease with increasing Ca concentrations, especially for the high-pH soil, which is likely due to decreased DOM concentrations at higher Ca concentrations (Römken *et al.*, 1996). In contrast with Cd and Zn, Cu is in most soil solution mainly present as complex with DOM. The Ca competition effect for sorption on the solid phase is cancelled out by the effect on Ca concentration on Cu complexation by DOM, and the Cu concentration in solution will therefore largely depend on the DOM concentration, as will be discussed in more detail later on. In the high-pH soil, Pb concentrations also decrease with increasing Ca concentration in solution, suggesting that most Pb is complexed with DOM. At low pH, however, Pb concentrations increase with increasing Ca concentrations in a manner similar to that observed with Cd and Zn, suggesting that complexation with DOM in solution is of minor importance at this pH and that the competition effect of Ca for sorption on the solid phase predominates.

While dilute salt extracts apparently fail to give a good prediction of total solution concentrations for ions that occur mainly as complexes, because of the large difference in ligand (DOM) concentration between *in situ* soil solution and an extract, they should provide a good estimate of the free ion concentration, provided that the pH and the Ca concentration of the extract corresponds to that of the soil solution (Sauvé *et al.*, 1997b).

In addition to the chemical composition, the liquid/solid ratio of an extract is likely to affect the metal solution concentration. Extracts with larger L/S ratios generally have smaller DOM concentrations, and therefore smaller solution concentrations (and larger K_d) of Cu (Ponizovsky *et al.*, 2006). Also when DOM is unlikely to affect the solid-liquid distribution of the metal, as is the case for Cd and Zn if $\text{pH} < 6.5$, the K_d tends to be larger at larger L/S ratio (Yin *et al.*, 2002), a phenomenon also known as the particle concentration effect (Di Toro *et al.*, 1986). In case of a linear sorption curve and fast desorption, no effect of L/S ratio on the K_d of these metals is expected. Non-linearity of the sorption curve may explain the observed effect; at larger solution to soil ratios, the concentration on the solid phase as well as the concentration in solution decreases. In case of a concave sorption curve ($n < 1$ in Equation 2), the ratio of solid phase to solution concentration (K_d) increases with decreasing metal concentrations. Alternatively, the effect of L/S ratio on the metal partitioning may be related to slow desorption of solid-phase metal, as more metal must be extracted into solution at large L/S ratio to maintain the same K_d value. In that case, the effect of L/S ratio should decrease as reaction time for desorption is prolonged, as was indeed observed by Filius *et al.* (1998).

In conclusion, a dilute salt extract is expected to give good estimates of the free ion concentration of metals in soil solution. Dilute salt extracts usually also provide reasonable estimates of the total soil solution concentration for Cd and Zn, but the concentrations of Cu, Pb and Ni in a dilute salt extract may differ by orders of magnitude from the soil solution concentration.

Solution concentrations. Solutions are usually analyzed for total dissolved metal concentrations by emission or absorption spectroscopy or by mass spectrometry. For some metals, especially Zn, background laboratory contamination can limit the quantification of metals at low concentrations (Ivahnenko *et al.*, 2001). While detection limits of 1 µg litre⁻¹ or lower may be achievable based on the sensitivity of the instrument, this limit may be considerably larger in practice because of laboratory contamination. This has practical consequences for the quantification of Zn in solutions of non-polluted calcareous soils, for which Zn concentrations in the soil solution are often in the µg litre⁻¹ level.

Solution phases are traditionally filtered (often on a 0.45 µm filter) before analysis. Metals in the filtered solution are operationally defined as dissolved, while the non-filterable metals are considered to be in particulate form. Both fractions encompass colloids, usually defined as particles with linear dimensions in the nm- to µm-range. Filtering may considerably reduce the metal concentrations in solutions where a large part of the metal is present as colloids that are partly retained on the filter. For instance, Jopony & Young (1994) found that up to 50% of Pb in an unfiltered supernatant of a soil suspension was retained on a 1-µm filter. Colloidal metals may play a role in metal transport. Denaix *et al.* (2001) found that about 50% of Pb in lysimeter-leachates was present in colloids (separated by ultracentrifugation), while Cd and Zn were mainly in dissolved form. The presence of colloidal metal species in solution complicates obtaining a representative soil solution, as the amount of colloidal species in an isolated soil solution or extract will most likely differ from that *in situ*. Therefore, the *in situ* collection of soil solutions with lysimeters is the preferred method to assess colloidal movement (Denaix *et al.*, 2001). Colloidal transport often shows an erratic pattern, since the stability of colloids depends, among other factors, on the ionic strength of the soil solution, which may show strong temporal and spatial variability. Because of its complicated nature, colloidal transport under field conditions is difficult, if not impossible, to predict *a priori*.

Solution speciation. Metals in soil solution may be present as a free ion or as a complex with inorganic (Cl^- , SO_4^{2-} , CO_3^{2-} , ...) or organic (DOM) ligands, or associated with mineral colloids. Models for metal leaching in soil do not strictly require information on the speciation of the metal in solution if the species conversion is fast (see further) since all metal species in solution can migrate. However, information on solution speciation is required for predicting bioavailability and, in general, for the interpretation of K_d values since the free metal ion is the most reactive species that interacts with solid phase. Depending on the element, the free ion may be the dominant species in the soil solution, or may account for only a minor fraction of the total metal in solution. For instance, Cd is usually mainly present as free ion in soil solution, whereas Cu is mainly complexed with DOM for soils with $\text{pH} > 5$ (Nolan *et al.*, 2003b).

Analytical techniques to measure or estimate 'free-ion' concentrations of metals in solution include Donnan dialysis, potentiometric techniques (ion selective electrodes, ISE), voltammetric techniques, resin exchange methods, and chromatographic techniques (Nolan *et al.*, 2003a). Many of these methods have been reviewed by Zhang & Young (2006). Dialysis techniques use a semipermeable membranes that allow only certain species to cross, based on size or charge. The Donnan dialysis uses a small-volume acceptor (receiving) solution to minimize errors resulting from perturbation of the chemical equilibrium in solutions with limited buffering capacity for trace elements. The technique has been applied to measure soil solution speciation by, among others, Helmke (2000), Nolan *et al.* (2003b) and Weng *et al.* (2001b). The latter authors used a soil column technique to allow for larger acceptor volumes. Determination of free-ion fractions of Pb and Cu with the Donnan technique becomes unreliable in uncontaminated or calcareous soils as concentrations in the acceptor solution may be below the detection limit. Addition of a complexing ligand with known complexation constants to the acceptor solution can possibly be used to overcome this problem, but this results in very long equilibration times.

A dynamic approach has been proposed where the acceptor solution is sampled before equilibrium is attained (Kalis *et al.*, 2006; Marang *et al.*, 2006). However, this approach cannot be applied when the transport is controlled by diffusion in solution, which may be the case when complexes dissociate relatively slowly. In that case, the rate of ion transport through the cation exchange membrane depends on the degree of complexation and the lability of the complexes in the donor solution, which is unknown in the solutions to be tested (Kalis *et al.*, 2007).

Resin exchange techniques to measure speciation are based on the equilibrium that is established between the free ion and metals bound on the resin. The free ion fraction is derived by comparing the metal partitioning in the test solution, after equilibration with the resin, to that in a reference solution with known metal speciation and a similar basal composition and therefore same partitioning of the free ion on the resin (Holm *et al.*, 1995). This approach assumes an excess ligand and a fast re-equilibration between free ion and complexes so that addition of the resin to the solution does not affect the free ion fraction. Very small free ion fractions, such as for Cu in most soil solutions, are hard to measure with this technique, since metal sorption on the resin is very limited in this case and the amount of metal sorbed, which is calculated from the difference between the initial and equilibrium concentration, cannot be accurately determined.

Measurements with ion selective electrodes (ISEs) in natural samples may be affected by fouling of the electrode by organic matter (Fish & Brassard, 1997). The use of ISEs in high Cl⁻ media is also not advisable, and other interferences may occur, resulting in an overestimation of the free-ion concentration (Westall *et al.*, 1979). During the last decade, much progress has been made in lowering the detection limits of ISEs (Pretsch, 2007). Most studies that have used ISEs to measure trace metal speciation in soil solutions are on Cu²⁺, for which detection limits of 10⁻¹³ M or even lower have been reported (Rachou *et al.*, 2007).

Voltammetric techniques determine the concentrations of labile metal species from a current measured in solution as a metal is taken up into or released from a mercury electrode. Analytical problems that may occur with voltammetric measurements are overlapping stripping peaks, adsorption of surface-active organic compounds on the Hg surface inhibiting the metal deposition, or formation of intermetallic compounds that are insoluble or that affect peak size and position. The most commonly used variants of voltammetry are anodic stripping voltammetry (ASV), and adsorptive cathodic stripping voltammetry (AdCSV). In the ASV technique, a current is measured when reoxidising the metals that have been accumulating in the mercury electrode. The ASV technique does not measure the concentration of the free ion only, but of the electro-labile species. As the free metal (M) becomes depleted near the electrode, labile metal complexes (ML) that are present will dissociate:



where K_{ML} is the stability constant for complex formation, and k_a and k_d or the first order rate constants for association and dissociation of the complex. The extent to which metal complexes contribute depends on the thickness of the diffusive boundary layer (DBL), and hence on the stirring conditions. Contribution of complexes is expected if the ‘reacto-diffusive length’ or reaction layer thickness, μ , is smaller than the diffusion layer thickness δ (Hudson, 1998):

$$\mu = \sqrt{\frac{D}{k_a \cdot [\text{L}_{\text{free}}]}} = \sqrt{\frac{D}{k_d} \cdot \frac{[\text{M}]}{[\text{ML}]}} < \delta. \quad (6)$$

Equation 6 shows that metal complexes are more likely to contribute as the complexes dissociate faster (k_d larger), the buffering is stronger ($[\text{ML}]/[\text{M}]$ larger), or the diffusion layer thickness δ is larger. In theory, it can be calculated which species, in terms of dissociation constant k_d , are measured with ASV but, to do so, the experimental conditions,

such as the stirring rate, must be well controlled and well known. It is usually assumed that ASV measures the free ion and inorganic and weak organic complexes of metals. Rotating disk electrodes, which allow varying the rotation rate, have been used to study kinetic processes. Depending on the rotation rate, δ ranges from about 5 μm (fast rotation) to 60 μm (slow rotation). This technique is capable of measuring dissociation constants (roughly) ranging between 10^{-1} and 10^2 s^{-1} (Shuman & Michael, 1978).

The ASV technique is not suitable for Co and Ni, which do not form an amalgam with the mercury electrode. For these elements, the AdCSV technique combined with ligand exchange has frequently been used (Lam *et al.*, 2002; Morfobos *et al.*, 2004). This technique is based on ligand exchange equilibria between a well characterized ligand that is added to the sample and the natural ligands. The selection of type and concentration of added ligand is essential, since the ‘detection window’ is rather small: no conclusion can be made about the metal speciation if the degree of complexation with the added ligand is too high (in which case nearly all metal is complexed with the added ligand) or too low (almost no metal complexed with the added ligand). The added ligand forms a complex with the metal of interest and adsorbs at the surface of the electrode, after which it is stripped to obtain a signal. The free ion fraction can be calculated from the measured concentration of the complex and the degree of complexation of the metal with the added ligand, which is estimated based on speciation calculations using known stability constants. The free ion concentration under ‘field conditions’ can then be calculated assuming that the ratio between free metal and metal bound to natural ligands is not changed by addition of the competing ligand. As pointed out by Xue & Sunda (1997), the fulfilment of this criterion cannot be taken for granted. Van Leeuwen & Town (2005) theoretically showed that metal speciation and stability constants of natural organic ligands derived with this technique may often have resulted from non-equilibrium conditions,

leading to an underestimation of the free ion concentration and overestimation of the stability constants.

While it is analytically a completely different technique, similar concepts can be used in the interpretation of DGT (diffusive gradients in thin films) results as for the ASV technique. The DGT device consists of a chelating resin gel layer, overlaid by a hydrogel layer that is in contact with the solution and through which ions can freely diffuse (Zhang & Davison, 1995). The DGT measured concentration, c_{DGT} , is determined by measuring the mass of metal accumulated on the resin after a certain deployment time, and is proportional to the diffusional flux of metal through the hydrogel layer. The DGT-timescale depends on the thickness of the diffusion layer, which is usually between 400 and 2000 μm (mostly 800 μm), and therefore, contribution of metal complexes will be more important than for ASV. The kinetic window, which defines the measurable species, can be varied by varying the thickness of the diffusion layer. A larger thickness of the diffusion layer allows for more dissociation – and hence larger contribution – of the complexes. Warnken *et al.* (2007) used this approach to obtain information on the dissociation rate of metal complexes *in situ* in a river.

Only few studies have compared different metal speciation techniques in environmental samples. Figura & McDuffie (1980) used several speciation techniques to differentiate metals on the basis of relative lability ranging from very labile (ASV), over moderately labile (retained on a Chelex column; 7 s contact time) and slowly labile (retained on Chelex resin during a 3 day batch equilibration), to inert. They found that Cd and Zn in natural waters and a sewage effluent were highly labile, while large parts of Cu and Pb were associated with the slowly labile fractions ($k_d \leq 10^{-3} \text{ s}^{-1}$). Minnich & McBride (1987) measured Cu activity in saturation extracts of sludge- and Cu-salt-treated soils. They found that Cu activities measured with ISE were one order of magnitude larger than those obtained with the Donnan system. Xue & Sunda (1997) measured free Cu^{2+}

concentrations in lake water, using ISE or a ligand exchange/CSV technique. The ISE gave erroneously high Cu^{2+} values at the lower Cu concentrations (total Cu below 30 nM). Luider *et al.* (2004) found that DGT-measured Cu in water with natural organic matter (NOM) of various sources was 2- to 10-fold larger than ISE-measured concentrations, indicating the contribution of labile complexes to DGT measurements. Turner *et al.* (1987) compared potentiometric (ISE) and voltammetric techniques to measure copper and lead complexation by fulvic acid. Estimated complexation capacities were smaller using the voltammetric technique than when using an ISE. This discrepancy was likely due to contribution of labile metal complexes in the voltammetric measurements. Ge *et al.* (2005) measured speciation on soil solutions of smelter polluted soils. They found reasonably good agreement between Cu^{2+} concentrations as measured with a resin exchange technique and ISE-measured concentrations, though the difference ranged up to an order of magnitude at the lower Cu^{2+} concentrations. Free cadmium measured with the resin exchange technique corresponded well with ASV-measured values, not surprisingly as most Cd was present as free ion. For Pb, the difference between these methods was larger, but still within a factor of 3 for most solutions, indicating that most Pb-complexes were not ASV-labile.

Overall, it can be concluded that measurement of metal speciation in soil solutions or waters often suffers from one or more shortcomings such as chemical interferences (ISE), detection limits at low concentrations (Donnan), and uncertain data interpretation as to exactly which species are measured (ASV, DGT). Figure 4 shows which kinetic fraction is theoretically measured with the different techniques. It also shows which fraction is expected to be important in environmental processes, and the (presumable) range of dissociation constants for metal complexes in soil solutions, as will be discussed further on. It follows from the above that methods used to measure metal partitioning and

speciation in soils and soil solutions are not only operationally defined but that they should also be selected to meet the objective of their application.

Slow reactions of metals in soil

The initial sorption reaction of metals in soil takes place within minutes or hours after metal addition in stirred soil suspension. This reaction is often followed by slower reactions that gradually decrease the metal availability in the months or years after metal addition. These slow reactions, which have also been termed ‘ageing’ or fixation reactions, should be taken into account to convert short-term data obtained with adsorption experiments to field contaminated soils. The number of studies where metal sorption in soils or soil components was studied over a long period of time is limited. Slow reactions can be demonstrated by a decrease in the solution concentration with time if all other factors influencing the solid–liquid distribution remain constant (Fischer *et al.*, 2007). It is however difficult to maintain critical factors such as pH or DOM concentrations constant over a longer period of time. Alternatively, changes in labile metal can be measured. Fixation reactions decrease the fraction of added metal that is in dynamic equilibrium with the solution phase. The labile fractions are less sensitive to changes in soil properties over time than solution concentrations and can, therefore, be used as an index of fixation in soil (Tye *et al.*, 2003; Buekers *et al.*, 2007). These long-term incubation studies with freshly metal-salt amended soil showed that the labile fraction of a metal added to soil decreases from initially 100% to <20–100% depending on metal and soil properties. After 850 days of ageing, the radio-labile fraction of added metal was, averaged over 28 soils, 57% for Cu, 59% for Zn, 59% for Ni and 72% for Cd (Buekers *et al.*, 2007). Fixation was most pronounced in soils with high pH or in soils with elevated concentrations of iron oxyhydroxides. Barrow (1998) used the “null point method” (Barrow, 1983) to assess

sorption kinetics of Cd, Zn, Co and Ni in a loamy sand soil (pH 5.6). The slow reactions were most pronounced for Zn and especially for Co and Ni, whereas Cd solubility changed little over time. These slow reactions are probably related to solid-state diffusion of metals into the interior of (hydr)oxides, though other mechanisms such as (surface) precipitation may also play a role, especially at high pH (Ma *et al.*, 2006b). A similar order for slow reactions on oxides has indeed been observed. Fischer *et al.* (2007) studied the reaction kinetics of sorption of 10 metals on goethite. Slow reactions were most pronounced for Co and least pronounced for Pb. In general, slow reactions were correlated with the ionic radius of the metals: the larger the radius, the slower the reaction.

There is little information whether fixation depends on the metal loading. Ma *et al.* (2006b) assessed aging of freshly added Cu^{2+} salt in 19 soils at two total Cu concentrations, during 2 years of outdoors incubation. They found that there was little difference in labile fraction between the two concentrations, suggesting that the total concentration (within relevant range) does not greatly affect the rate and extent of fixation. On the other hand, Buekers *et al.* (2008a) measured slow reactions of Co, Ni and Zn on four synthetic oxyhydroxides and found that slow reactions were more pronounced at small than at large metal concentrations for sorption of Ni and Zn on goethite.

The slow reactions of metals with (hydr)oxides are usually modeled with diffusion-based kinetics (Trivedi & Axe, 2000; Fischer *et al.*, 2007). Ma *et al.* (2006b) developed a semi-mechanistic model to describe slow reactions of Cu across soils, assuming that precipitation/nucleation occurs at high pH and slow diffusion at all pH values. Crout *et al.* (2006) described the slow reactions of Cd and Zn in soils with a reversible first-order model (cf. Figure 1), assuming a pH dependent labile fraction at equilibrium. Buekers *et al.* (2008b) used the same model to describe slow reactions of Cd, Cu, Ni and Zn in soils (Figure 5). It should be realized that the slow reactions in soil are not first-order reactions, but most likely a combination of intraparticle diffusion, (surface) precipitation, co-

precipitation and possible other mechanisms. Nevertheless, reversible first-order kinetics describe the decrease in labile metal fraction with ageing time reasonably well.

The fact that the slow reactions of metals in soil can be described with reversible kinetics, suggests that metal ‘fixation’ is a reversible process. The model predicts that ‘fixed’ metals will be released slowly under conditions of continuous metal removal (for instance, prolonged leaching with clean water). Moreover, fixation in high pH soils may (partly) be caused by (co)precipitation of metals in carbonates or other minerals, in which case the metals will be released if the soil subsequently acidifies (Hamon *et al.*, 2002).

Prediction of the solid–liquid partitioning of metals in soils

Different models for predicting K_d values are in use, which can be divided in two groups: multisurface models that describe the interactions of metals with different soil constituents (organic matter, oxides, clay) and empirical regression models.

Multisurface models

Multisurface models, also termed assemblage models, consider the soil as a set of independent reactive surfaces, and combine several models to describe sorption onto organic matter (both solid and dissolved), (hydr)oxides, and clay. The speciation calculations are performed with geochemical programs, such as ECOSAT (Weng *et al.*, 2001a), WHAM (Tipping *et al.*, 2003), or ORCHESTRA (Schröder *et al.*, 2005). A surface complexation model is used to describe sorption on (hydr)oxides, while sorption on clay minerals is usually modeled with an ion exchange approach. Sorption on organic matter is modeled with the NIC(C)A-Donnan model (Kinniburgh *et al.*, 1999) in ECOSAT and ORCHESTRA, or with Model VI (Tipping, 1998) in WHAM. Though the NICA model and model VI are mathematically quite different, the models are alike in that they assume

two types of sites (typically associated with carboxylic and phenolic groups) on which protons and metals compete for binding (specific sorption) together with non-specific electrostatic sorption (Tipping, 1998). These models are conceptually attractive, but they require extensive input information, often not available in more routine research. Moreover, assumptions are required to define the reactivity of surfaces compared with model constituents. These include assumptions about the fraction active organic matter and the surface area of oxyhydroxides.

These mechanistic models can be used to describe metal partitioning between soil and solution or to calculate the solution speciation only (Weng *et al.*, 2002; Nolan *et al.*, 2003b). Figure 6 depicts measured free-ion fractions of metals in soil solution, and free-ion fractions predicted by WHAM (Model VI) for a soil solution with a generic composition. This model predicts that the affinity of DOM for metals increases in the order: $\text{Co} < \text{Ni} < \text{Cd} \sim \text{Zn} \ll \text{Pb} \sim \text{Cu}$. Complexation of Co and Ni in soil solution is expected to be small at $\text{pH} < 7$. However, the description of complexation of DOM with Co and Ni in WHAM is based on sparse data, and results from Sanders (1983) suggest that Co in soil solution may be more complexed with DOM than predicted by WHAM. The available data indicate that complexation of Cu and Pb with DOM, though considerable, is less pronounced than predicted by WHAM (Nolan *et al.*, 2003b; Sauvé *et al.*, 1997a). These deviations between predicted and observed values for Cu and Pb may also be due to analytical problems in determining the free ion fractions of these ions. Measurement of free-ion concentrations of Cu and Pb in soil solutions is often problematic since the free-ion concentrations are mostly near or below the detection limit of the Donnan dialysis technique (Nolan *et al.*, 2003b), and ASV may overestimate free ion fractions of Pb if labile Pb-DOM complexes are present (Sauvé *et al.*, 1997a).

Only a few studies have compared observed solid–liquid distribution of metals in soils with predictions of mechanistic models (Weng *et al.*, 2002; Tipping *et al.*, 2003; Schröder

et al., 2005; MacDonald & Hendershot, 2006). It is often found that the observed and predicted solid–solution distribution differ considerably without parameter adjustment. Solution concentrations of Pb are often overestimated (Weng *et al.*, 2002; Schröder *et al.*, 2005). Although these models predict that Pb binds more strongly on oxides than the other metals, they still predict that a large part of Pb is associated with organic matter, especially at low pH. However, the K_d of Pb is usually much larger than the solid–liquid distribution of organic matter ($[SOC]/[DOC] \sim 100\text{--}2000$ litre kg^{-1} in most soils). Unless the solid organic matter has much larger affinity for Pb than DOM, which seems unlikely, this means that organic matter is not the main factor in controlling Pb solubility. It has been suggested that mineral phases (such as chloropyromorphite, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) control Pb solubility, but spectroscopic (Morin *et al.*, 1999) and isotopic dilution studies (Tongtavee *et al.*, 2005; Degryse *et al.*, 2007) indicate the importance of sorption processes in soils unamended with phosphate, suggesting that sorption of Pb on hydrous oxides is particularly underestimated by these models.

Until more validation for real soil systems is carried out, *a priori* prediction of metal partitioning with multisurface models seems still unreliable at present. These models are preferentially validated on datasets for which free-ion concentrations are also known, since this allows evaluating the partitioning of the free ion between solution and solid phase and the complexation in solution separately. However, obtaining reliable measurements of free-ion concentrations remains an analytical challenge, especially in high pH soils.

Regression models

Alternatively, the solution concentrations of metals in soil can be predicted with regression models that relate the sorption of an element to soil properties. Most of these models take the form of a multivariate, linear relation between $\log K_d$ and soil properties (Anderson &

Christensen, 1988; Sauvé *et al.*, 2000a), or a Freundlich-type equation (Equation 3) that takes into account the effect of pH, organic C content and sometimes ionic strength (IS) or Ca concentration. Such regression models can be developed for K_d values that are based on free ion concentration or on total solution concentration. The partitioning of the free ion can be determined either by measuring the free ion concentration (Sauvé *et al.*, 1997b; Nolan *et al.*, 2003b) or by predicting free ion concentrations from total solution concentration and soil solution composition (Tye *et al.*, 2004; Tipping *et al.*, 2003). Models that describe the K_d^{free} , which gives the partitioning of the free ion, offer the advantage that they describe a single mechanism, but they rely on an accurate measurement of prediction of the free ion concentration. Moreover, when the objective is to predict metal transport, the total solution concentration, and not the free ion concentration, must be known. In that case, if the free ion concentration is predicted from the total metal concentration in soil and the estimated partitioning of the free ion (K_d^{free}), additional modeling has to be carried out to estimate the total solution concentration from the free ion concentration and the soil solution composition (see, for instance, Tye *et al.*, 2004). Regression equations that predict K_d values based on total solution concentration, allow a direct estimate of the total concentration, but the model may fail to describe the partitioning adequately, since it does not describe a single mechanism, but both the sorption of the free ion and the complexation of the free ion in solution (Figure 1). In practice, both approaches (total solution concentration of free ion concentration based) will give similar results for elements such as Cd and Zn that are usually for a large part as free ion in solution, although the pH slope will usually be smaller when regressing K_d than for K_d^{free} , since the complexation increases with increasing pH (Figure 6). For Cu, on the other hand, regression equations for K_d or K_d^{free} strongly differ. The free ion based models usually also have much larger coefficients of determination than those based on total solution concentration (see Table 2 and discussion below).

The statistical models relating K_d to soil properties, calibrated to a set of observations, are obviously empirical but their mathematical form can be explained by soil chemical reactions. For example, the most simplified regression models predict that $\log K_d$ increases linearly with pH (Anderson & Christensen, 1988; see also Table 2). Such relationship can be explained by sorption reactions assuming that (i) the binding site capacity is well above the amount of metal sorbed, (ii) the binding site capacity is similar among all soils and (iii) protons and metals compete for sorption on the same binding sites and have a quasi-gaussian (Sips) distribution of their binding constants (Rusch *et al.*, 1997). Clearly, the assumption of a constant binding site capacity (implying a similar concentration of organic matter and oxyhydroxides) among soils is usually not valid, but a large part of the variation in K_d values can be explained nevertheless with such a simplified model, because the variation of binding site capacity is much smaller than the effect provoked by differences in pH. A change in pH with 2 units generally affects the K_d of Cd, Zn and Ni more than 20-fold whereas a 20-fold variation in binding site capacity between topsoils is unlikely.

From a practical point of view, it is preferable that only routinely measured soil properties (pH, %OC) are included in the model. When using a regression model, the soil properties should be measured with the same methods, or methods that give similar results, as those used in the original development of the model. For instance, if the regression model is based on pH measured in 0.01 M CaCl₂, different results will be obtained if pH measured in 1 M KCl or in water is used for the K_d prediction, since pH values may differ more than 1 unit depending on the method used (de Groot *et al.*, 1998). Clearly, any regression model should not be extrapolated beyond the range of soil properties with which it was originally developed. An advantage of regression models over the multisurface models is that the former models are usually calibrated on a larger number of soils.

In Table 2, regression equations are reported that were derived from pore water based K_d values. These regression equations allow estimating porewater concentrations from the total (or labile) metal content in soil and the predicted K_d (or K_d^{lab}) value:

$$[M]_{\text{pred}} = M_{\text{tot}} / K_{d,\text{pred}}, \quad (7)$$

$$[M]_{\text{pred}} = M_{\text{labile}} / K_{d,\text{pred}}^{\text{lab}}. \quad (8)$$

Ideally, solutions concentrations should be estimated from the labile metal pool, using regression equations or models that predict the partitioning between labile metal and metal in solution (Equation 8). Often, only the total metal concentration is known without any information about the labile metal fraction, which adds an additional source of error. However, labile metal fractions ($M_{\text{labile}}/M_{\text{tot}}$) generally only vary 10-fold (Degryse *et al.*, 2003), whereas the K_d^{lab} may vary nearly 1000-fold between soils. As a result, differences in sorption (related to differences in pH, organic C content, etc.) between soils usually explain most of the variation in metal solubility between soils. This explains why the improvement in prediction of metal solubility when based on labile metal in soil (Equation 8) instead of total metal (Equation 7) is often small (Tye *et al.*, 2003; Degryse *et al.*, 2003). Moreover, the labile metal fraction in soil may be pH dependent, and the variation in labile fraction between soils may partly be accounted for by the pH term in the K_d equation (Tye *et al.*, 2003).

For Cd, the regression equation that relates *in situ* K_d values to soil properties, predicts similar values as regression equations reported in literature derived from adsorption measurements in dilute salt extracts (Anderson & Christensen, 1988). For Zn and Ni, however, the proposed equations tend to predict higher K_d values than regression equations based on adsorption K_d values (Figure 7). These metals are often for a large part in non-labile form (Buekers *et al.*, 2007). As a result, adsorption K_d values in salt extracts, which give the partitioning of labile metal, are smaller than K_d values that express the partitioning of the native metal, that was already present in the soil. When the partitioning of the native

Zn is based on (native) labile Zn as measured by isotopic dilution, the obtained regression equation is in better agreement with adsorption K_d based regression equations (Figure 7a). Similarly, the K_d values of Ni in NiCl₂ amended soils agree much better with the regression equation of Anderson & Christensen (1988) than those in unamended soils (Figure 7b; data of Oorts *et al.*, 2006). The Ni dose in the amended soils was relatively small (between 20 and 86 mg Ni kg⁻¹) and pore water composition (Ca, pH) was in most cases unaffected by the metal amendment. The larger K_d values in the unamended soils therefore indicate that a considerable fraction of the background metal is in non-labile form.

While the sorption of the free Cu²⁺ ion on the solid phase is strongly related to pH (Table 2; Yin *et al.*, 2002), the relationship between pH and log K_d is often not very pronounced for Cu (Sauvé *et al.*, 2000a; Figure 8a). This can be explained by the strong complexation of Cu with dissolved organic matter. An increase in pH strongly increases the binding of free Cu²⁺ on the solid phase, but often has only a minor effect on the total solution concentration, because the pH increase also enhances complexation of Cu²⁺ with dissolved organic matter (Yin *et al.*, 2002). Assuming that Cu binds solely on organic matter and that there is no inorganic complexation in solution, the K_d of Cu can be calculated as follows:

$$K_d = \frac{K_d^{\text{SOC}} \cdot [\text{SOC}]}{1 + K_d^{\text{DOC}} \cdot [\text{DOC}]}, \quad (9)$$

where [SOC] (kg OC per kg soil) and [DOC] (kg OC per liter) are the concentrations of solid and dissolved organic C respectively, and K_d^{SOC} and K_d^{DOC} are the distribution coefficients (in litre per kg OC) of free Cu on the organic C. If the solid and dissolved organic C have the same affinity for Cu and if the free ion fraction is much smaller than 1 (or $K_d^{\text{DOC}} \times [\text{DOC}] \gg 1$), which is usually the case in soils with pH >5, Equation 9 can be reduced to:

$$K_d \approx \frac{[\text{SOC}]}{[\text{DOC}]}$$

Figure 8b indeed shows a significant ($P < 0.0001$) positive correlation between K_d values of Cu and the partitioning of organic C in soils with $\text{pH} > 5$, if the data of Nolan *et al.* (2003b) are excluded. The R^2 was 0.53, compared with an R^2 of 0.17 for $\log K_d$ versus pH for the same soils. Clearly, the partitioning of Cu in soils with moderate to high pH is related to the partitioning of organic C, as was previously demonstrated by Temminghoff *et al.* (1997). In the study of Nolan *et al.* (2003b), the K_d of organic C was consistently smaller (in general about an order of magnitude) than the K_d of Cu. The DOC concentrations in the study were very large, likely because the soils were dried at 40°C , and only incubated (at 25°C) for 16 hours after rewetting. Drying-rewetting is known to result in a flush of DOC, most of which is decomposed – in uncontaminated soils – after about 1 month of incubation (Merckx *et al.*, 2001). This DOC released during drying-rewetting has very low metal affinity (Amery *et al.*, 2007), explaining why Cu is associated more strongly with solid organic matter than with DOM in recently rewetted soils (Figure 8b). Speciation programs do not consider this variation in DOM quality, but use default parameters to predict complexation. Amery *et al.* (2008) showed that the prediction of Cu complexation with DOM could be improved by taking into account the variable quality of DOM, using the specific UV absorbance as an indicator.

Use of K_d values

The K_d concept is strictly an equilibrium concept, so that equilibrium is implicitly assumed when calculations are performed with K_d values. The assumption of equilibrium can be justified if appropriate choices are made for the parameters required. For instance, some reactions, such as the release of metals incorporated in crystal lattices, may be slow enough to ignore on a relevant time scale. Other reactions are fast compared with the process of

interest, and equilibrium may be assumed. This is illustrated for two relevant environmental processes: metal transport and bioavailability.

Metal transport (leaching)

Metals adsorb on the solid phase and therefore migrate more slowly through the soil than the water. The retardation coefficient R gives the ratio of the water velocity relative to the solute velocity for a homogenous medium in case of linear sorption and is related to the K_d :

$$R = 1 + \frac{\rho}{\theta} \cdot K_d, \quad (10)$$

where ρ is the soil bulk density, and θ is the volumetric water content. In a soil profile, the soil properties vary with depth. The sorption parameters (K_d or Freundlich parameters in case of non-linear sorption) for each depth increment are then estimated from an equation that relates the sorption parameters to soil properties such as pH and organic matter content (Streck & Richter, 1997). Solute transport in soils is often modeled with the convection-dispersion equation, assuming local equilibrium. Several studies have shown that this local equilibrium assumption does not always hold for metal transport. However, many of the studies where non-equilibrium in metal transport was observed, were conducted in columns at large pore-water velocities (50 cm day⁻¹ or more), and may not be representative for the field situation. Streck & Richter (1997), Seuntjens (2002) and Degryse & Smolders (2006) found that Cd transport at field scale could be successfully modelled based on the local equilibrium assumption, if spatial variability of sorption was taken into account. However, soils in these studies were all sandy soils, and it cannot be concluded that the local equilibrium assumption is always valid for modelling metal transport at field scale. Preferential flow is likely to occur in more structured soil, and could affect metal leaching. Moreover, metals as Cu and Pb may be present for a large part as metal complex or under colloidal form. Citeau *et al.* (2003) found that 75% of Pb in the

solution (collected by zero-tension lysimeters) of two Luvisols was in colloidal form, and that a substantial fraction was present as stable or slowly dissociating metal complex, while Cd and Zn were mainly present as free ion or labile complexes. As discussed below, the presence of slowly dissociating complexes may lead to more rapid leaching of metals.

Kinetic limitations in desorption from the solid phase. Metal transport can be modeled assuming that sorption is in equilibrium if the rate of the sorption reaction is large compared with the advection rate. A theoretical analysis has been conducted by Valocchi (1985) and Bahr & Rubin (1987), and criteria were derived to assess whether local equilibrium may be assumed. In an attempt to simplify and synthesize the findings of these studies, we propose as rule of thumb that the breakthrough curve can be reasonably well described with the equilibrium assumption if following condition holds:

$$\frac{v \cdot T_c}{\lambda} < 0.1, \quad (11)$$

where T_c is the response time of the reaction (the time to reach 63% of the equilibrium value) and λ is the dispersivity (normal range: 0.5–10 cm). Thus, if v is $\sim 1 \text{ m year}^{-1}$ (normal value for field situation in humid temperate regions) and λ is 1 cm, equilibrium can be assumed if the response time of the reaction is smaller than 9 hours. The response time of the fast sorption reaction between solution and labile metal pool (described with k_{ads} and k_{des} in Figure 1) is probably a few minutes (Ernstberger *et al.*, 2002), and can therefore be modeled as an equilibrium reaction unless very large pore water velocities are employed (as often the case in column experiments). The response time for the transfer from labile to non-labile pool is much larger; Crout *et al.* (2006) estimated a response time of *c.* 200 days for Zn. Figure 9 illustrates the effect of chemical non-equilibrium on leaching of metals from a soil profile. Figure 9a shows a theoretical breakthrough curve if it is assumed that all metal is in equilibrium with the solution phase. In Figure 9c, the presence of a non-labile pool is taken into account, and it is assumed that this pool is

totally inert. Figure 9b shows the intermediate case in which it is assumed that metals of the non-labile pool are not in immediate equilibrium with the solution, but are slowly released (according to the concept in Figure 1a), causing tailing in the breakthrough curve. Little is known about the release rate of metals from non-labile pools, especially in field contaminated soils where metals may originate from different sources, some of which may act as labile metal, while other may be quasi-inert. Without any information about the kinetics of desorption, the best estimate of metal transport can probably be made assuming that the labile metal pool, which may be estimated by isotope dilution (Degryse & Smolders, 2006) or EDTA extraction (Streck & Richter, 1997), and not the total metal pool is in equilibrium with the solution.

Kinetic limitations in dissociation of complexes. Metals in soil solution are partly present as complexes with inorganic or organic ligands. The rate of dissociation of these complexes will affect the metal transport in soil. Only few experimental studies have assessed the importance of dissociation kinetics of complexes in metal transport, and most of these studies dealt with colloidal complexes of actinides and lanthanides (Artinger *et al.*, 1998; van de Weerd & Leijnse, 1997), known to form slowly dissociating complexes with humic substances. Artinger *et al.* (1998) found that transport of ^{241}Am in column experiments with quartz sand was enhanced in the presence of humic substances, and this enhancement increased with increasing flow rate, which was attributed to the slow dissociation of the complexes. Schmitt *et al.* (2003) observed fast breakthrough of a fraction of Al, Fe and Pb (but not of Zn) complexed by natural organic matter in column experiments with quartz sand, which could be related to the dissociation rate of the complexes.

Slow dissociation of complexes results in enhanced transport (faster breakthrough than expected based on equilibrium calculations) if the rate of dissociation of the metal

complexes is slow compared to the pore water velocity. We performed numerical transport calculations for a step input of metal taking into account advection, dispersion, (linear) immediate sorption on the solid phase and kinetic complex formation in solution described with first order kinetics (cf. Equation 5). The theoretical breakthrough is shown for a metal for which the K_d^{free} is 100 litre kg^{-1} and half of the metal in soil solution is present as free ion. The calculations were made for a pore water velocity of 0.3 cm day^{-1} , relevant for the field situation. It was assumed that the concentration of the ligand is constant in time and space. The model calculations show that the local equilibrium assumption (for the reaction between complex and free ion) is valid if the dissociation rate constant, k_d , is larger than 10^{-5} s^{-1} (Figure 10a). On the other hand, slowly dissociating complexes ($k_d < 10^{-8} \text{ s}^{-1}$) leach through the soil without retardation (Figure 10c), unless the complex itself is sorbed on the solid phase. In the intermediate case where complexes dissociate, but not fast enough to attain equilibrium, no immediate breakthrough occurs, but the predicted breakthrough is earlier than expected from equilibrium assumptions (Figure 10b).

Data for the dissociation kinetics of divalent metals in soil solutions are scarce, but the available information (Citeau *et al.*, 2003; Degryse & Smolders, 2005) suggests that a fraction of Cu, Pb and, to a lesser extent, Ni complexes in solution may dissociate so slowly that the local equilibrium assumption is violated, especially at high flow rates (Figure 4). Ma *et al.* (2006a) found that part of Cu in 0.2- μm filtered soil water extracts was non-isotopically exchangeable, also indicating that part of Cu in soil solution is inert or only very slowly reacting. Non-equilibrium in the dissociation of the complexes may certainly affect transport of these metals in column experiments where large water fluxes are often applied to obtain results within a short timeframe. For instance, when the porewater velocity is 30 cm day^{-1} , which is not exceptionally high for column experiments, kinetic constraints in dissociation of the complexes will already enhance the metal transport if the dissociation rate constant is in the order of 10^{-3} s^{-1} or smaller. For Cd and

Zn, which are usually mainly present as free ion or as labile complexes in soil solutions, dissociation of complexes is not expected to be a rate determining step in metal transport, unless the metals were added to the soil as stable complexes, which may be the case for solid waste leachates (Christensen, 1989a).

In summary, the K_d^{lab} , the ratio of labile metal concentration (measured by isotopic dilution or extraction with EDTA) to total solution concentration, seems the best choice to describe the metal partitioning for transport calculations. Most metal complexes probably dissociate fast enough to model retardation with the equilibrium approach (using total solution concentration), while release from the 'non-labile' metal pool on the solid phase is likely often slow enough to ignore on relevant time-scales. However, slow dissociation of metal complexes and the slow release of non-labile metals potentially may increase metal mobility in soil. The relevance at field scale of these non-equilibrium processes is still unknown. The few examples of field validation confirm that the K_d^{lab} – or a similar Freundlich equation – is indeed the preferred input parameter to describe metal sorption in transport calculations (Streck & Richter, 1997; Degryse & Smolders, 2006). These model validations are based on retrospective modeling and depend heavily on the history of metal addition to soil which is never accurately known, and therefore, the models can only be validated to a limited extent. More field research is needed to validate the existing concepts.

Bioavailability

To predict metal uptake by plants, it is essential to know which metal species are taken up. If uptake can be well modeled, it should also be possible to predict phytotoxicity, since toxic effects usually occur at a critical tissue concentration (Beckett & Davis, 1977). The free-ion activity model (FIAM) postulates that the uptake of metal by an organism is related to the free-ion concentration of the metal in the surrounding solution (Parker *et al.*,

1995). Over a range of pH values, the free ion is not a constant predictor of bioavailability. The gill surface interaction model (Pagenkopf, 1983) and the (more generalized) biotic ligand model (BLM) do not only take into account the metal-ligand complexation in solution, but also the competitive binding of cations (base cations and protons) at the uptake sites. The same concept can also be used to predict metal toxicity in soil, using a terrestrial BLM. It has indeed been found that both uptake (Hough *et al.*, 2005) and toxicity of the free metal ion in solution (Oorts *et al.*, 2006) increase with increasing soil pH, indicating competition between protons and free metal ions for uptake from solution. Using these concepts, the bioavailability of metals in soil can be estimated from the labile (reactive) metal concentration, soil properties (pH, %OC) that allow an estimate of the partitioning of the free ion between solution and solid phase ($K_d^{\text{lab/free}}$), and the concentration of 'protecting' cations (Lofts *et al.*, 2004).

Several exceptions to the FIAM have been reported, especially for higher plants for which greater uptake has often been observed when metal complexes were present in solution as compared to ligand-free solutions with a same free-ion activity (Bell *et al.*, 1991). It has been speculated that these deviations from the FIAM are due to uptake of intact complexes, or are related to buffering of the free ion around the uptake site when metal transport to the uptake sites is limiting (Parker *et al.*, 2001). In the latter case, the contribution of complexes to metal uptake is expected to depend on the dissociation rate of the complexes, as was indeed found for Cd uptake by spinach in hydroponics (Degryse *et al.*, 2006). Diffusive limitations in metal uptake by plants explain why plant concentrations correlate better with DGT-measured concentrations than with total solution or free ion concentrations (Zhang *et al.*, 2001). In summary, the bioavailability theoretically depends on the activities of the free metal ion and of competing ions if there are no transport limitations. In that case, bioavailability in soil should be predicted based on a free ion based model (Lofts *et al.*, 2004) In case of transport-limited uptake, however, labile

complexes, that may be picked up as 'labile metal' depending on the solution speciation technique used, may also contribute (Figure 4).

Conclusions

It is well established that the solid–liquid partitioning of metals in soil is a critical parameter to predict the fate of metals in soil, namely their mobility and availability. The solid–liquid distribution coefficient, K_d , of a metal varies over multiple orders of magnitude among different soils, mainly due to differences in soil and soil solution properties (pH, soil organic matter, DOC, ionic strength), origin of the metals, and differences in fixed fraction. Water or weak salt extracts are not recommended to estimate total dissolved metal concentrations of Cu and Pb in soil solution due to dilution of DOC and colloids, however the free metal ion activity can be quantified in these extract due to its buffering by the solid phase. Metal partitioning is usually described with equilibrium models. This equilibrium assumption is justified when the reactions converting one metal species into another (such as sorption and complexation) are fast compared with the process of interest. Often, a fraction of metal on the solid phase reacts slowly with the solution phase or is even inert. Therefore, it is preferable to take into account only the labile metal in the solid phase to describe the metal partitioning (for instance, as nominator of the K_d value). This labile metal can be measured with isotope dilution or EDTA extraction. Another kinetic limitation that may be important in transport and availability of metals is the slow dissociation of complexes in solution. Slowly dissociating metal complexes may accelerate leaching of metals, and labile complexes may contribute to metal uptake by biota. The measure of the solution concentration (which appears as denominator in the K_d) should fit the process of interest, but more research is needed to assess which metal species in solution are relevant for which processes. We recommend

the benchmarking of different solution speciation techniques with processes of interest rather than a comparison among methods.

Acknowledgements

F. Degryse acknowledges a grant from the Research Foundation, Flanders (F.W.O.-Vlaanderen). This work was supported by the International Copper Association.

References

- Ahnstrom, Z.A.S. & Parker, D.R. 2001. Cadmium reactivity in metal-contaminated soils using a coupled stable isotope dilution-sequential extraction procedure. *Environmental Science & Technology*, **35**, 121–126.
- Amery, F., Degryse, F., Degeling, W., Smolders, E. & Merckx, R. 2007. The copper-mobilizing-potential of dissolved organic matter in soils varies 10-fold depending on soil incubation and extraction procedures. *Environmental Science & Technology*, **41**, 2277–2281.
- Amery, F., Degryse, F., Cheyns, K., De Troyer, I., Mertens, J., Merckx, R. & Smolders, E. 2008. The UV-absorbance of dissolved organic matter predicts the fivefold variation in its affinity for mobilizing Cu in an agricultural soil horizon. *European Journal of Soil Science*, **59**, 1087–1095.
- Anderson, P.R. & Christensen, T.H. 1988. Distribution coefficients of Cd, Co, Ni, and Zn in soils. *Journal of Soil Science*, **39**, 15–22.
- Artinger, R., Kienzler, B., Schussler, W. & Kim, J.I. 1998. Effects of humic substances on the Am-241 migration in a sandy aquifer: column experiments with Gorleben groundwater/sediment systems. *Journal of Contaminant Hydrology*, **35**, 261–275.
- Bahr, J.M. & Rubin, J. 1987. Direct comparison of kinetic and local equilibrium formulations for solute transport affected by surface reactions. *Water Resources Research*, **23**, 438–452.

- Barrow, N.J. 1983. A discussion of the methods for measuring the rate of reaction between soil and phosphate. *Fertilizer Research*, **4**, 51–61.
- Barrow, N.J. & Cox, V.C. 1992. The effects of pH and chloride concentration on mercury sorption. II. By a soil. *European Journal of Soil Science*, **43**, 305–312.
- Barrow, N.J. 1998. Effects of time and temperature on the sorption of cadmium, zinc, cobalt, and nickel by a soil. *Australian Journal of Soil Research*, **36**, 941–950.
- Barrow, N.J. & Whelan, B.R. 1998. Comparing the effects of pH on the sorption of metals by soil and by goethite, and on uptake by plants. *European Journal of Soil Science*, **49**, 683–692.
- Barrow, N.J. 2008. The description of sorption curves. *European Journal of Soil Science*, **59**, 900–910.
- Beckett, P.H.T. & Davis R.D. 1977. Upper critical levels of toxic elements in plants. *New Phytologist*, **79**, 95–106.
- Bell, P.F., Chaney, R.L. & Angle, J.S. 1991. Free metal activity and total metal concentrations as indices of micronutrient availability to barley [*Hordeum vulgare* (L.) 'Klages']. *Plant and Soil*, **130**, 51–62.
- Bowers, A.R. & Huang, C.P. 1986. Adsorption characteristics of metal-EDTA complexes onto hydrous oxides. *Journal of Colloid and Interface Science*, **110**, 575–590.
- Buchter, B., Davidoff, B., Amacher, M.C., Hinz, C., Iskandar, I.K. & Selim, H.M. 1989. Correlation of Freundlich K_d and n retention parameters with soils and elements. *Soil Science*, **148**, 370–379.
- Buekers, J., Van Laer, L. Amery, F., Van Buggenhout, S., Maes, A. & Smolders, E., 2007. Role of soil constituents on fixation of soluble Zn, Cu, Ni and Cd added to soils. *European Journal of Soil Science*, **58**, 1514–1524.
- Buekers, J., Amery, F., Maes, A. & Smolders E. 2008a. Long-term reactions of Ni, Zn and Cd with iron oxyhydroxides depend on crystallinity and structure and on metal concentrations. *European Journal of Soil Science*, **59**, 706–715.

- Buekers, J., Degryse, F., Maes, A. & Smolders E. 2008b. Modelling the effects of ageing on Cd, Zn, Ni and Cu solubility in soils using an assemblage model. *European Journal of Soil Science*, **59**, 1160–1170.
- Christensen, T.H. 1989a. Cadmium soil sorption at low concentrations. VII. Effect of stable solid-waste leachate complexes. *Water Air and Soil Pollution*, **44**, 43–56.
- Christensen, T.H. 1989b. Cadmium soil sorption at low concentrations. VIII. Correlation with soil parameters. *Water, Air, and Soil Pollution*, **44**, 71–82.
- Citeau, L., Lamy, I., van Oort, F. & Elsass, F. 2003. Colloidal facilitated transfer of metals in soils under different land use. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **217**, 11–19.
- Crout, N.M.J., Tye, A.M., Zhang, H., McGrath, S.M. & Young, S.D. 2006. Kinetics of metal fixation in soils: Measurement and modeling by isotopic dilution. *Environmental Toxicology and Chemistry*, **25**, 659–663.
- de Groot, A.C., Peijnenburg, W.J.G.M., van den Hoop, M.A.G.T., Ritsema, R. & van Veen, R.P.M. 1998. *Heavy metals in Dutch field soils: an experimental and theoretical study on equilibrium partitioning*. National Institute of Public Health and the Environment (RIVM), The Netherlands.
- Degryse, F., Broos, K., Smolders, E. & Merckx, R. 2003. Soil solution concentration of Cd and Zn can be predicted with a CaCl₂ soil extract. *European Journal of Soil Science*, **54**, 149–157.
- Degryse, F., Buekers, J. & Smolders, E. 2004. Radio-labile cadmium and zinc in soils as affected by pH and source of contamination. *European Journal of Soil Science*, **55**, 113–121.
- Degryse, F. & Smolders, E. 2005. Kinetic speciation of metal complexes in relation to metal mobility in soils. In: *Proceedings of the 8th International Conference on the Biogeochemistry of Trace Elements* (eds E. Lombi *et al.*), Adelaide, Australia.
- Degryse, F. & Smolders, E. 2006. Mobility of Cd and Zn in polluted and unpolluted Spodosols. *European Journal of Soil Science*, **57**, 122–133.

- Degryse, F., Smolders, E. & Merckx, R. 2006. Labile Cd complexes increase Cd availability to plants. *Environmental Science & Technology*, **40**, 830–836.
- Degryse, F., Waegeneers, N. & Smolders, E. 2007. Labile lead in polluted soils measured by stable isotope dilution. *European Journal of Soil Science*, **58**, 1–7.
- Denaix, L., Semlali, R.M. & Douay, F. 2001. Dissolved and colloidal transport of Cd, Pb, and Zn in a silt loam soil affected by atmospheric industrial deposition. *Environmental Pollution*, **114**, 29–38.
- Di Toro, D.M., Mahony, J.D., Kirchgraber, P.R., Obyrne A.L., Pasquale, L.R. & Piccirilli, D.C. 1986. Effects of nonreversibility, particle concentration, and ionic-strength on heavy-metal sorption. *Environmental Science & Technology*, **20**, 55–61.
- Elzinga, E.J., Van Grinsven, J.J.M. & Swartjes, F.A. 1999. General purpose Freundlich isotherms for cadmium, copper and zinc in soils. *European Journal of Soil Science*, **50**, 139–149.
- Ernstberger, H., Davison, W., Zhang, H., Tye, A. & Young, S. 2002. Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS. *Environmental Science & Technology*, **36**, 349–354.
- Figura, P. & McDuffie, B. 1980. Determination of labilities of soluble trace metal species in aqueous environmental samples by anodic stripping voltammetry and chelex column and batch methods. *Analytical Chemistry*, **52**, 1433–1439.
- Filius, A., Streck, T. & Richter, J. 1998. Cadmium sorption and desorption in limed topsoils as influenced by pH: Isotherms and simulated leaching. *Journal of Environmental Quality*, **27**, 12–18.
- Fischer, L., Brümmer, G.W. & Barrow, N.J. 2007. Observations and modelling of the reactions of 10 metals with goethite: adsorption and diffusion processes. *European Journal of Soil Science*, **58**, 1304–1315.
- Fish, S.J. & Brassard, P. 1997. Dialysis membrane to prevent cadmium ion specific electrode fouling. *Talanta*, **44**, 939–945.

- Gäbler, H.E., Bahr, A., Heidkamp, A. & Utermann, J. 2007. Enriched stable isotopes for determining the isotopically exchangeable element content in soils. *European Journal of Soil Science*, **58**, 746–757.
- Ge, Y., Sauvé, S. & Hendershot, W.H. 2005. Equilibrium speciation of cadmium, copper, and lead in soil solutions. *Communications in Soil Science and Plant Analysis*, **36**, 1537–1556.
- Gerritse, R.G. & van Driel, W. 1984. The relationship between adsorption of trace metals, organic matter and pH in temperate soils. *Journal of Environmental Quality*, **13**, 197–204.
- Gray, C.W., McLaren, R.G. & Shioyatana, J. 2003. The determination of labile cadmium in some biosolids-amended soils by isotope dilution plasma mass spectrometry. *Australian Journal of Soil Research*, **41**, 589–597.
- Hamon, R.E., McLaughlin, M.J. & Cozens G. 2002. Mechanisms of attenuation of metal availability *in situ* remediation treatments. *Environmental Science & Technology*, **36**, 3991–3996.
- Helmke, P.A. 2000. The chemical composition of soils. In: *Handbook of Soil Science* (Ed. M.E. Sumner), pp. B3-B24. CRC Press, Boca Raton, FL.
- Hendrickson L.L. & Corey R.B. 1981. Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes. *Soil Science*, **131**, 163–171.
- Holm, P.E., Christensen, T.H., Tjell, J.C. & McGrath, S.P. 1995. Speciation of cadmium and zinc with application to soil solutions. *Journal of Environmental Quality*, **24**, 183–190.
- Hough, R.L., Tye, A.M., Crout, N.M.J., McGrath, S.P., Zhang, H. & Young, S.D. 2005. Evaluating a 'Free Ion Activity Model' applied to metal uptake by *Lolium perenne* L. grown in contaminated soils. *Plant and Soil*, **270**, 1–12.
- Hudson, R.J.M. 1998. Which aqueous species control the rates of trace metal uptake by aquatic biota? Observations and predictions of non-equilibrium effects. *Science of the Total Environment*, **219**, 95–115.

- Ivahnenko, T., Szabo, Z. & Gibs, J. 2001. Changes in sample collection and analytical techniques and effects on retrospective comparability of low-level concentrations of trace elements in ground water. *Water Research*, **35**, 3611–3624.
- Jopony, M. & Young, S.D. 1994. The solid–solution equilibria of lead and cadmium in polluted soils. *European Journal of Soil Science*, **45**, 59–70.
- Kalis, E.J.J., Weng, L.P., Dousma, F., Temminghoff, E.J.M. & van Riemsdijk, W.H. 2006. Measuring free metal ion concentrations in situ in natural waters using the Donnan membrane technique. *Environmental Science & Technology*, **40**, 955–961.
- Kalis, E.J.J., Weng, L.P., Temminghoff, E.J.M. & van Riemsdijk, W.H. 2007. Measuring free metal ion concentrations in multicomponent solutions using the Donnan membrane technique. *Analytical Chemistry*, **79**, 1555–1563.
- Kinniburgh, D.G., van Riemsdijk, W.H., Koopal, L.K., Borkovec, M., Benedetti, M.F. & Avena, M.J. 1999. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloids and Surfaces. A. Physicochemical and Engineering Aspects*, **151**, 147–166.
- Lam, M.T., Murimboh, J., Hassan, N.M. & Chakrabarti, C.L. 2002. Competitive ligand exchange/adsorptive cathodic stripping voltammetry (CLE/AdCSV) for kinetic studies of nickel speciation in aqueous environmental samples containing heterogeneous, macromolecular, organic complexants. *Analytica Chimica Acta*, **402**, 195–209
- Litaor, M.I. 1988. Review of soil solution samplers. *Water Resources Research*, **24**, 727–733.
- Lofts, S., Spurgeon, D.J., Svendsen, C. & Tipping, E. 2004. Deriving soil critical limits for Cu, Zn, Cd, and Pb: A method based on free ion concentrations. *Environmental Science & Technology*, **38**, 3623–3631.
- Luidier, C.D., Crusius, J., Playle, R.C. & Curtis, P.J. 2004. Influence of natural organic matter source on copper speciation as demonstrated by Cu binding to fish gills, by ion selective electrode, and by DGT gel sampler. *Environmental Science & Technology*, **38**, 2865–2872.

- Ma, Y.B., Lombi, E., Nolan, A.L. & McLaughlin, M.J. 2006a. Determination of labile Cu in soils and isotopic exchangeability of colloidal Cu complexes. *European Journal of Soil Science*, **57**, 147–153.
- Ma, Y.B., Lombi, E., Oliver, I.W., Nolan, A.L. & McLaughlin, M.J. 2006b. Long-term aging of copper added to soils. *Environmental Science & Technology*, **40**, 6310–6317.
- MacDonald, J.D. & Hendershot, W.H. 2006. Modelling trace metal partitioning in forest floors of northern soils near metal smelters. *Environmental Pollution*, **143**, 228–240.
- Marang, L., Reiller, P., Pepe, M. & Benedetti, M.F. 2006. Donnan membrane approach: from equilibrium to dynamic speciation. *Environmental Science & Technology*, **40**, 5496–5501.
- Massoura, S.T., Echevarria, G., Becquer, T., Ghanbaja, J., Leclere-Cessac, E. & Morel, J.L. 2006. Control of nickel availability by nickel bearing minerals in natural and anthropogenic soils. *Geoderma*, **136**, 28–37.
- McBride, M., Sauvé, S. & Hendershot, W. 1997. Solubility control of Cu, Zn, Cd and Pb in contaminated soils. *European Journal of Soil Science*, **48**, 337–346.
- Meijboom, F. W. & van Noordwijk, M. 1992. Rhizon soil solution samplers as artificial roots. In: *Root ecology and its practical application, Proceedings of the 3rd ISSR symposium* (eds L. Kutschera *et al.*), pp. 793–795. Wien, Austria.
- Merckx, R., Brans, K. & Smolders, E. 2001. Decomposition of dissolved organic carbon after soil drying and rewetting as an indicator of metal toxicity in soils. *Soil Biology & Biochemistry*, **33**, 235–240.
- Minnich, M.M. & McBride, M.B. 1987. Copper activity in soil solution: I. Measurement by ion-selective electrode and Donnan dialysis. *Soil Science Society of America Journal*, **51**, 568–572.
- Morfobos, M., Economou, A. & Voulgaropoulos, A. 2004. Simultaneous determination of nickel(II) and cobalt(II) by square wave adsorptive stripping voltammetry on a rotating-disc bismuth-film electrode. *Analytica Chimica Acta*, **519**, 57–64.

- Morin, G., Ostergren, J.D., Juillot, F., Ildefonse, P., Calas, G. & Brown, G.E.Jr. 1999. XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: importance of adsorption processes. *American Mineralogist*, **84**, 420–434.
- Nakhone, L.N. & Young, S.D. 1993. The significance of (radio-)labile cadmium pools in soil. *Environmental Pollution*, **82**, 73–77.
- Nolan, A.L., Lombi, E. & McLaughlin, M.J. 2003a. Metal bioaccumulation and toxicity in soils - Why bother with speciation? *Australian Journal of Chemistry*, **56**, 77–91.
- Nolan, A.L., McLaughlin, M.J. & Mason, S.D. 2003b. Chemical speciation of Zn, Cd, Cu and Pb in pore waters of agricultural and contaminated soils using Donnan dialysis. *Environmental Science & Technology*, **37**, 90–98.
- Nolan, A.L., Ma, Y.B., Lombi, E. & McLaughlin, M.J. 2004. Measurement of labile Cu in soil using stable isotope dilution and isotope ratio analysis by ICP-MS. *Analytical and Bioanalytical Chemistry*, **380**, 789–797.
- Oorts, K., Ghesquiere, U., Swinnen, K. & Smolders, E. 2006. Soil properties affecting the toxicity of CuCl₂ and NiCl₂ for soil microbial processes in freshly spiked soils. *Environmental Toxicology and Chemistry*, **25**, 836–844.
- Pagenkopf, G.K. 1983. Gill surface interaction model for trace-metal toxicity to fishes: Role of complexation, pH and water hardness. *Environmental Science & Technology*, **17**, 342–347.
- Parker, D.R., Chaney, R.L. & Norvell, W.A. 1995. Chemical equilibrium models: applications to plant nutrition research. In: *Chemical Equilibrium and Reaction Models* (eds R.H. Loeppert *et al.*). Soil Sci. Soc. Amer. Spec. Pub. No. 42, Madison, WI.
- Parker, D.R., Pedler, J.F., Ahnstrom, Z.A.S. & Resketo, M. 2001. Reevaluating the free-ion activity model of trace metal toxicity toward higher plants: experimental evidence with copper and zinc. *Environmental Toxicology and Chemistry*, **20**, 899–906.
- Percival, H.J., Speir, T.W. & Parshotam, A. 1999. Soil solution chemistry of contrasting soils amended with heavy metals. *Australian Journal of Soil Research*, **37**, 993–1004.

- Ponizovsky, A.A., Metzler, D.M., Allen, H.E. & Ackerman, A.J. 2006. The effect of moisture content on the release of organic matter and copper to soil solutions. *Geoderma*, **135**, 204–215.
- Pretsch E. 2007 The new wave of ion-selective electrodes. *Trends in Analytical Chemistry*, **26**, 46–51.
- Rachou, J., Gagnon, C. & Sauvé, S. 2007. Use of an ion-selective electrode for free copper measurements in low salinity and low ionic strength matrices. *Environmental Chemistry*, **4**, 90–97.
- Roberts, D.R., Scheinost, A.C. & Sparks, D.L. 2002. Zinc speciation in a smelter-contaminated soil profile using bulk and microspectroscopic techniques. *Environmental Science & Technology*, **36**, 1742–1750.
- Römkens, P.F., Bril, J. & Salomons, W. 1996. Interaction between Ca^{2+} and dissolved organic carbon: implications for metal mobilization. *Applied Geochemistry*, **11**, 109–115.
- Römkens, P.F. & Salomons, W. 1998. Cd, Cu and Zn solubility in arable and forest soils: Consequences of land use changes for metal mobility and risk assessment. *Soil Science*, **163**, 859–871.
- Römkens, P.F., Hoenderboom, G. & Dolfing, J. 1999. Copper solution geochemistry in arable soils: Field observations and model application. *Journal of Environmental Quality*, **29**, 776–783.
- Rusch, U., Borkovec, M., Daicic, J. & van Riemsdijk, W.H. 1997. Interpretation of competitive adsorption isotherms in terms of affinity distributions. *Journal of Colloid and Interface Science*, **191**, 247–255.
- Salam, A.K. & Helmke, P.A. 1998. The pH dependence of free ionic activities and total dissolved concentrations of copper and cadmium in soil solution. *Geoderma*, **83**, 281–291.
- Sanders, J.R. 1983. The effect of pH on the total and free ionic concentrations of manganese, zinc and cobalt in soil solutions. *Journal of Soil Science*, **34**, 315–323.
- Sarret, G., Balesdent, J., Bouziri, L., Garnier, J.M., Marcus, M.A., Geoffroy, N., Panfili, F. & Manceau, A. 2004. Zn speciation in the organic horizon of a contaminated soil by micro-X-

- Ray fluorescence, micro- and powder-EXAFS spectroscopy, and isotopic dilution. *Environmental Science & Technology*, **38**, 2792–2801.
- Sauvé, S., McBride, M.B. & Hendershot, W. 1997a. Speciation of lead in contaminated soils. *Environmental Pollution*, **98**, 149–155.
- Sauvé, S., McBride, M.B., Norvell, W.A. & Hendershot, W. 1997b. Copper solubility and speciation of *in situ* contaminated soils: Effects of copper level, pH and organic matter. *Water, Air, and Soil Pollution*, **100**, 133–149.
- Sauvé, S., Hendershot, W. & Allen, H.E. 2000a. Solid–solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environmental Science & Technology*, **34**, 1125–1131.
- Sauvé, S., Norvell, W.A., McBride, M. & Hendershot, W. 2000b. Complexation and speciation of cadmium in extracted soil solutions. *Environmental Science & Technology*, **34**, 291–296.
- Schmitt, D., Saravia, F., Frimmel, F. H., Schuessler, W., 2003. NOM-facilitated transport of metal ions in aquifers: Importance of complex-dissociation kinetics and colloid formation. *Water Research*, **37**, 3541–3550.
- Schröder, T.J., Hiemstra, T., Vink, J.P.M. & van der Zee, S.E.A.T.M. 2005. Modeling of the solid–solution partitioning of heavy metals and arsenic in embanked flood plain soils of the rivers Rhine and Meuse. *Environmental Science & Technology*, **39**, 7176–7184.
- Seuntjens, P. 2002. Field-scale cadmium transport in a heterogeneous layered soil. *Water, Air, and Soil Pollution*, **140**, 401–423.
- Shuman, M.S. & Michael, L.C. 1978. Application of rotated disk electrode to measurement of copper complex dissociation rate constants in marine coastal samples. *Environmental Science & Technology*, **12**, 1069–1072.
- Sinaj, S., Dubois, A. & Frossard, E. 2004. Soil isotopically exchangeable zinc: A comparison between *E* and *L* values. *Plant and Soil*, **261**, 17–28.

- Smolders, E., Degryse, F., De Brouwere, K., Van Den Brande, K., Cornelis, C. & Seuntjens, P. 2000. *Pore water based K_d values of heavy metals in soils from Flanders*. Internal Report (in Dutch) to the Flemish Waste Agency, OVAM.
- Smolders, E., Buekers, J., Oliver, I. & McLaughlin, M.J. 2004. Soil properties affecting toxicity of zinc to soil microbial properties in laboratory-spiked and field-contaminated soils. *Environmental Toxicology and Chemistry*, **23**, 2633–2640.
- Sposito, G. 1984. *The surface chemistry of soils*. Oxford University Press, NY.
- Streck, T. & Richter, J. 1997. Heavy metal displacement in a sandy soil at the field scale. 1. Measurements and parameterization of sorption. *Journal of Environmental Quality*, **26**, 49–56.
- Stevens, P.D., McLaughlin, M.J. & Heinrich, R. 2003. Determining toxicity of lead and zinc runoff in soils: salinity effects on metal partitioning and on phytotoxicity. *Environmental Toxicology and Chemistry*, **22**, 3017–3024.
- Suarez, D.L. 1986. A soil water extractor that minimizes CO₂ degassing and pH errors. *Water Resources Research*, **22**, 876–880.
- Temminghoff, E.J.M., van der Zee, S.E.A.T.M. & de Haan, F.A.M. 1995. Speciation and calcium competition effects on cadmium sorption by sandy soil at various pHs. *European journal of Soil Science*, **46**, 649–655.
- Temminghoff, E.J.M., van der Zee, S.E.A.T.M. & de Haan, F.A.M. 1997. Copper mobility in a copper contaminated sandy soil as affected by pH, solid and dissolved organic matter. *Environmental Science & Technology*, **31**, 1109–1115.
- Tipping, E. 1998. Humic ion-binding model VI: an improved description of the interactions of protons and metal ions with humic substances. *Aquatic Geochemistry*, **4**, 3–48.
- Tipping, E., Rieuwerts, J., Pan, G., Ashmore, M.R., Lofts, S., Hill, M.T.R., Farago, M.E. & Thornton, I. 2003. The solid–solution partitioning of heavy metals (Cu, Zn, Cd, Pb) in upland soils of England and Wales. *Environmental Pollution*, **125**, 213–225.

- Trivedi, P. & Axe, L. 2000. Modeling Cd and Zn sorption to hydrous metal oxides. *Environmental Science & Technology*, **34**, 2215–2223.
- Tongtavee, N., Shiowatana, J., McLaren, R.G. & Gray, C.W. 2005. Assessment of lead availability in contaminated soil using isotope dilution techniques. *Science of the Total Environment*, **348**, 244–256.
- Turner, D.R., Varney, M.S., Whitfield, M., Mantoura, R.F.C. & Riley, J.P. 1987. Electrochemical studies of copper and lead complexation by fulvic-acid. 2. A critical comparison of potentiometric and polarographic measurements. *Science of the Total Environment*, **60**, 17–34.
- Tye, A.M., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Barbosa-Jefferson, V.L., Davison, W., McGrath, S.P., Paton, G.I., Kilham, K. & Resende, L. 2003. Predicting the activity of Cd²⁺ and Zn²⁺ in soil pore water from the radio-labile metal fraction. *Geochimica et Cosmochimica Acta*, **67**, 375–385.
- Tye, A.M., Young, S.D., Crout, N.M.J., Zhang, H., Preston, S., Zhao, F.J. & McGrath, S.P. 2004. Speciation and solubility of Cu, Ni and Pb in contaminated soils. *European Journal of Soil Science*, **55**, 579–590.
- Valocchi, A.J. 1985. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resources Research*, **21**, 808–820.
- van de Weerd, H. & Leijnse, A. 1997. Assessment of the effects of kinetics on colloid facilitated radionuclide transport in porous media. *Journal of Contaminant Hydrology*, **26**, 245–256.
- van Leeuwen, H.P. & Town, R.M. 2005 Kinetic limitations in measuring stabilities of metal complexes by Competitive Ligand Exchange-Adsorptive Stripping Voltammetry (CLE-AdSV). *Environmental Science & Technology*, **39**, 7217–7225.
- Vulkan, R., Zhao, F.J., Barbosa-Jefferson, V., Preston, S., Paton, G.I., Tipping, E. & McGrath, S.P. 2000. Copper speciation and impacts on bacterial biosensors in the pore water of copper-contaminated soils. *Environmental Science & Technology*, **34**, 5115–5121.

- Warnken, K.W., Davison, W., Zhang, H., Galceran, J. & Puy, J. 2007. *In situ* measurements of metal complex exchange kinetics in freshwater. *Environmental Science & Technology*, **41**, 3179–3185.
- Welp, G. & Brümmer, G.W. 1999. Adsorption and solubility of ten metals in soil samples of different composition. *Journal of Plant Nutrition and Soil Science*, **162**, 155–161.
- Weng, L.P., Temminghoff, E.J.M. & van Riemsdijk, W.H. 2001a. Contribution of individual sorbents to the control of heavy metal activity in sandy soil. *Environmental Science & Technology*, **35**, 4436–4443.
- Weng, L.P., Temminghoff, E.J.M. & van Riemsdijk, W.H. 2001b. Determination of the free ion concentration of trace metals in soil solution using a soil column Donnan membrane technique. *European Journal of Soil Science*, **52**, 629–637.
- Weng, L.P., Temminghoff, E.J.M., Lofts, S., Tipping, E. & van Riemsdijk, W.H. 2002. Complexation with dissolved organic matter and solubility control of heavy metals in a sandy soil. *Environmental Science & Technology*, **36**, 4804–4810.
- Westall, J.C., Morel, F.M.M. & Hume, D.N. 1979. Chloride interference in cupric ion-selective electrode measurements. *Analytical Chemistry*, **51**, 1792–1798.
- Xue, H.B. & Sunda, W.G. 1997. Comparison of $[\text{Cu}^{2+}]$ measurements in lake water determined by ligand exchange and cathodic stripping voltammetry and by ion-selective electrode. *Environmental Science & Technology*, **31**, 1902–1909.
- Yin, Y., Impellitteri, C. A., You, S. J. & Allen, H. E. 2002. The importance of organic matter distribution and extract soil:solution ratio on the desorption of heavy metals from soils. *Science of the Total Environment*, **287**, 107–119.
- Young, S.D., Tye, A., Carstensen, A., Resende, L. & Crout, N. 2000. Methods for determining labile cadmium and zinc in soil. *European Journal of Soil Science*, **51**, 129–136.
- Young, S.D., Crout, N., Hutchinson, J., Tye, A., Tandy, S. & Nakhone, L. 2007. Techniques for measuring attenuation: isotopic dilution methods. In: *Natural attenuation of trace element*

- availability in soils* (eds R. Hamon, M. McLaughlin & E. Lombi), pp. 19–55. CRC Press (Taylor and Francis Group), Boca Raton, FL.
- Zhang, H. & Davison, W. 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. *Analytical Chemistry*, **67**, 3391–3400.
- Zhang, H. & Young, S.D. 2006. Characterizing the availability of metals in contaminated soils. II. The soil solution. *Soil Use and Management*, **21**, 459–467.
- Zhang, H., Zhao, F.J., Sun, B., Davison, W. & McGrath, S.P. 2001. A new method to measure effective soil solution concentration predicts copper availability to plants. *Environmental Science & Technology*, **35**, 2602–2607.

FIGURE CAPTIONS

Figure 1 Schematic descriptions of metal partitioning in soil, in increasing order of simplicity. (a) Adsorption and desorption from metal ions (M^{2+}) onto and from the solid phase and association and dissociation of metal complexes (ML) in solution are described as kinetic processes using (1st order) rate constants (respectively k_{ads} , k_{des} , k_a , k_d). Slow reactions (such as solid-state diffusion) may convert the labile adsorbed metal (M_{labile}) to non-labile metal ($M_{non-lab}$), which is described as a reversible process (rate constants k_1 and k_{-1}). Inert metals (M_{inert}) on the solid phase cannot be released into solution and inert metal complexes (ML_{inert}) cannot dissociate. (b–d) More simplified schemes, where the double arrow denotes that equilibrium is assumed and M_{sol} denotes the total metal in solution. The solid–liquid distribution coefficients give the concentration ratios of labile metal on the solid phase and free metal ion ($K_d^{lab/free}$) or total metal in solution (K_d^{lab}), or the concentration ratio of total metal on the solid phase, M_{solid} , and total metal in solution (K_d^{tot}).

Figure 2 Illustration of the pH dependence of cation sorption and the effect of liquid/solid (L/S) ratio on adsorption envelopes (example representative for sorption of Cd on soil). The K_d was assumed to be independent of the L/S ratio and to be related to the pH as follows: $\log K_d = -1.59 + 0.60pH$. The theoretical adsorption envelopes (calculated with Equation 4), that show the percentage of metal sorbed on the surface as a function of pH, are given for a L/S ratio of 5 litre kg^{-1} or 50 litre kg^{-1} .

Figure 3 Effect of Ca concentration on solution concentrations of Cu, Pb and Zn (mean \pm standard error) for two metal-contaminated soils (pH 4.3 and pH 7.1). Soil was suspended in solutions with varying $Ca(NO_3)_2$ concentration (ionic strength maintained by matching with $NaNO_3$) at a liquid/solid ratio of 10 litre kg^{-1} , and equilibrated for 3 days. Zinc

concentrations differed strongly between the two soils, and are therefore shown on a different scale, as indicated by the arrows (Degryse, unpublished).

Figure 4 The contribution of metal complexes – with respect to their dissociation rate – (a) in detection by analytical techniques and (b) in environmental processes, and (c) the estimated range of dissociation rates of metal complexes in soil solutions. The contribution of complexes in measurement by DGT or ASV, or in diffusion-controlled uptake by biota was calculated with the reaction layer theory (Hudson, 1998; Equation 6). The values are approximate since also the degree of buffering affects the contribution. The range of complexes expected (a) to contribute to the analytical measurement or (b) to be retarded during transport or to contribute to diffusion-limited uptake is given by the lines. The retardation of complexes during leaching was estimated with numerical transport calculations (cf. Figure 10), for fast ($v \sim 25 \text{ cm day}^{-1}$) or slow water velocity ($v \sim 0.25 \text{ cm day}^{-1}$). Dashed lines indicate that (a-b) the contribution (for analytical measurements or biouptake) or retardation (during leaching) is only partial, or that (c) these complexes are in most soil solutions of minor importance.

Figure 5 The fraction radio-labile Zn as a function of incubation time for four soils that were amended with $\text{Zn}(\text{NO}_3)_2$ ($250 \text{ mg Zn kg}^{-1}$) and incubated under field conditions. The lines show the fit of reversible first-order kinetics (half-life 330 days, pH dependent labile fraction f at equilibrium: $f=1.60-0.20\text{pH}$). Data from Buekers *et al.* (2008b).

Figure 6 Free-ion fractions of metals in soil solution measured with Donnan dialysis (● Weng *et al.*, 2001b; ○ Nolan *et al.*, 2003b; ▲ Weng *et al.*, 2002), ISE (Δ Vulkan *et al.*, 2000), or a resin exchange method (□ Sanders, 1983), or free ion fractions in a 10 mM $\text{Ca}(\text{NO}_3)_2$ extract measured with ISE (× Sauv   *et al.*, 1997b) or in a 10 mM KNO_3 extract measured with ASV (+ Sauv   *et al.*, 1997a). The lines show the free-ion fractions predicted with WHAM6 for a generic composition of solution (not attempting to predict

the individual observations), for either ‘low’ (full line) or ‘high’ (dotted line) concentration of the trace metals. Solution composition used for the prediction: $\text{Ca}(\text{NO}_3)_2$ 2 mM; Fe in equilibrium with $\text{Fe}(\text{OH})_3$ ($\log\{(\text{Fe}^{3+})/(\text{H}^+)^3\}=2.5$); Al in equilibrium with $\text{Al}(\text{OH})_3$ ($\log\{(\text{Al}^{3+})/(\text{H}^+)^3\}=8.5$), except for soils with $\text{pH} < 4.5$: $(\text{Al}^{3+})=10^{-5}$ M; trace metals: Cd 10^{-8} M, Co 10^{-7} M, Cu $5 \cdot 10^{-7}$ M, Ni $5 \cdot 10^{-7}$ M, Pb 10^{-8} M, Zn 10^{-6} M (‘low’) or 10 times higher concentrations (‘high’), 50 mg/l DOM (65% fulvic acid, 35% inert), pCO_2 $10^{-3.5}$ atm.

Figure 7 Pore-water based K_d values of (a) Zn and (b) Ni, representing the partitioning of total (+) or labile metal (◆). The full lines show the regression equation of Anderson & Christensen (1998) based on adsorption K_d s in 1 mM CaCl_2 . (×) ‘Total’ K_d values for field contaminated and uncontaminated soils (Zn: data from de Groot *et al.*, 1998; Degryse *et al.*, 2003; and Zhao, unpublished; Ni: de Groot *et al.*, 1998; Smolders *et al.*, 2000; Oorts *et al.*, 2006). (●) K_d^{lab} for Zn based on isotopically exchangeable Zn (E value) (Degryse *et al.*, 2003; Zhao, unpublished); ‘total’ K_d for Ni but in soils that were freshly amended with NiCl_2 and where most Ni is consequently in labile form (Oorts *et al.*, 2006).

Figure 8 The K_d of Cu for soils with $\text{pH} > 5$ (a) as a function of pH, or (b) as a function of the solid–liquid distribution of organic C, $K_{d\text{-OC}}$ (dotted line is the 1:1 line). The K_d values are pore-water based (de Groot *et al.*, 1998; Smolders *et al.*, 2000; Römkens *et al.*, 1999; Nolan *et al.*, 2003b; Vulkan *et al.* 2000) or based on concentrations in a ‘recirculating’ 2 mM $\text{Ca}(\text{NO}_3)_2$ ($S:L$ 1:2) soil column extract (Weng *et al.*, 2001a, 2002). Full lines are regression lines relating $\log K_d$ of Cu to pH or to $\log K_{d\text{-OC}}$ (data of Nolan *et al.* (+) not included in regression; see text).

Figure 9 Theoretical leaching curves of metals from soil when (a) all solid-phase metal is in equilibrium with the solution phase, (b) part of the solid phase metal is non-labile, but slowly released, or (c) part of the solid-phase metal is inert. The area under the breakthrough curves corresponds to the amount of metal that is leached from the soil (white: from labile pool; striped: from non-labile pool). Symbols are explained in the legend of Figure 1. ($K_d^{\text{tot}}=100$ litre kg^{-1} , $K_d^{\text{lab}}=50$ litre kg^{-1}).

Figure 10 Theoretical breakthrough curves of a step input of metal (half as free ion, half as complex), when (a) complexes dissociate fast in which case equilibrium between the free ion and the complex can be assumed, (b) complexes dissociate slowly (dissociation rates k_d in s^{-1}), or (c) the complexes are inert. Symbols are explained in the legend of Figure 1. Input parameters for the numerical model calculations were: $K_d^{free} = 100$ litre kg^{-1} , $f_{free} = 0.5$, $v = 0.3$ cm d^{-1} , $\lambda = 1$ cm, $\theta = 0.25$, $\rho = 1.5$ kg litre $^{-1}$; breakthrough at 50 cm of depth.

Table 1 Literature examples of how solid–liquid distribution of metals in soils is determined, and which definition of K_d corresponds with the observations: $K_d^{\text{tot}/(\text{free})}$: ratio of total solid phase concentration to total solution (or free ion) concentration; $K_d^{\text{lab}/(\text{free})}$: ratio of labile solid phase concentration to total solution (or free ion) concentration (cf. Figure 1).

K_d	Solid phase	Solution phase		Metals studied	Reference
		Isolation/extract	Analysis		
K_d^{tot}	hot acid digestion	pore water (centrifugation)	(GF)AAS	Cd, Cr, Cu, Ni, Pb, Zn	de Groot <i>et al.</i> , 1998; Römkens & Salomons, 1998
K_d^{tot}	hot acid digestion	pore water (Rhizon samplers)	GFAAS, ICP-AES	Cd, Cu, Zn	Vulkan <i>et al.</i> , 2000
$K_d^{\text{tot}/\text{free}}$			+ ISE for Cu		
$K_d^{\text{tot}/\text{free}}$	hot acid digestion	KNO ₃ 10 mM (S/L 1:2)	ASV	Cd, Pb	Sauvé <i>et al.</i> , 1997a, 2000b
K_d^{lab}	<i>E</i> value	pore water (centrifugation)	ICP-AES	Cd, Zn	Degryse <i>et al.</i> , 2003
K_d^{lab}	<i>E</i> value	pore water (Rhizon samplers)	(GF)AAS, ICP-MS	Cd, Zn	Tye <i>et al.</i> , 2003
K_d^{lab}	EDTA 0.025 M	CaCl ₂ 2.5 mM (S/L 1:1)	(GF)AAS	Cd, Zn	Streck & Richter, 1997
K_d^{lab}	adsorption	CaCl ₂ 1 mM (S/L 1:5)	GFAAS	Cd	Christensen, 1989b
K_d^{lab}	adsorption	dilute salt (IS 0.011 M; S/L 1:5)	ASV ^a	Cd	Gerritse & van Driel, 1984
K_d^{lab}	adsorption	Ca(NO ₃) ₂ 5 mM (S/L 1:10)	ICP-AES	Cd, Co, Cr, Cu, Ni, Pb, Zn	Buchter <i>et al.</i> , 1989
K_d^{lab}	adsorption	CaCl ₂ 1 mM (S/L 1:100, 1:20 if pH<5)	Zn, Cd, Ni: AAS ^b ⁶⁵ Co: counting	Cd, Co, Ni, Zn	Anderson & Christensen, 1988
K_d^{lab}	(cold) HNO ₃ 2 M	Ca(NO ₃) ₂ 2 mM	ICP-MS	Cd, Cu, Ni, Pb, Zn	Weng <i>et al.</i> , 2001a, 2002
$K_d^{\text{lab}/\text{free}}$		(S/L 1:2, column extraction)	Donnan dialysis		

^a measure of total solution concentration, as DOM was decomposed with ozone before measurement with ASV;

^b Organic extraction (preconcentration) used for Cd and Ni

Table 2 Selected regression models for $\log K_d$ (in litre kg^{-1}), derived from pore water-based K_d values. The regression equations were fitted on K_d values that were based on total solid phase concentrations ($K_d^{\text{tot}/(\text{free})}$) or on labile solid phase concentration (K_d^{lab}).

Metal	K_d	Regression coefficients			Based on data from		
		intercept	pH	$\log\%OC^e$	n	R^2	
Cd	K_d^{tot}	-0.83	0.56		123	0.65	de Groot <i>et al.</i> (1998), Degryse <i>et al.</i> (2003), Zhao ^a
		-1.04	0.55	0.70	123	0.72	
	K_d^{lab}	-1.59	0.65		86	0.66	Degryse <i>et al.</i> (2003), Zhao ^a
		-1.7	0.62	0.61	86	0.71	
Zn	K_d^{tot}	-1.54	0.68		143	0.65	de Groot <i>et al.</i> (1998), Degryse <i>et al.</i> (2003), Zhao ^a
		-1.77	0.66	0.79	143	0.72	
	K_d^{lab}	-2.31	0.72		97	0.66	Degryse <i>et al.</i> (2003), Zhao ^a
		-2.48	0.69	0.67	97	0.71	
Cu	K_d^{tot}	0.60	0.37		129	0.34	de Groot <i>et al.</i> (1998), Smolders <i>et al.</i> (2000), Nolan <i>et al.</i> (2003b), Vulkan <i>et al.</i> (2000), Weng <i>et al.</i> (2001a) ^b , Römken <i>et al.</i> (1999) ^b
		0.45	0.34	0.65	128	0.44	
	$K_d^{\text{tot}/\text{free}}$	-1.88	1.05	0.65	32	0.97	Weng <i>et al.</i> (2001a) ^c
Pb	K_d^{tot}	1.43	0.42		79	0.58	de Groot <i>et al.</i> (1998), Smolders <i>et al.</i> (2000), Nolan <i>et al.</i> (2003b), Weng <i>et al.</i> (2001a) ^b
		1.32	0.40	0.50	78	0.66	
Ni ^d	K_d^{tot}	0.99	0.30		63	0.36	de Groot <i>et al.</i> (1998), Smolders <i>et al.</i> (2000), Oorts <i>et al.</i> (2006)
	K_d^{lab}	-0.58	0.44		16	0.71	Oorts <i>et al.</i> (2006)

^a F.J. Zhao, personal communication; ^b only data for the topsoils were used; ^c free ion concentration determined with Donnan dialysis; ^d K_d^{tot} values based on partitioning of native Ni in soil, K_d^{lab} based on partitioning of Ni in NiCl_2 amended soils (cf. Figure 7b); ^e If organic matter (OM) content was reported, the OM content was converted to OC content assuming 50% C in organic matter

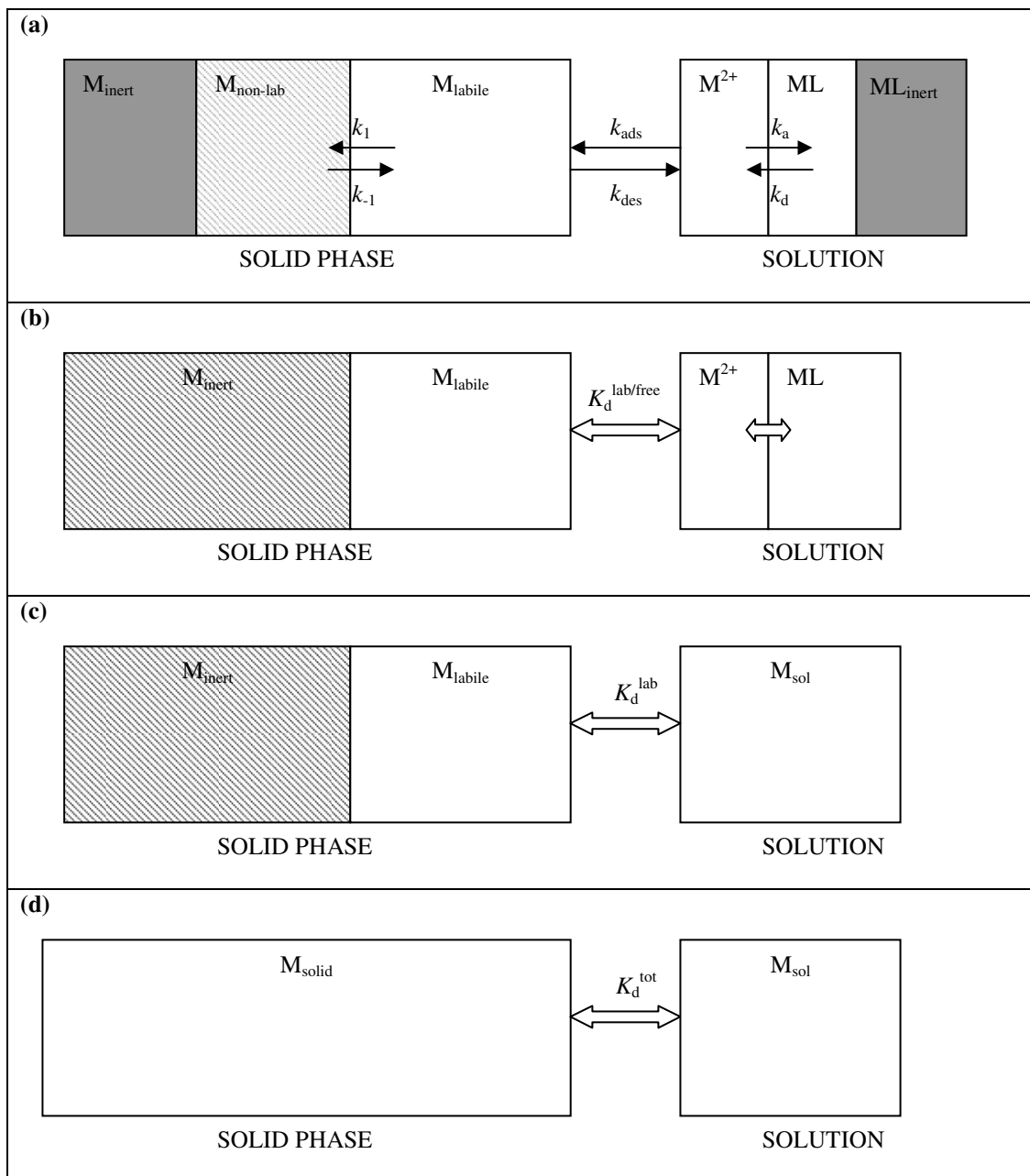


Figure 1

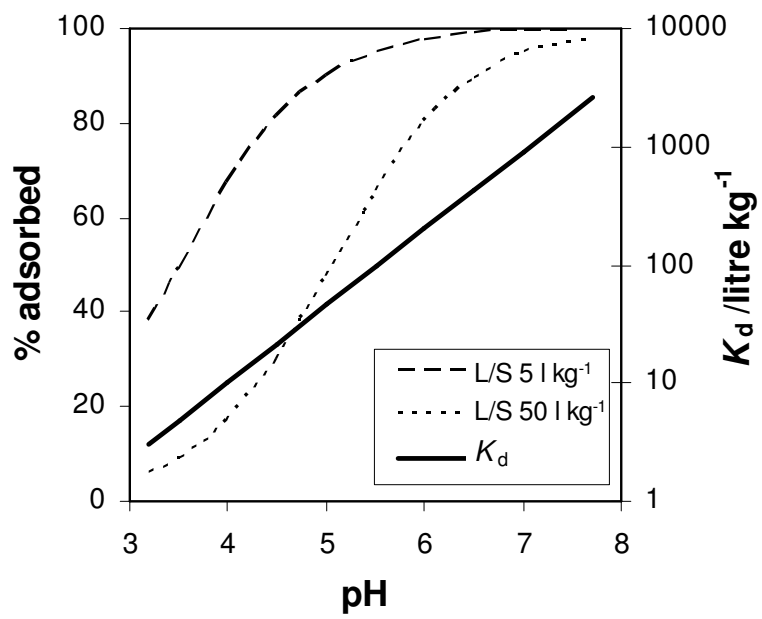


Figure 2

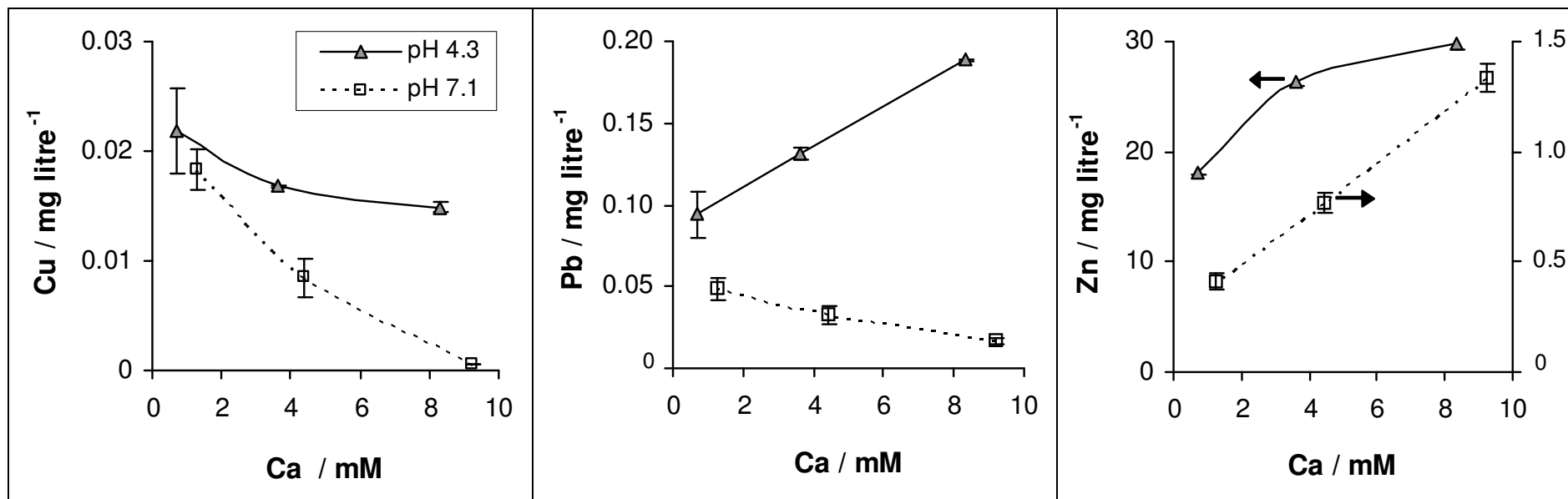


Figure 3

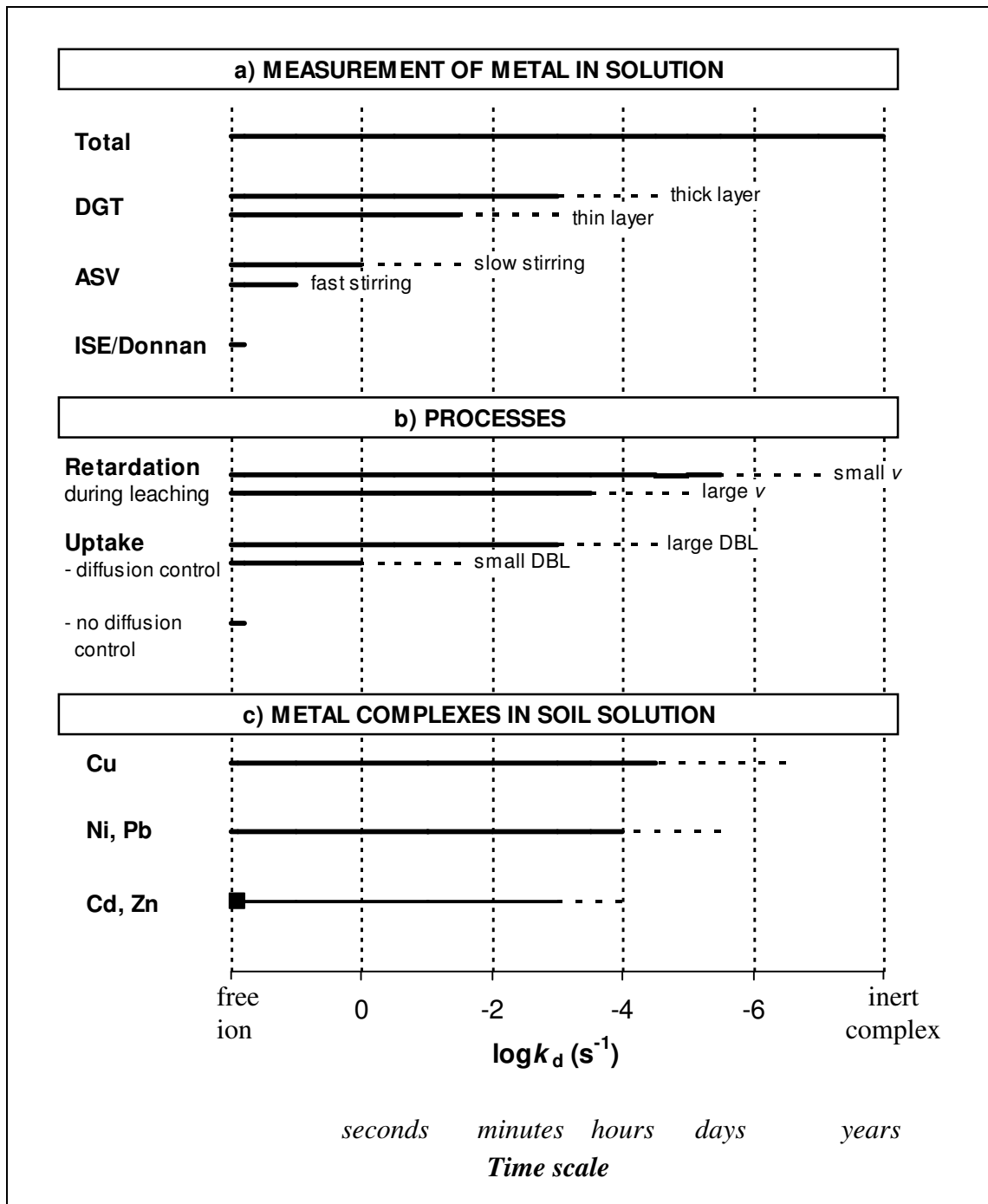


Figure 4

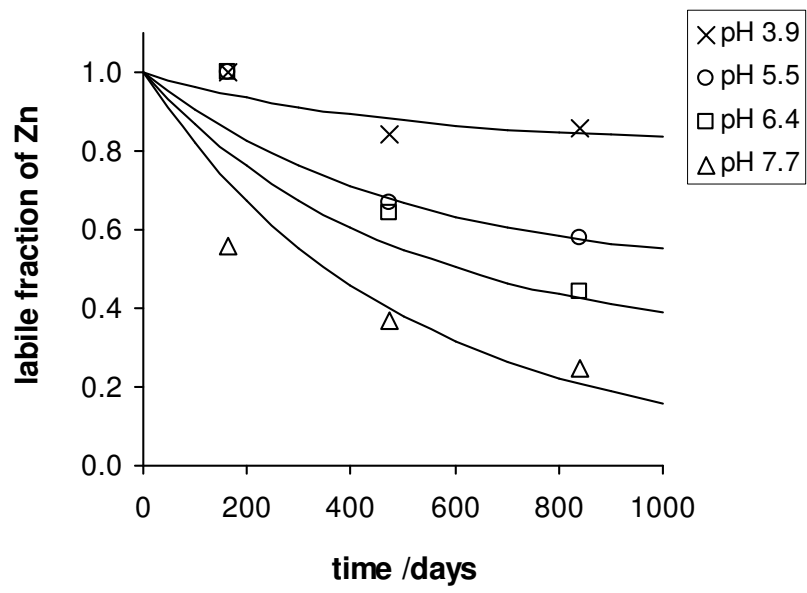


Figure 5

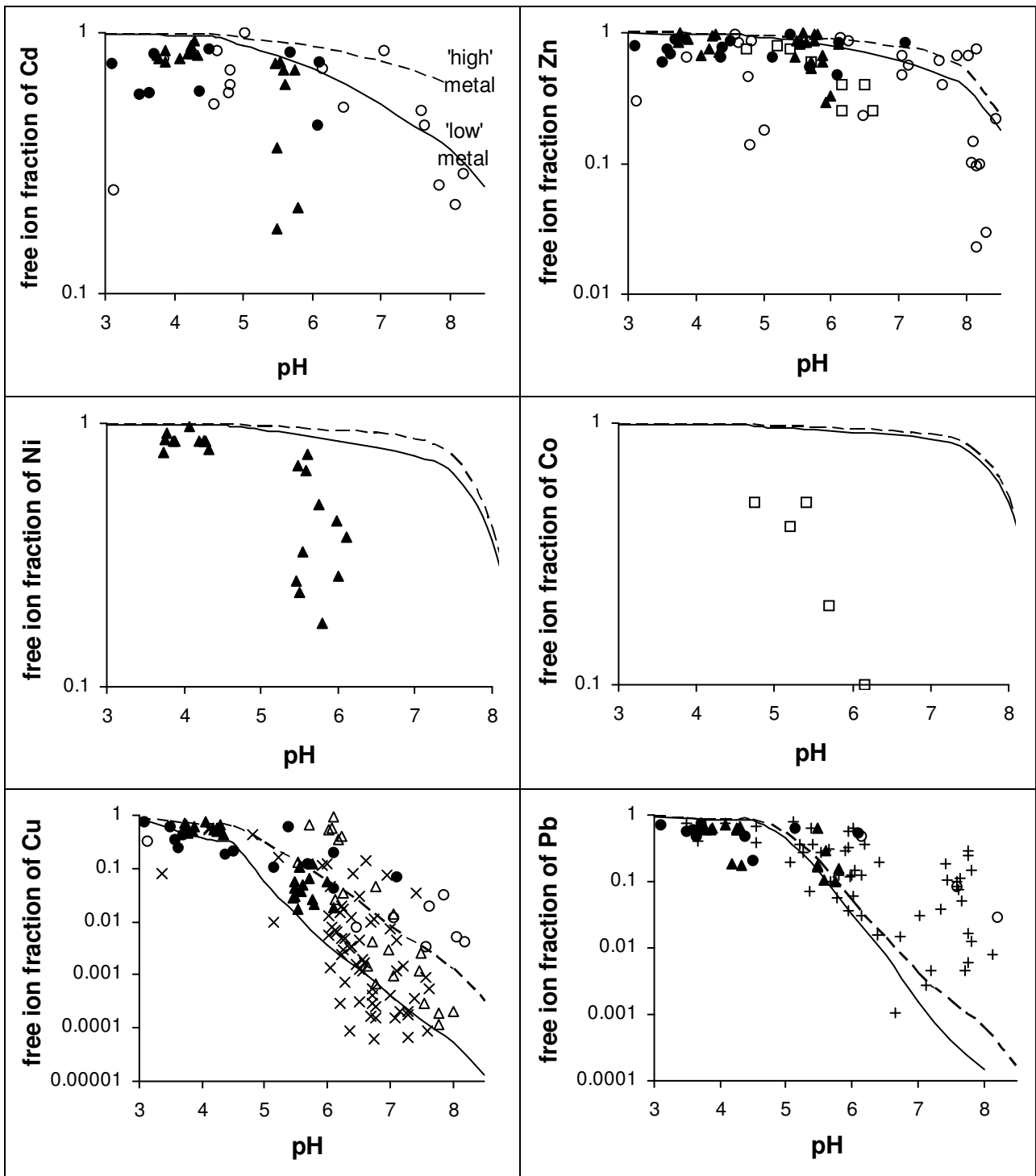


Figure 6

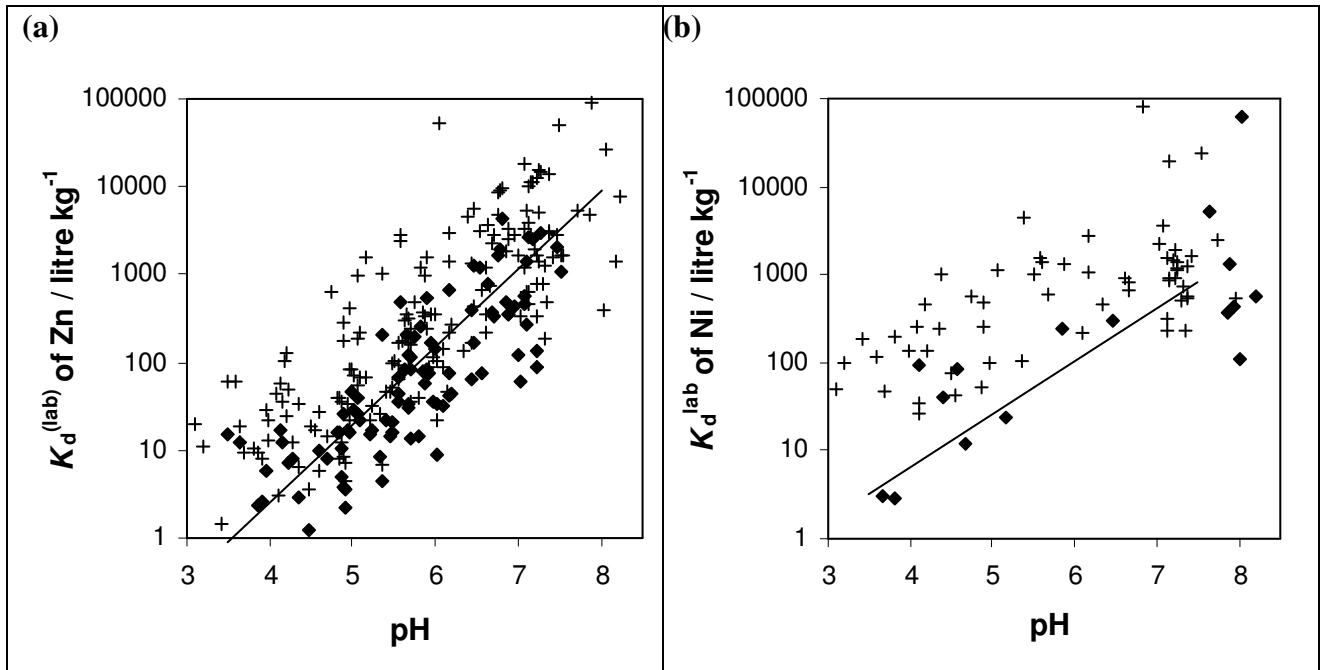


Figure 7

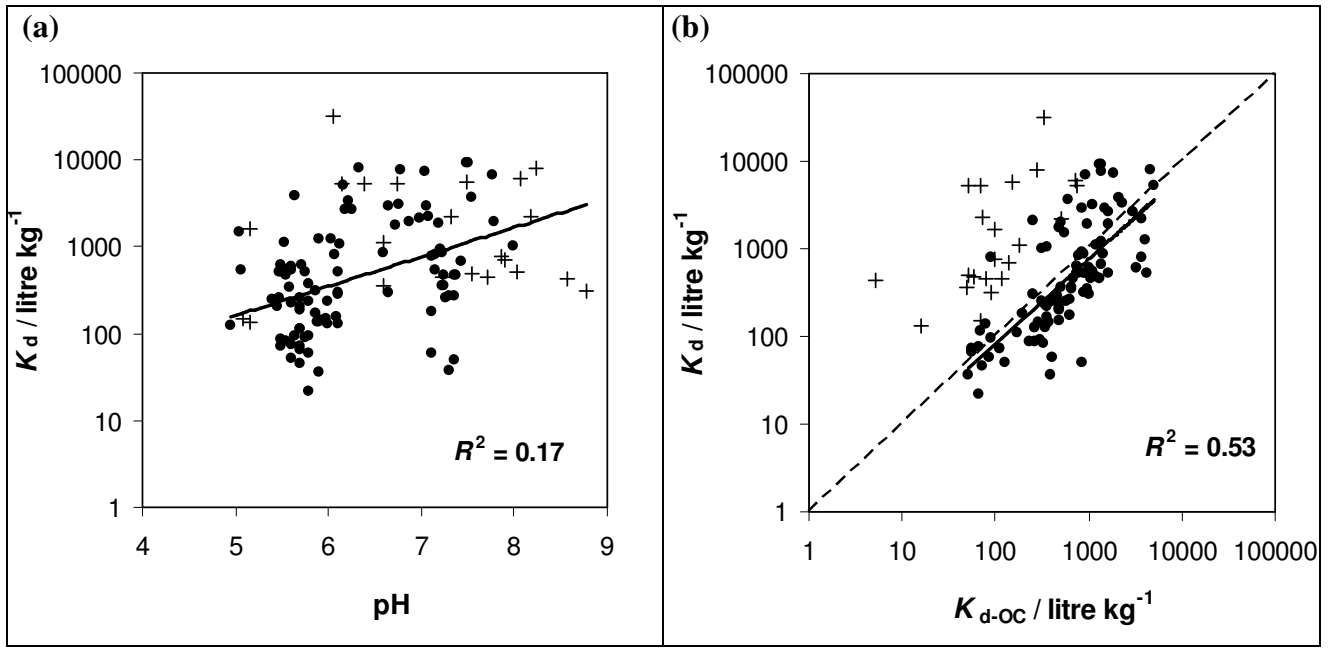


Figure 8

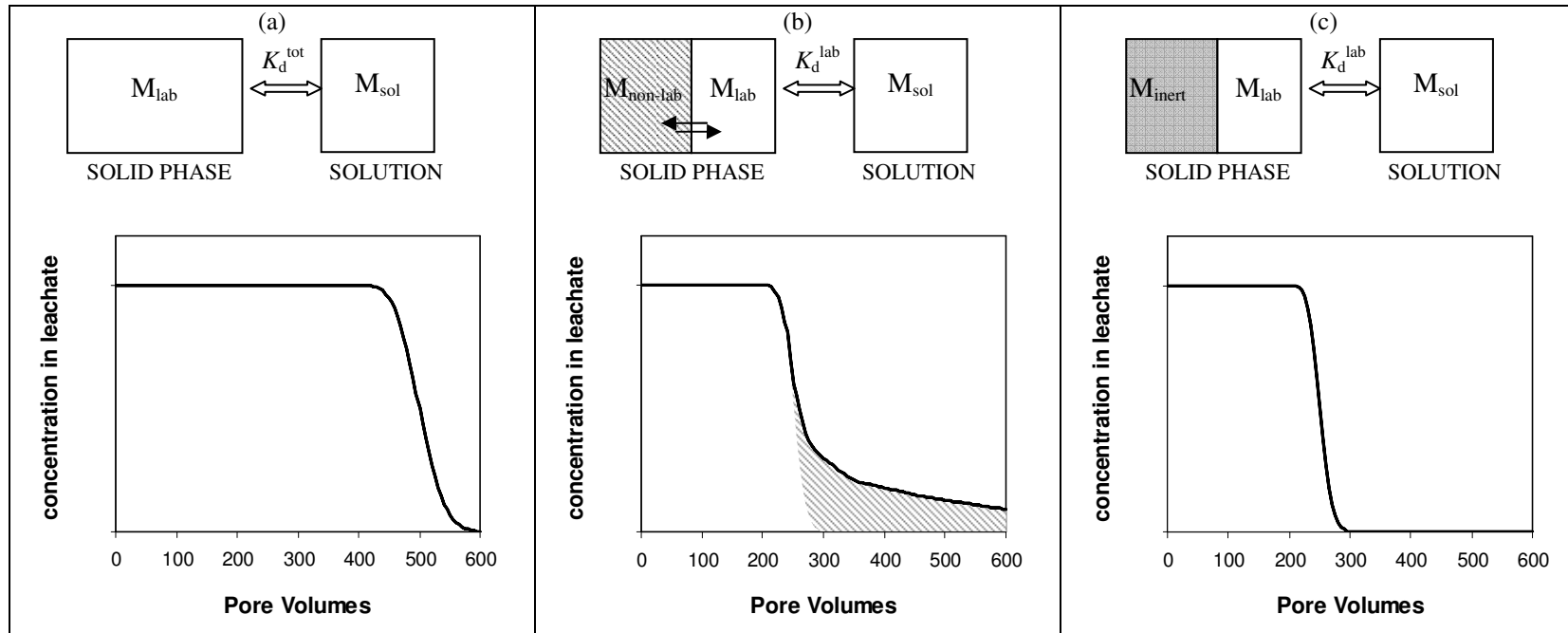


Figure 9

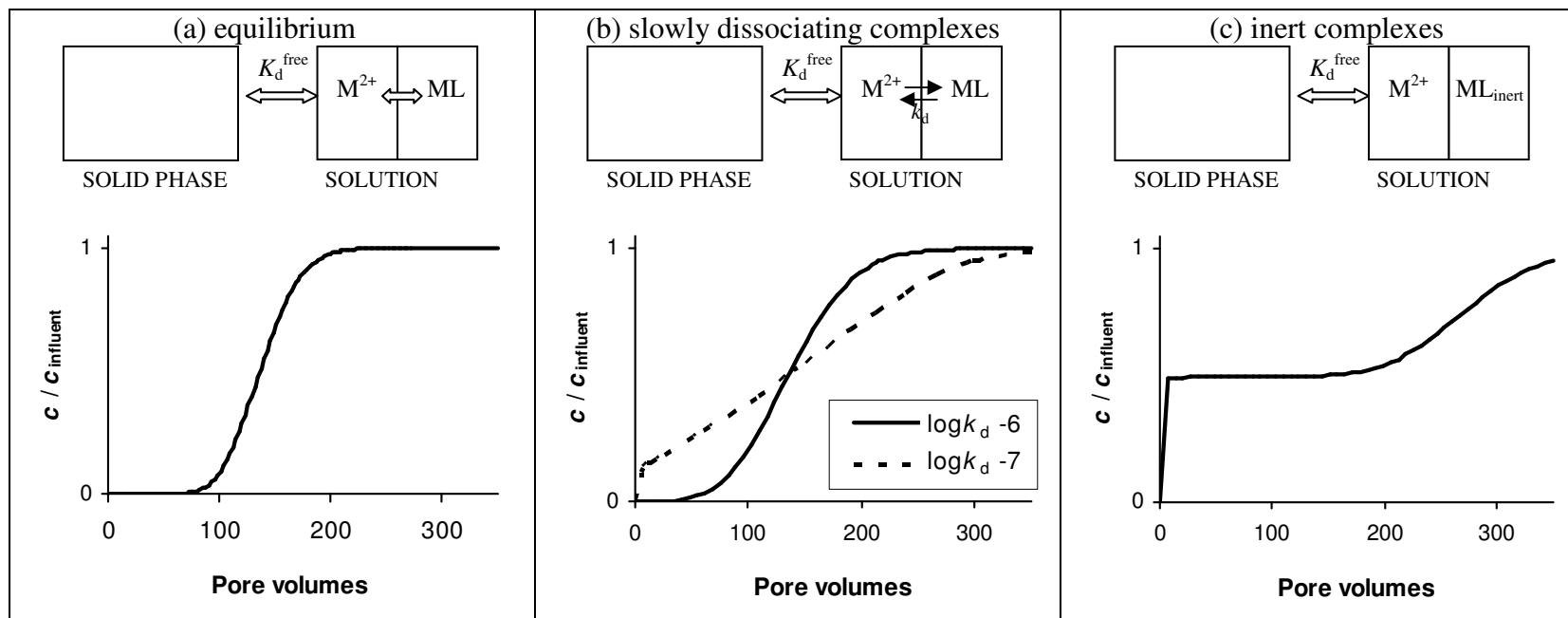


Figure 10